One-electron Transfer Reactions of Cyclooctatetraene (cot) Complexes: Electron Spin Resonance Studies of ^{60}Co γ-Irradiated [Fe(CO)$_2$L(η^4-cot)] [L = CO or P(OPh)$_3$] *

Martyn C. R. Symons,[a] **Jane L. Wyatt**[a] **and Neil G. Connelly**[b]
[a] *Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, UK*
[b] *School of Chemistry, University of Bristol, Bristol BS8 1TS, UK*

Exposure of [Fe(CO)$_2$L(η^4-cot)] [cot = cyclooctatetraene, L = CO or P(OPh)$_3$] in CFCl$_3$ at 77 K to ^{60}Co γ-rays gave the cation [Fe(CO)$_2$L(C$_8$H$_8$)]$^+$ the ESR spectrum of which is consistent with a metal-based radical with considerable spin density on the C$_8$ ring. In 2-methyltetrahydrofuran or CD$_3$OD ^{60}Co γ-irradiation of [Fe(CO)$_3$(η^4-cot)] gave two different radical anions. ESR spectroscopy suggests the primary centre, **A**, is [Fe(CO)$_3$(η^4-cot)]$^-$ in which the unpaired electron is localised largely on the unbound diene fragment of the C$_8$ ring. On annealing above 77 K, centre **A** gave a second species, **B**, the ESR spectrum of which is consistent with migration of the unpaired electron to a d$_{z^2}$-type metal orbital; one of the alkene–metal bonds of **A** is cleaved and **B** is formulated as the 17-electron anion [Fe(CO)$_3$(η^2-cot)]$^-$. For [Fe(CO)$_2${P(OPh)$_3$}(η^4-cot)], the primary centre, **A′**, is very similar to **A**, the singly occupied molecular orbital being strongly confined to the cot ligand. The second species, **B′**, is similar to **B** but gave a large ^{31}P hyperfine splitting, suggesting the phosphite ligand lies close to the *z* axis.

Our studies of the oxidative dimerisation[1] of cyclooctatetraene (cot) co-ordinated to Fe,[2] Ru,[3] Co[4] and Rh[5] have led to the stereo- and regio-specific syntheses of a wide range of novel polycyclic hydrocarbon complexes.[6] Throughout this work, we have assumed that 17-electron cations such as [M(CO)$_2$L(η^4-cot)]$^+$ (M = Fe or Ru, L = CO or phosphine) and [M(η^4-cot)(η-C$_5$R$_5$)]$^+$ (M = Co, R = Me; M = Rh, R = H) are the primary products of oxidation, with subsequent rearrangements and C–C bond coupling reactions leading to the isolated diamagnetic dimers.[1] In none of this chemistry, however, have we been able to characterise spectroscopically the proposed paramagnetic intermediates although we, and others, have isolated the stable analogues [Fe(CO){P(OMe)$_3$}$_2$(η^4-C$_4$Ph$_4$)]$^+$ (C$_4$Ph$_4$ = tetraphenylcyclobutadiene)[7,8] and [Fe(PMe$_3$)$_3$(η^4-C$_4$H$_6$)]$^+$ (C$_4$H$_6$ = trimethylenemethane),[9] and there is good electrochemical evidence for the radical cation [Rh(η^4-cot)(η-C$_5$H$_5$)]$^+$.[5]

Electron spin resonance studies of compounds subjected to ^{60}Co γ-irradiation at 77 K have provided a wealth of information on the geometric and electronic structures of otherwise inaccessible organic and inorganic radicals.[10] We have therefore studied the effects of ^{60}Co γ-rays on [Fe(CO)$_2$L(η^4-cot)][L = CO or P(OPh)$_3$] and present evidence both for the elusive radical cations [Fe(CO)$_2$L(C$_8$H$_8$)]$^+$ and for two different types of radical anion formed by electron capture.

Results and Discussion

Electron-loss Centres in CFCl$_3$.—One advantage of using CFCl$_3$ with the ^{60}Co γ-irradiation technique is that for very dilute solutions (*ca.* 1:1000) it is certain that only primary radical cations or their unimolecular breakdown products will be formed from the substrate. Also, only a broad underlying feature is associated with the electron-capture products.[11] Thus when [Fe(CO)$_3$(η^4-cot)] in CFCl$_3$ at 77 K was exposed to ^{60}Co γ-irradiation, the pale yellow product showed an ESR spectrum which can be assigned confidently to the radical cation [Fe(CO)$_3$(C$_8$H$_8$)]$^+$.

The spectrum of [Fe(CO)$_3$(C$_8$H$_8$)]$^+$ [Fig. 1(*a*)] shows three distinct *g* features (Table 1) with subsidiary proton-hyperfine splitting on each. There are clearly five components on the *x* feature which are assigned to four equivalent protons. The computer-simulated spectrum [Fig. 1(*b*)] is based on the assumption of coupling to four protons. The hyperfine splitting shows that there is quite high unpaired electron density on the C$_8$ ring, most likely on a C$_4$ segment. Judging from the isotropic coupling of *ca.* (−)5 G, the spin density on the ring is probably greater than 60%. However, the g_x shift, although very small for a transition-metal complex having a predominantly 3d singly occupied molecular orbital (SOMO), is far too large for a SOMO confined to the hydrocarbon ligand. A 60:40% distribution (ring:metal) though not proven is quite reasonable. Features marked α were most intense at 77 K but were never totally lost on annealing. They are clearly due to some minor radical centre, which is quite distinct from the species of interest.

With one *g* value close to free spin, a $(d_{yz})^2(d_{xz})^2(d_{z^2})^1$ partial electron configuration is indicated; the absence of any electronic band in the visible region, indicated by the pale yellow colour of the complex, shows that the d_{z^2} orbital is well separated from the d_{xz} and d_{yz} pair which are clearly quite different from each other.

The ESR spectrum of [Fe(CO)$_2${P(OPh)$_3$}(C$_8$H$_8$)]$^+$ is very similar to that of the tricarbonyl cation except that the proton-hyperfine splitting is less defined; there was no resolved coupling to the ^{31}P atom. The *g* values are not greatly altered when one CO ligand is replaced by P(OPh)$_3$ so that a large spin density probably remains on the C$_8$ ring, and the phosphorus atom is not in a σ configuration with respect to the d_{z^2} orbital. We therefore suggest that the SOMO involves one major lobe of the d_{z^2} orbital centred on the C$_8$ ring with the P(OPh)$_3$ ligand making an angle of *ca.* 90° to the *z* axis. (The absence of any defined ^{13}C satellites means that there is no ESR information pertinent to the siting of the CO ligands.)

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* *Non-SI unit employed:* G = 10^{-4} T.

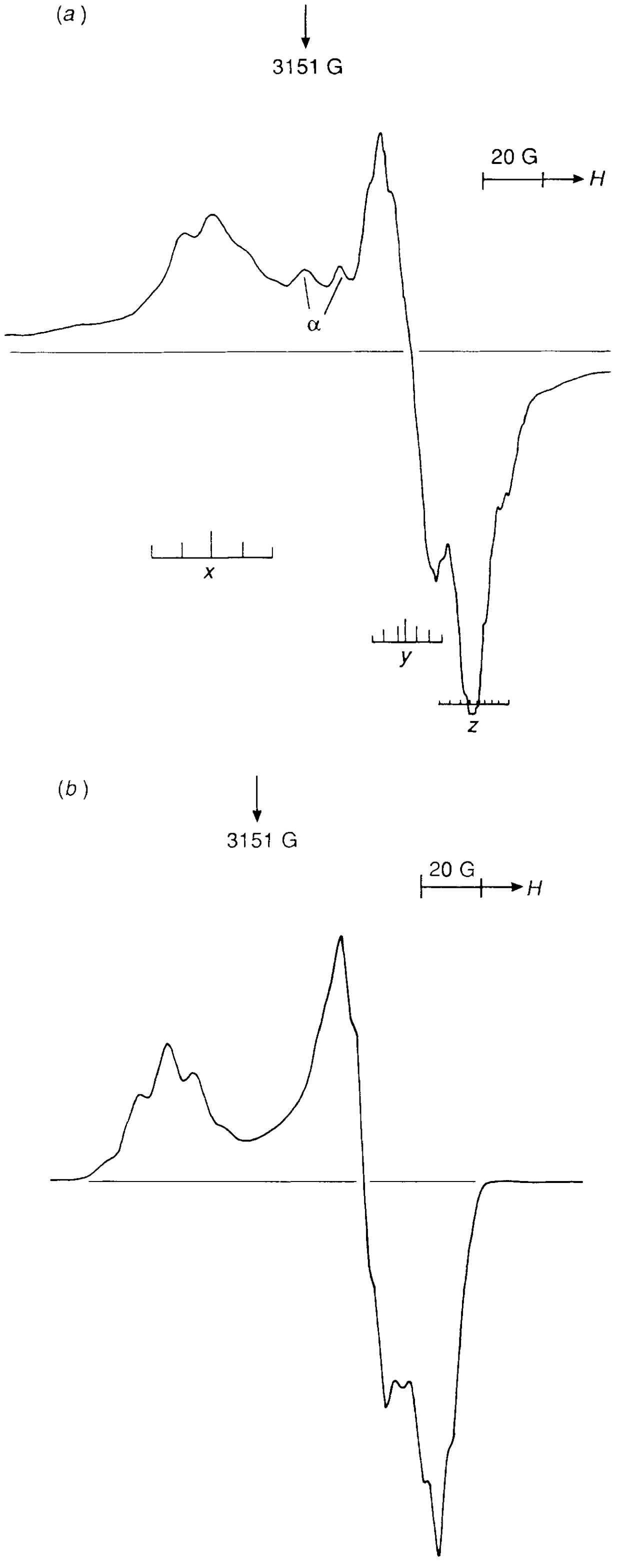

Fig. 1 (*a*) First derivative X-band ESR spectrum of a dilute solution (1:1000) of [Fe(CO)$_3$(η^4-cot)] in CFCl$_3$ after exposure to ^{60}Co γ-rays at 77 K, assigned to the radical cation [Fe(CO)$_3$(C$_8$H$_8$)]$^+$. The features marked α are due to unknown impurities. (*b*) Computer simulation based on the ESR parameters given in Table 1, using four equivalent protons. The lines were Gaussian, with 3 G widths

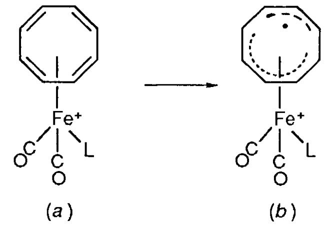

Fig. 2 Isomerisation of the primary radical cation [Fe(CO)$_2$-L(C$_8$H$_8$)]$^+$ to an allyl-based radical cation [L = CO or P(OPh)$_3$]

Our published mechanism[1] for the oxidative dimerisation of [Fe(CO)$_3$(η^4-cot)] suggested that the primary radical cation shown in Fig. 2(*a*), where the unpaired electron is localised on the 17-electron metal centre, isomerises to the allyl-based radical cation shown in Fig. 2(*b*), where the unpaired electron is localised on a C$_3$ fragment of the ring (and the metal has regained the 18-electron configuration). The present study suggests the formation of one radical cation intermediate (preceding the dimerisation step) with unpaired electron distribution intermediate between the somewhat simplistic extremes of Fig. 2. The delocalisation of the unpaired electron density onto the C$_8$ ring leads to the subsequent dimerisation reaction. There is no evidence for a second radical species on annealing above 77 K. At *ca.* 160 K the spectrum of [Fe(CO)$_2$L(C$_8$H$_8$)]$^+$ was irreversibly lost.

The radical cations [Fe(CO)$_2$L(C$_8$H$_8$)]$^+$ clearly differ from the stable 17-electron tetraphenylcyclobutadiene complexes [Fe(CO)$_{3-n}$L$_n$(η^4-C$_4$Ph$_4$)]$^+$ [n = 1, L = PPh$_3$; n = 2, L = P(OMe)$_3$] which show[7] anisotropic ESR spectra (Table 1) with g values markedly different from the spin only value and for which X-ray structural studies[8] show metal-based radical character (there is little or no difference between the ring structure of [Fe(CO){P(OMe)$_3$}$_2$(η^4-C$_4$Ph$_4$)]$^+$ and its neutral, 18-electron parent). Similarly, the radicals [Fe(CO)$_2$L(C$_8$H$_8$)]$^+$ seem to differ from [Co(η^4-L)(η-C$_5$R$_5$)]$^+$ (R = H, L = cycloheptatriene;[15] R = Me, L = cyclooctadiene[16]), which, on generation *via* electrochemical oxidation[16,17] of [Co(η^4-L)(η-C$_5$R$_5$)], show ESR spectra consistent with 17-electron metal-based radical cations.* It is noteworthy that neither the cyclobutadiene derivatives nor the cobalt complexes have been observed to dimerise.

Electron Gain Centres in CD$_3$OD *or 2-Methyltetrahydrofuran.*—Whereas CFCl$_3$ is the solvent of choice for the study of radiolytically generated radical cations, other media can be chosen[19] specifically to induce electron *capture* by the substrate. The use of CD$_3$OD is ideal provided that the radical anions are not protonated readily; radicals formed from this solvent show only narrow features in the $g = 2$ region, which obscure a minimum of the spectra of interest. The alternative is 2-methyltetrahydrofuran (mthf). In this case, although electron capture is promoted the solvent radicals give rise to an eight-line spectrum covering *ca.* 140 G. Fortunately, however, these features are often lost prior to the loss of those from the electron adducts and the complete spectra can be measured. When both media give similar adduct spectra there can be little doubt as to the assignment. It should be noted, however, that electron adducts often dissociate by loss of an anionic or neutral fragment, as in the case of alkyl halides, for example, which give alkyl radicals and halide ions in either medium.[20]

In the present study, two different electron adducts were formed with each of [Fe(CO)$_2$L(η^4-cot)] [L = CO or P(OPh)$_3$]. The first [**A**, L = CO; **A′**, L = P(OPh)$_3$] has g values relatively close to 2.0 and the unpaired electron is largely confined to the C$_8$H$_8$ ligand; the second, **B**, is formed irreversibly on annealing **A** and has the added electron on the metal.

The ESR spectrum observed when [Fe(CO)$_3$(η^4-cot)] was irradiated at 77 K in CD$_3$OD is shown in Fig. 3. There are three well defined g features, one of which (g_z) appears to be either a triplet or a quintet with *ca.* 5 G splitting. A very similar

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* Detailed studies of these species are in progress.[18]

Table 1 ESR spectroscopic data for radical cations (in $CFCl_3$) and anions (in mthf) generated by exposure of $[Fe(CO)_2L(\eta^4\text{-cot})]$ to ^{60}Co γ-irradiation and for related compounds

	g Values					^1H Hyperfine coupling[a]/G					
Radical	g_x		g_y	g_z	g_{av}	A_x		A_y	A_z	A_{av}	Ref.
$[Fe(CO)_3(C_8H_8)]^+$	2.057		2.017	2.002	2.025	9		5	5	6.3[b]	
$[Fe(CO)_2\{P(OPh_3\}(C_8H_8)]^+$	2.055		2.015	2.002	2.024			c			
$[Fe(CO)_2(PPh_3)(\eta^4\text{-}C_4Ph_4)]^+$	2.132		2.033	2.012	2.059[d]			—			7
$[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]^+$	2.156		2.053	2.017	2.075[e]			—			7
$[Fe(CO)_3(\eta^4\text{-}C_8H_8)]^-$ **A**	2.016		2.009	1.980	2.002	—		—	5[f]	—	
$[Fe(CO)_3(\eta^4\text{-}C_8H_8)]^-$	2.016		2.009	1.980	2.002[g]			—			12
$[Fe(CO)_3(\eta^2\text{-}C_8H_8)]^-$ **B**		2.056		2.002	2.038			—			
$[Fe(CO)_3(\eta^2\text{-}C_8H_8)]^-$	2.059		2.052	2.002	2.038[f]			—			
$[Fe(CO)_2(PPh_3)(\eta^4\text{-}C_8H_8)]^-$	2.014		2.009	1.979	2.001[g]						12
$[Fe(CO)_2\{P(OPh)_3\}(\eta^2\text{-}C_8H_8)]^-$ **B′**		2.058		2.002	2.039		120		135	125[h]	
$[Fe(CO)_2\{P(OPh)_3\}(\eta^2\text{-}C_8H_8)]^-$ **B′**		2.059		~2.002	2.04[f]		120		135	125[h]	
$[Fe(CO)_2(PPh_3)(\eta^2\text{-}C_6H_8)]^-$	2.075		2.062	2.006	2.048[k]	56		54	68	59[h]	13
$[Fe(CO)_3(\eta^2\text{-}L'')]^-$[j]	2.0599		2.0511	2.0063	2.0391[k]	—		—	~3[l]	—	14
$[Fe(CO)_2\{P(OMe)_3\}(\eta^2\text{-}L')]^-$[m]					2.0418[n]	—		—	—	12.5[h] 3.2[o]	14

[a] $A(^1H)$ unless stated otherwise. [b] Five lines resolved. [c] No resolved coupling to ^{31}P or ^1H. [d] In CH_2Cl_2 at 143 K. [e] In CH_2Cl_2 at 113 K. [f] In CD_3OD. [g] In dimethylformamide at 163 K. [h] $A(^{31}P)$. [i] Solid sample at 77 K. [j] L″ = Dimethyl fumarate. [k] In mthf at 103 K. [l] Coupling to two protons. [m] L′ = methylmaleic anhydride. [n] In mthf at 193 K. [o] Coupling to one proton.

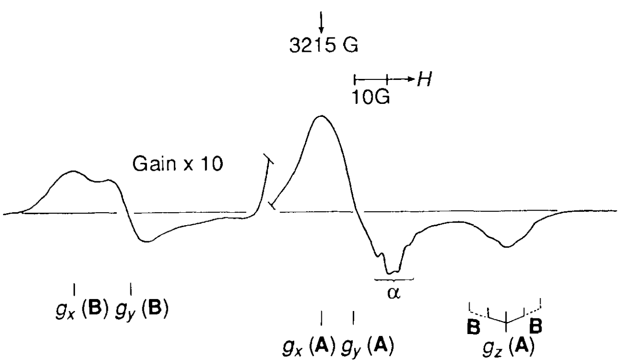

Fig. 3 First derivative X-band ESR spectrum of a dilute solution (1:100) of $[Fe(CO)_3(\eta^4\text{-cot})]$ in CD_3OD after exposure to ^{60}Co γ-rays at 77 K and annealing to *ca.* 130 K. The major features are assigned to species **A**, and the minor low-field features to g_x and g_y of species **B**: The α lines are from solvent radicals. The g_z feature for **B** must be concealed beneath the far more intense **A** features (It is assumed to be close to 2.002.)

spectrum is observed on ^{60}Co γ-irradiation of $[Fe(CO)_2\{P(OPh)_3\}(\eta^4\text{-cot})]$ although neither the ^1H coupling observed for the tricarbonyl anion **A′** nor ^{31}P hyperfine splitting was resolved for the primary radical anion **A**. The analyses of these spectra, indicated in Fig. 3, give data (Table 1) which are identical with those obtained from frozen solutions of the radical anions formed by the room temperature, electrolytic one-electron reduction of $[Fe(CO)_2L(\eta^4\text{-cot})]$ (L = CO or PPh_3) in dimethylformamide.[21]

On the basis of the near identity of the ESR spectra of the anions formed from both $[Fe(CO)_3(\eta^4\text{-cot})]$ and $[Fe(CO)_2(PPh_3)(\eta^4\text{-cot})]$ (*i.e.* there is also no ^{31}P splitting in the spectrum of the PPh_3 complex), the relatively small deviations of the g values from the free electron value, and the results of molecular orbital (MO) calculations,[12] the radical anions were formulated as $[Fe(CO)_2L(\eta^4\text{-cot})]^-$, *i.e.* the unpaired electron was thought to reside largely on the uncoordinated diene part of the cot ring with the metal atom retaining its 18-electron configuration. Clearly, the proton-hyperfine splitting observed in the ESR spectrum of **A** adds further support to this bonding description.

Although g shifts (from the free electron value) are quite small they do require significant delocalisation of the unpaired electron density onto the metal. Indeed, the MO calculations[12] on $[Fe(CO)_3(\eta^4\text{-cot})]$ suggest that the lowest unoccupied molecular orbital (LUMO) includes *ca.* 30% $Fe(CO)_3$ character. It is noteworthy, then, that a recent spectro-electrochemical study[22] of the one-electron reduction of $[Fe(CO)_3(\eta^4\text{-cot})]$ indicated substantial delocalisation of unpaired electron density onto the carbonyl ligands; when $[Fe(CO)_3(\eta^4\text{-cot})]$ in acetonitrile was electrolysed at the potential required to generate only the monoanion, the IR spectrum showed carbonyl absorptions (1940 and 1890 cm^{-1}) at very much lower energies than those of the neutral precursor [$\tilde{\nu}$(CO) 2050 and 1980 cm^{-1}].

No other electron adducts were observed in any of the electrochemical studies noted above. However, our studies show that unimolecular breakdown or rearrangement is possible for $[Fe(CO)_2L(\eta^4\text{-cot})]^-$ [L = CO or $P(OPh)_3$].[2] It is well established that the course of reactions of species that are matrix isolated often differ from liquid-phase reactions; the bimolecular reactions which usually dominate in solution are prevented in the solid state. Thus, under careful conditions of annealing, the species $[Fe(CO)_2L(\eta^4\text{-cot})]^-$ were lost and new centres having far greater spin density on iron were formed; the initial stage of this process can be seen in Fig. 3. On annealing, features for **A** were lost, and those for **B** grew in, revealing the g_z feature at *ca.* 2.002 which is hidden in the spectrum shown. There is a clear *x*–*y* splitting for solutions in CD_3OD, but only a perpendicular feature at the average value was detected for annealed solutions in mthf. This suggests some degree of hydrogen bonding in the former solvent, but complete proton transfer is unlikely since g_{av} remains constant.

The centre **B**, formed from the tricarbonyl, **A**, has an ESR spectrum with near axial symmetry. With g_z' close to 2.00, it seems probable that a $d_{z'}{}^2$ type orbital is once again involved.* Centre **B′**, formed from the $P(OPh)_3$ derivative **A′**, displays a similar spectrum in terms of the anisotropic g values, but in addition there is large ^{31}P doublet splitting, as shown in Fig. 4. The facts that $A_{max}(^{31}P)$ occurs at the free-spin g value and that $A_x \cong A_y$ strongly suggest that the g and A tensors share common directions. The feature marked α, close to the free-spin

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* We stress that the conventional nomenclature used here is not meant to imply that the axis selected as z′ for these electron adducts is the same as that for the radical cations. Hence we use z′ rather than z.

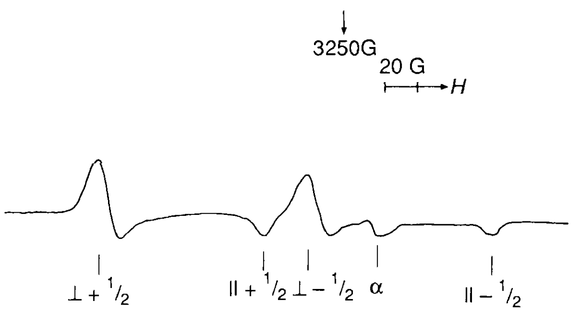

Fig. 4 First derivative X-band ESR spectrum of a dilute solution (1:500) of $[Fe(CO)_2\{P(OPh)_3\}(\eta^4\text{-cot})]$ in mthf after exposure to ^{60}Co γ-rays at 77 K and annealing to remove solvent radical features, showing features assigned to species **B**′. Feature α is due to an impurity

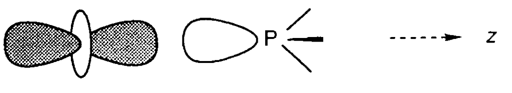

Fig. 5 Proposed SOMO for the electron adduct of species **B**′ showing the antibonding combination of the $3d_{z^2}$ (Fe) orbital and the *ca.* sp^3 hybrid orbital on phosphorus

position, is clearly not part of the spectrum of interest, since the features marked || and | in Fig. 4 all decayed at the same rate, leaving α relatively unchanged.

Assuming that the ^{31}P data are close to principal values, and that both are positive, then $A_{iso} \cong 125$ G and $2B \cong 10$ G. Using A^0 and $2B^0$ values for ^{31}P of 3663 and 201 G respectively,[23] the approximate orbital populations on phosphorus are 6.2% 3p and 3.4% 3s giving a total of *ca.* 9.6%. This accords with the partial structure, for the SOMO, shown in Fig. 5.

Although **B** (and **B**′) can be formulated as a 19-electron species we prefer a structure in which the C_8 ring is bound *via* one alkenic double bond in a 17-electron metal complex, *i.e.* as in the formula $[Fe(CO)_2L(\eta^2\text{-}C_8H_8)]^-$. There are several precedents for this type of structure (Table 1). For example, potassium reduction of $[Fe(CO)_3(\eta^4\text{-diene})]$(diene = cyclohexa-1,3-diene, 2,3-dimethylbutadiene, *etc.*) gives[14] species with ESR spectra very similar to those obtained when $[Fe(CO)_4(\eta^2\text{-alkene})]$ is reduced. The observation of hyperfine coupling only to protons bound to two carbons provided strong evidence for the formation of $[Fe(CO)_3(\eta^2\text{-diene})]^-$. Similarly the reduction of the benzylideneacetone complex $[Fe(CO)_3(\eta^4\text{-}C_6H_5CH{=}CHCOMe)]$ resulted[24] in detachment of the iron-co-ordinated C=O group, giving $[Fe(CO)_3(\eta^2\text{-}C_6H_5CH{=}CHCOMe)]^-$ (hyperfine coupling to only one hydrogen atom), and ^{60}Co γ-irradiation of solid $[Fe(CO)_2(PPh_3)(\eta^4\text{-}C_6H_8)]$ (C_6H_8 = cyclohexadiene) gave an ESR spectrum again consistent with $[Fe(CO)_2(PPh_3)(\eta^2\text{-}C_6H_8)]^-$.[13] The ESR spectrum of the last anion showed substantial spin density on phosphorus, though less than for **B**′, and a partial structure for the SOMO similar to that in Fig. 5 was postulated.

Although the electrochemical reduction of $[Fe(CO)_2L(\eta^4\text{-cot})]$ provided evidence for only one type of radical anion, identical to the primary radical formed by ^{60}Co γ-irradiation (**A** or **A**′), similar studies have revealed two types of radical anion for the cobalt complexes $[Co(\eta^4\text{-diene})(\eta\text{-}C_5H_5)]$. For example, the cot complex gives $[Co(\eta^4\text{-1,3-cot})(\eta\text{-}C_5H_5)]^-$, with the unpaired electron on the unbonded diene, whereas $[Co(\eta^4\text{-cod})(\eta\text{-}C_5H_5)]^-$ [1,3- or 1,5-bound cyclooctadiene (cod)] are formulated as metal-based radicals.[25] (Note that the latter are thought to be 19-electron η^4-diene, rather than 17-electron η^2-diene, complexes.) It appears, therefore, that where there is a choice between electron addition to the metal or to an unbound diene unit (*i.e.* only in the case of cot) the latter is observed. Where there is no choice (*i.e.* where there is no unbound diene) addition to the metal must occur. Interestingly, the reduction of $[Co(\eta^4\text{-dbcot})(\eta\text{-}C_5H_5)]$ (dbcot = dibenzo[*a*,*e*]cyclooctatetraene) gives a metal-based radical anion. In this case, the unbound alkene units of the dbcot ligand remain part of the aromatic rings.

Conclusion

Electron spin resonance spectroscopy of ^{60}Co γ-irradiated samples in $CFCl_3$ at 77 K has finally provided direct evidence for the radical cations postulated as intermediates in the oxidative dimerisation of $[Fe(CO)_2L(\eta^4\text{-cot})]$. These radical cations are largely metal-based though there is significant delocalisation of the unpaired electron density onto the C_8 ring. This delocalisation provides the means by which the subsequent dimerisation, *via* C–C bond formation, can occur.

In CD_3OD or mthf, two radical anions are formed from $[Fe(CO)_2L(\eta^4\text{-cot})]$ [L = CO or $P(OPh)_3$]. The primary species is identical to that generated by room temperature electrolytic reduction and is formulated as $[Fe(CO)_2L(\eta^4\text{-cot})]^-$. The unpaired electron is localised largely on the unbound diene unit of the C_8 ring although there is significant delocalisation onto the metal. On annealing, the primary radical anion forms a second species, formulated as $[Fe(CO)_2L(\eta^2\text{-cot})]^-$, in which the single electron is located substantially on the 17-electron metal centre.

Experimental

The complexes $[Fe(CO)_2L(\eta^4\text{-cot})]$[L = CO[26] or $P(OPh)_3$[2]] were prepared by published methods. Samples for ESR spectroscopy were prepared as dilute solutions (between 1:100 and 1:1000 v/v) in purified $CFCl_3$, CD_3OD or mthf and frozen as small beads in liquid nitrogen after degassing. Samples were exposed to ^{60}Co γ-rays at 77 K in a Vicrad source to doses up to *ca.* 1 Mrad. ESR spectra were measured using a Varian E 109 X-band spectrometer at 77 K. They were annealed with continuous monitoring of the spectra, and re-cooled to 77 K for measurement.

References

1 N. G. Connelly, in *Paramagnetic Organometallic Species in Activation/Selectivity, Catalysis*, eds. M. Chanon, M. Julliard and J. C. Poite, Kluwer Academic Publishers, Holland, 1989, p. 71; N. G. Connelly, *Chem. Soc. Rev.*, 1989, **18**, 153.

2 N. G. Connelly, R. L. Kelly, M. D. Kitchen, R. M. Mills, R. F. D. Stansfield, M. W. Whiteley, S. M. Whiting and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 1317.

3 N. G. Connelly, P. G. Graham and J. B. Sheridan, *J. Chem. Soc., Dalton Trans.*, 1986, 1619.

4 M. Gilbert, Ph.D. Thesis, University of Bristol, 1988; N. G. Connelly and M. Gilbert, unpublished work.

5 L. Brammer, N. G. Connelly, J. Edwin, W. E. Geiger, A. G. Orpen and J. B. Sheridan, *Organometallics*, 1988, **7**, 1259.

6 N. G. Connelly, A. R. Lucy, R. M. Mills, J. B. Sheridan and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1985, 699; N. G. Connelly, M. J. Freeman, A. G. Orpen, J. B. Sheridan, A. N. D. Symonds and M. W. Whiteley, *J. Chem. Soc., Dalton Trans.*, 1985, 1027; N. G. Connelly, A. R. Lucy, R. M. Mills, M. W. Whiteley and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1984, 161.

7 N. G. Connelly, R. L. Kelly and M. W. Whiteley, *J. Chem. Soc., Dalton Trans.*, 1981, 34.

8 A. G. Orpen, N. G. Connelly, M. W. Whiteley and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1989, 1751.

9 J.-M. Grosselin, H. LeBozec, C. Moinet, L. Toupet, F. H. Köhler and P. H. Dixneuf, *Organometallics*, 1988, **7**, 88.

10 M. C. R. Symons, J. R. Morton and K. F. Preston, *ACS Symp. Ser.*, 1987, **333**, 169; M. C. R. Symons, in *Paramagnetic Organometallic Species in Activation/Selectivity, Catalysis*, eds. M. Chanon, M. Julliard and J. C. Poite, Kluwer Academic Publishers, Holland, 1989, p. 447.

11 M. C. R. Symons, *Chem. Soc. Rev.*, 1984, **13**, 393.

12 T. A. Albright, W. E. Geiger, J. Moraczewski and B. Tulyathan, *J. Am. Chem. Soc.*, 1981, **103**, 4787.

13 O. P. Anderson and M. C. R. Symons, *Inorg. Chem.*, 1973, **12**, 1932.

14 P. J. Krusic and J. San Filippo, jun., *J. Am. Chem. Soc.*, 1982, **104**, 2645.

15 W. E. Geiger, T. H. Gennett, G. A. Lane, A. Salzer and A. L. Rheingold, *Organometallics*, 1986, **5**, 1352.

16 J. Moraczewski and W. E. Geiger, *Organometallics*, 1982, **1**, 1385.

17 U. Koelle, *Inorg. Chim. Acta*, 1981, **47**, 13.

18 W. E. Geiger and P. H. Rieger, personal communication.

19 M. C. R. Symons, *Pure Appl. Chem.*, 1981, **53**, 223.

20 M. C. R. Symons and I. G. Smith, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1180.

21 B. Tulyathan and W. E. Geiger, *J. Electroanal. Interfacial Electrochem.*, 1980, **109**, 325.

22 M. N. Golovin and M. J. Weaver, *Inorg. Chim. Acta*, 1988, **142**, 177.

23 M. C. R. Symons, *Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy*, Van Nostrand, London, 1978.

24 N. El Murr, M. Riveccie and P. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1978, 552.

25 W. E. Geiger, T. Gennett, M. Grzeszczuk, G. A. Lane, J. Moraczewski, A. Salzer and D. E. Smith, *J. Am. Chem. Soc.*, 1986, **108**, 7454.

26 R. B. King, *Organomet. Synth.*, 1965, **1**, 126.

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