the analogous diiodide ion.[17] Agreement with the I_3^- fundamental and overtone progressions from solution spectra listed in Table II confirms the assignment to I_3^- and the matrix identification of the $M^+I_3^-$ species.

Several points are worthy of contrast between the matrix and solution spectra. The $M^+I_3^-$ vibrational potential function is slightly more anharmonic in the cubic sense as the vibrational spacing decreases with increasing quantum number slightly more for the $M^+I_3^-$ ion pair. Resonance enhancement was attained with 476.5-nm excitation in the $M^+I_3^-$ species, which is rather far out the red wing of the absorption, whereas the solution species required ultraviolet excitation in the $\pi_g \rightarrow \sigma_u^*$ absorption band.[10,11]

The shoulder at 145 ± 5 cm^{-1} in the Raman spectrum is appropriate for the ν_3 mode of I_3^-, and similar features have been assigned accordingly in the earlier resonance Raman investigations.[10,11] However, a very recent Raman study of triiodide ion in solution as a function of iodide concentration has demonstrated a concentration dependence for the 155-cm^{-1} signal which indicates the presence of a higher polyhalide.[18] The matrix data provide no additional information on this feature. The broad band at 170 cm^{-1} is probably due to a higher aggregate species. Since the Raman intensity at 170 cm^{-1} varied relative to the $(I_2)_n$ fundamental at 180 cm^{-1} and the I_3^- mode at 113 cm^{-1} in the experiments performed here, the 170-cm^{-1} signal is due to a different molecular species, most likely a higher polyiodide. The $Cs^+I_5^-$ ion pair could be formed in a CsI matrix reaction with $(I_2)_2$ or by the reaction of another I_2 molecule with $Cs^+I_3^-$.

A final comparison between the resonance Raman spectra of the $Cs^+I_2^-$ and $Cs^+I_3^-$ iodide species is appropriate; vibrational data for the former are given in the last column in Table II.[17] Two pieces of evidence show that different spectra are obtained for diiodide ion and triiodide ion: the fundamental and overtones differ by more than the error of measurement even though the values are close, and red excitation produces a resonance Raman spectrum of I_2^- owing to a strong 686-nm absorption for this anion whereas blue excitation gives a resonance Raman spectrum for I_3^-. Both I_2^- and I_3^- involve "one-electron" or "half-order" bonds, and their symmetric stretching vibrational fundamentals are nearly the same, and both are about half of the I_2 fundamental value (212 cm^{-1})[15] which, of course, involves an electron-pair bond.

Conclusions

Matrix reactions of alkali iodide and iodine molecules were performed to synthesize the $M^+I_3^-$ ion pair for spectroscopic study. Strong ultraviolet absorptions at 287 and 355 nm and a strong resonance Raman fundamental at 113 ± 1 cm^{-1} and five overtones with regularly decreasing intensities were observed for the $Cs^+I_3^-$ species. These data are in excellent agreement with ultraviolet and resonance Raman spectra of triiodide ion solutions.[10,11] The $M^+X_3^-$ salt–molecule matrix reaction product is representative of the triiodide ion, which substantiates the use of this synthetic technique to produce new unstable polyhalide ions like the trifluoride ion.[1]

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Registry No. $Cs^+I_3^-$, 12297-72-2; $Na^+I_3^-$, 12593-83-8; $Na^+BrI_2^-$, 72138-51-3; $Na^+IBr_2^-$, 72138-52-4; $Na^+Br_3^-$, 21109-91-1; $Cs^+Br_3^-$, 17060-10-5; $Cs^+ClBr_2^-$, 22325-19-5; CsI, 7789-17-5; NaI, 7681-82-5; NaBr, 7647-15-6; CsBr, 7787-69-1; CsCl, 7647-17-8; I_2, 7553-56-2; Br_2, 7726-95-6.

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(16) Howard, W. F., Jr.; Andrews, L. *J. Am. Chem. Soc.* **1973**, *95*, 2056; *Inorg. Chem.* **1975**, *14*, 767.

(17) Howard, W. F., Jr.; Andrews, L. *J. Am. Chem. Soc.* **1975**, *97*, 2956.

(18) Loos, K. R.; Jones, A. C. *J. Phys. Chem.* **1974**, *78*, 2306.

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Paramagnetic Organometallic Molecules. 8.[1] An ESR Study of the Redox Chemistry of Iron Carbonyl Species

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An ESR study of THF or CH_2Cl_2 solutions of $Fe_3(CO)_{12-n}L_n$ (L = CO, $P(OR)_3$, PR_3), $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$, which have been reduced by electrolytic methods or by alkali metals or have been photolyzed, is presented. The radical anions of the above compounds have been characterized at low temperature. However, the iron-containing radical anions readily undergo what are believed to be disproportionation reactions to Fe(II), Fe(−I), and Fe(−II) via the intermediacy of the dianions $[Fe_3(CO)_{12-n}L_n]^{2-}$. The hydrido anion $[HFe_3(CO)_{11}]^-$ is an ultimate product in reductions in THF or when $Fe_3(CO)_{12}$ is photolyzed. No evidence was found for an oxidation or reduction mode for $Fe_3(CO)_{11}^{2-}$. Solutions of $Fe_2(CO)_9$ in THF on reduction give essentially the same ESR spectra as $Fe_3(CO)_{12}$. It is found that small concentrations of $Fe_3(CO)_{12}^{-}\cdot$ are produced in THF solutions of $Fe_3(CO)_{12}$ and $Fe_2(CO)_9$, even in the absence of an external reducing agent.

Introduction

Previous papers[2-4] on the tricobalt carbon clusters demonstrated that the redox behavior of this type of metal carbonyl can be elucidated if both electrochemical and spectral techniques are utilized. Since the unpaired electrons occupy a σ^* Co_3 orbital in the tricobalt carbon clusters, it was of interest to compare other trinuclear clusters which do not have a nonmetal capping group. The iron group carbonyls $M_3(CO)_{12}$, with which this paper is concerned, make an interesting comparison because there is formally one extra carbonyl group per metal atom[5] and, at least in the solid phase, some carbonyls may bridge the metal–metal bond.[6] Further, a large number

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(1) Part 7: Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *J. Organomet. Chem.*, **1979**, *172*, C63.

(2) Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 405.

(3) Bond, A. M.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 410.

(4) Bond, A. M.; Dawson, P. A.; Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.*, **1979**, *18*, 1413.

(5) (a) Abel, E.; Stone, F. G. A. *Q. Rev., Chem. Soc.* **1969**, *23*, 325. (b) *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 471.

(6) Cotton, F. A.; Hunter, P. L. *Inorg. Chim. Acta* **1974**, *11*, L9.

of reactions of iron carbonyls involve excited-state reactivity (i.e., photolysis) and even thermal reactions of $Fe(CO)_5$ or $Fe_2(CO)_9$ could well be partially free-radical in character, particularly in THF.

The electrochemical studies[7] showed that $M_3(CO)_{12}$ (M = Fe, Ru, Os) and $Fe_3(CO)_{12-n}L_n$ (L = $P(OR)_3$, PR_3) compounds underwent one-electron reduction but, in general, this was only reversible at low temperatures. Moreover, while the reduction of iron compounds was relatively "clean" in CH_2Cl_2, complex polarograms and cyclic voltammograms were obtained in ether solvents such as THF. The complexity arose from decomposition of the radical anions to mono- and dinuclear iron fragments but the identity of these was not established. Preliminary ESR work[8] had shown that paramagnetic species were produced on alkali metal reduction of iron carbonyls although our electrochemical results[7] (confirmed by a recent note[9]) indicated that our original interpretation of these spectra could be in doubt. Accordingly, a wide ranging ESR study of alkali metal and electrolytically reduced iron carbonyl solutions was carried out in an endeavor to characterize the paramagnetic species. Difficulties were anticipated because of the fact that the known chemistry of iron carbonyls in ether solvents is dominated by base-induced disproportionation and a decrease in nuclearity in reactions of $Fe_3(CO)_{12}$.[10] This proved to be the case for the systems reported in this paper. Vlcek and co-workers[9] have briefly mentioned the ESR spectra of $Fe_3(CO)_{12}$ in CH_2Cl_2 while paramagnetic species analogous to those reported in this paper have been detected[11] in DMF solutions of an anionic cluster $[HFe_3(CO)_{11}]^-$.

Experimental Section

General Procedures. The electrochemical and ESR procedures have been described previously.[2,3] The metal carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, and $M_3(CO)_{12}$ (M = Fe, Ru, Os) were obtained from Strem Chemicals but particular care was taken to obtain pure samples. $Fe(CO)_5$ was purified by vacuum distillation while $Fe_2(CO)_9$ was dried in vacuo at 323 K to remove traces of acetic acid. Repeated sublimation of $Fe_3(CO)_{12}$ at 335 K (0.05 mmHg) produced black crystals free from $Fe(CO)_5$ and paramagnetic impurity. The heteronuclear clusters $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ were prepared by a method based on that of Yawney and Stone.[12] All solid samples of carbonyls were checked for paramagnetic impurities before use, and blank spectra of freshly prepared solutions were obtained before reduction.

The phosphite derivatives were prepared[13] from $Fe_3(CO)_{12}$ and purified by preparative TLC. Literature methods with minor modifications were also used for mononuclear iron species, $[Et_3NH][Fe_3(CO)_{11}H]$,[14] $[PPN][HFe(CO)_4]$,[15] and $[Fe_3(CO)_{11}]^{2-}$ [16] salts. Solvents were rigorously degassed and dried as described previously.[2]

Reactivity of $Fe_2(CO)_9$ in THF. (a) In Vacuo. $Fe_2(CO)_9$ (0.36 g) and dry degassed THF (10 cm^3 distilled from K/naphthalene) were magnetically stirred for 2 h. The reaction mixture immediately acquired an orange-yellow color which deepened as more $Fe_2(CO)_9$ "dissolved". After 2 h the solution appeared deep purple-red and contained little solid $Fe_2(CO)_9$. The solvent and $Fe(CO)_5$ were distilled off under vacuum to leave a dark purple solid. This was redissolved in CH_2Cl_2 and a solution of Et_4NBr (0.2 g) in CH_2Cl_2 was added. Addition of hexane led to the separation of a dark red-brown precipitate. This compound was identified by infrared (ν(CO) ($CHCl_3$ solution) 2076 (w), 1998 (vs), 1983 (s), 1955 (m), 1736 cm^{-1}(w)) and electronic spectroscopy (λ_{max} = 540 nm) as $[Et_4N][HFe_3(CO)_{11}]$. An authentic sample of this compound used for comparison was prepared from $Fe_3(CO)_{12}$ by the method of Hieber.[17] The same electronic spectra were observed for aged solutions of $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ in THF made up under vacuum in a UV cell.

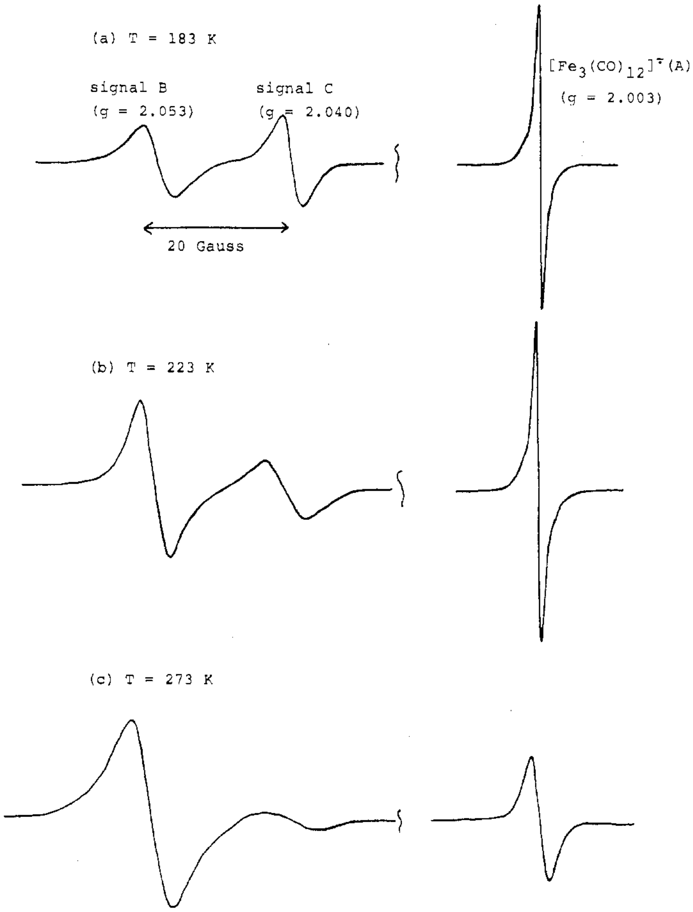

Figure 1. Temperature dependence of the ESR signals from the reduction of $Fe_3(CO)_{12}$.

(b) Under Nitrogen Flow. In this case the initial orange-yellow "solution" was steadily converted to the dark green color of $Fe_3(CO)_{12}$. The infrared spectrum of the resultant solution showed $Fe(CO)_5$ as well as $Fe_3(CO)_{12}$ were present. The solvent and $Fe(CO)_5$ were distilled off and the $Fe_3(CO)_{12}$ was extracted from the residue. Starting with 1.5 g of $Fe_2(CO)_9$, we obtained about 0.1 g of $Fe_3(CO)_{12}$; the material left was insoluble in organic solvents.

Results

Triiron Dodecacarbonyl. (a) Reduction and Chemistry in Dichloromethane. The electrochemical studies[7] showed that on the cyclic voltammetric time scale $Fe_3(CO)_{12}$ forms a radical anion stable in dichloromethane at 203 K and in acetone at temperatures below 268 K. Correspondingly, electrolytic reduction of $Fe_3(CO)_{12}$ in dichloromethane within the ESR cavity, at temperatures below 203 K, leads to the observation of a single sharp-line spectrum A (g = 2.003 (2), ΔB_{p-p} = 1.4 G, T = 233 K)[18,19] which can be assigned to the species $[Fe_3(CO)_{12}]^{-}\cdot$. The signal appears within seconds of the commencement of electrolysis and grows in intensity with time to reach a constant value. This suggests that reduction is diffusion controlled, as is also indicated by the electro-

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(7) Bond, A. M.; Dawson, P. A.; Peake, B. M.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1977**, *16*, 2199.

(8) Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *J. Chem. Soc., Chem. Commun.* **1974**, 945.

(9) Miholova, D.; Klima, J.; Vlcek, A. A. *Inorg. Chim. Acta* **1978**, *27*, L67.

(10) (a) King, R. B. *Adv. Organomet. Chem.* **1964**, *2*, 157. (b) Hieber, W.; Schubert, E. H. *Z. Anorg. Allg. Chem.* **1965**, *338*, 37.

(11) Gil'denber, E. Z.; Shuets, V. A.; Lapidus, A. L.; Kazanskii, V. B.; Eidus, Y. G. *Kinet. Catal.* **1975**, *16*, 930.

(12) Yawney, D. B. W., Stone, F. G. A. *J. Chem. Soc. A* **1969**, 502.

(13) (a) Pollick, P. J.; Wojcicki, A. *J. Organomet. Chem.* **1968**, *14*, 469. (b) Angelici, R. J.; Siefert, E. E. *Inorg. Chem.* **1966**, *5*, 1457.

(14) McFarlane, W.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 181.

(15) Case, J. R.; Whiting, M. C. *J. Chem. Soc.* **1960**, 4632.

(16) Hieber, W.; Sedlemeir, J.; Werner, R. *Chem. Ber.* **1957**, *90*, 278.

(17) Hieber, W.; Brendel, G. *Z. Anorg. Allg. Chem.* **1957**, *289*, 332.

(18) Figures given in parentheses are the estimated errors in final digits quoted.

(19) The anisotropic g factors, $g_{\parallel}$ = 1.990, $g_{\perp}$ = 2.007, were obtained from a frozen solution spectrum.

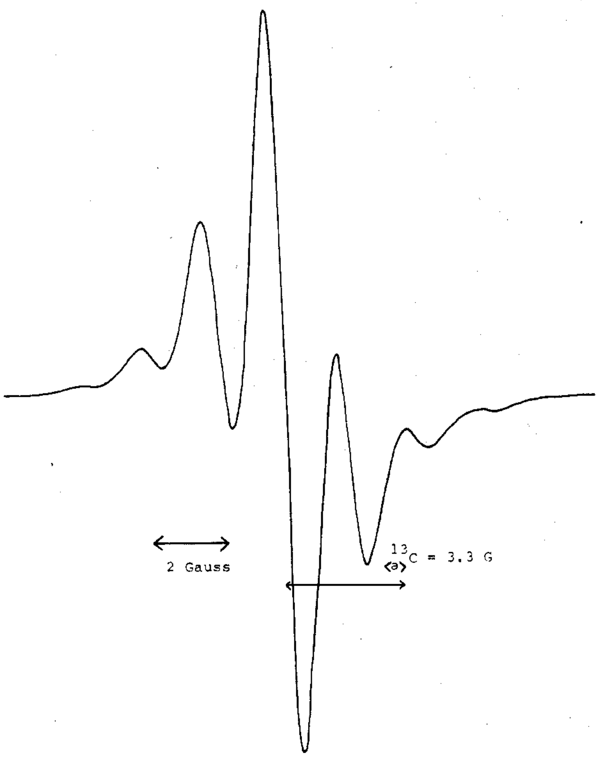

Figure 2. ESR spectrum of ^{13}C-enriched $[Fe_3(CO)_{12}]^{-}\cdot$ at 203 K.

chemical data. If a dichloromethane solution containing $[Fe_3(CO)_{12}]^{-}\cdot$ is warmed to above 203 K or if electrolysis in the same solvent is performed at above that temperature, two new broader single-line signals appear in the ESR spectrum: B ($g = 2.053$ (3), $\Delta B_{p-p} = 4$ G); C ($g = 2.040$ (3), $\Delta B_{p-p} = 6$ G; $T = 253$ K). Both these signals are very weak in comparison to that of the radical anion, at temperatures up to 263 K, but, at ambient temperatures, the latter are more intense (Figure 1). When electrolysis is carried out at room temperature both lines A and B grow steadily in intensity with time but, once the current is stopped, the relatively weak ($[Fe_3(CO)_{12}]^{-}\cdot$) decays rapidly, without a significant effect on the amplitude of B. If a solution containing all three paramagnetic species is recooled to temperatures where initially only $[Fe_3(CO)_{12}]^{-}\cdot$ was seen, all three remain observable. Admission of air to the solution, however, leads to the disappearance of all lines. Furthermore, infrared analysis of the solution following an ESR/electrolysis experiment reveals the presence of $Fe(CO)_5$ in addition to the remaining $Fe_3(CO)_{12}$. Thus, lines B and C can be attributed to products arising from the decomposition of $[Fe_3(CO)_{12}]^{-}\cdot$. These ESR observations are compatible with the cyclic voltammetric data in dichloromethane, which showed[7] that at 293 K the radical anion is only marginally stable on that time scale.

When a sample of ^{13}C-enriched $Fe_3(CO)_{12}$ ($\sim$10% enrichment) is reduced, ^{13}C hyperfine coupling is exhibited by $[Fe_3(CO)_{12}]^{-}\cdot$; this is best resolved at temperatures in the range 200–250 K (Figure 2). The hyperfine coupling shown in Figure 2 arises largely from the superposition of the 1:2:1 triplet due to $[Fe_3(^{12}CO)_{10}(^{13}CO)_2]^{-}\cdot$ and the 1:1 doublet of $[Fe_3(^{12}CO)_{11}(^{13}CO)]^{-}\cdot$ on the singlet line of $[Fe_3(^{12}CO)_{12}]^{-}\cdot$. The ^{13}C coupling constant is 3.3(2) G while all three species have a common g value of 2.002 (2).

The low-field signals, B and C, did not show ^{13}C coupling at any temperature. This does not necessarily preclude assignment of these signals to carbonyl-containing species, since their line widths, at all temperatures (>4 G), are broad compared to the ^{13}C-coupling constant observed for the trinuclear radical anion.

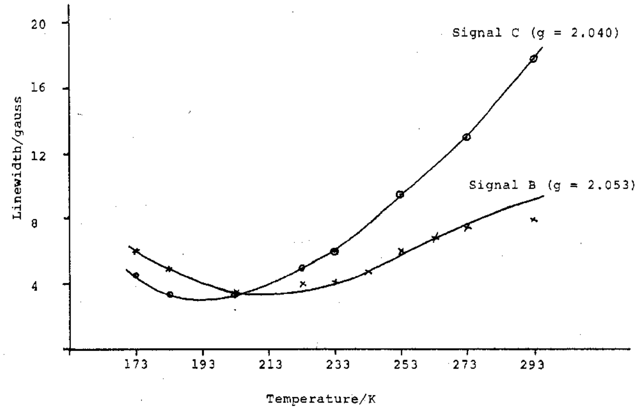

Figure 3. Effect of temperature on the ESR line widths of species B and C.

Further evidence that the high-field line (A) was due to $[Fe_3(CO)_{12}]^{-}\cdot$ came from the investigation of electron-transfer reactions. On mixing solutions of $[CH_3CCo_3(CO)_9]^{-}\cdot$ and $Fe_3(CO)_{12}$ in an ESR cell, we observed that the characteristic 22-line spectrum[2] of the former species disappeared and that a very strong singlet ($g = 2.003$) was observed instead. This electron transfer was anticipated since the electrochemical data indicate that the tricobalt species has a more negative reduction potential.[3]

$$[CH_3CCo_3(CO)_9]^{-}\cdot + Fe_3(CO)_{12} \xrightarrow[CH_2Cl_2]{273\ K} CH_3CCo_3(CO)_9 + [Fe_3(CO)_{12}]^{-}\cdot$$

The species $[Fe_3(CO)_{12}]^{-}\cdot$ can itself act as an electron-transfer agent to more powerful electron-accepting compounds, such as 1,4,5,8-tetranitronaphthalene (TNN). When a dichloromethane solution containing $[Fe_3(CO)_{12}]^{-}\cdot$ but neither of the other paramagnetic iron species was reacted with TNN, the ESR signal due to the triiron anion was replaced, as expected, by that of the TNN radical anion.[20]

$$[Fe_3(CO)_{12}]^{-}\cdot + TNN \xrightarrow[CH_2Cl_2]{233\ K} Fe_3(CO)_{12} + [TNN]^{-}\cdot$$

However, when a solution, whose ESR spectrum showed only line B ($g = 2.053$), was reacted with TNN, the TNN radical anion was not generated, although signal B did disappear.

(b) Electrolytic and Chemical Reduction in THF. Reduction of $Fe_3(CO)_{12}$ in THF leads to the observation of the same three ESR signals obtained from electrolyzed dichloromethane solutions. However, studies in THF are complicated by the fact that two of the signals, A and B ($g = 2.053$), are observed from solutions of $Fe_3(CO)_{12}$ *that have not been subjected to an external reducing agent* (vide infra). These signals appear within a few minutes of $Fe_3(CO)_{12}$ being dissolved in THF, under vacuum, at room temperature and both grow in intensity with time, with both the magnitude and rate of growth of line B being much greater. If a freshly prepared THF solution of $Fe_3(CO)_{12}$, for which the paramagnetic signals are only very weak, is reduced, the following observations are noted.

(i) Electrochemical reduction is qualitatively the same as in dichloromethane solution except that the rate of decay of $Fe_3(CO)_{12}^{-}\cdot$ is faster in THF and occurs at lower temperature. Prolonged electrolysis at 293 K leads to the replacement of signal B ($g = 2.053$) by C.

(ii) Reduction with a sodium mirror at temperatures below 240 K leads to the observation of all three ESR signals ($g = 2.053$, 2.041, 2.003) with considerably enhanced intensities. The relative amplitudes of the spectral lines vary considerably depending on the solution temperature (Figure 1). However,

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(20) Gerson, F.; Adams, R. N. *Helv. Chim. Acta* **1965**, *48*, 1539.

for the two low-field lines (B, C) this effect is reversible and can be attributed to a temperature dependence of the line width (Figure 3). Thus, below 203 K, line C is sharper and appears more intense while, above that temperature, it broadens at a much faster rate than line B. Estimates of the area under B and C indicated that the concentrations of the species giving rise to these signals do increase with an increase in temperature over a period of time. The intensity of line A is dependent on the stability of the radical; recooling of a sodium reduced solution from 298 K *does not restore its intensity to the original value*. The reduction of the dark green THF solutions of $Fe_3(CO)_{12}$ with sodium also causes a marked change in color. Solutions reduced at low temperatures and which exhibited all three ESR signals were mauve while further reduction at 293 K changed the color again to an orange-brown. No paramagnetic species were detected in the latter solution.

(iii) Reduction is much more facile with cesium, the same three signals being produced. There is no sign of hyperfine coupling to ^{133}Cs. Formation of a purple color is immediate and the conversion to an orange-brown solution is more rapid than with sodium.

(c) Solvent and Photolytically Induced Reactions. When $Fe_3(CO)_{12}$ is dissolved in dry THF under vacuum, a complicated decomposition process occurs and the following points have been noted:

(i) Within a few minutes of being prepared at ambient temperatures, the green solutions display two ESR signals A and B.

(ii) If a solution is left in sunlight, a gradual color change from green to mauve is observed over a period of some hours, together with an increase in the intensity of signal B. However, experiments carried out in the dark also produced the two paramagnetic species but the solutions remained green, even after several hours. Solutions kept away from light for several hours and which showed a strong signal B did, however, upon exposure to light rapidly become mauve, and this was accompanied by a decrease in the intensity of line B. The diamagnetic purple-red colored compound, shown by its electronic and infrared spectra to be $HFe_3(CO)_{11}^-$ is thus formed in a photolytic reaction, possibly involving species B.

(iii) Intense UV/visible photolysis ($\lambda > 350$ nm) leads to a much enhanced rate of formation of species B but also rapidly destroys the radical anion $[Fe_3(CO)_{12}]^{-}\cdot$. Following photolysis at 233 K, line B was observed to decrease with time while that of $[Fe_3(CO)_{12}]^{-}\cdot$ increased rapidly.

(iv) The addition of carbon monoxide to a solution containing both species B and $[Fe_3(CO)_{12}]^{-}\cdot$ led to the immediate disappearance of the ESR line of B while, in keeping with the electrochemical results, that of the radical anion was unaffected.

(v) Solutions prepared at low temperatures did not display any ESR signals until heated above 273 K.

(vi) On admission of air to any solution all paramagnetic species were rapidly destroyed and the mauve coloration was also lost. Analysis of the resultant solutions always showed the presence of $Fe(CO)_5$, $Fe_3(CO)_{12}$, and large amounts of insoluble material.[21]

Solutions of $Fe_3(CO)_{12}$ in 1,2-dimethoxyethane (DME) or acetone showed similar behavior to that described for THF solutions. The two paramagnetic species, B and $[Fe_3(CO)_{12}]^{-}\cdot$, gave lines of identical shape and g value in all solvents while the mauve coloration was also common to all aged solutions. The rate of production of species B and $[Fe_3(CO)_{12}]^{-}\cdot$ appeared to be greater in DME than in THF. In contrast, however, degassed dichloromethane solutions exhibited no ESR signals in the absence of an external reducing agent nor was any mauve coloration detected even in solutions several days old.

Iron Pentacarbonyl and Diiron Enneacarbonyl. A THF solution of $Fe(CO)_5$ when passed over a sodium mirror darkened to orange-brown. This solution gave a strong signal C. Immediately after exposure to air the solution became red and signal C was replaced by B and that of $[Fe_3(CO)_{12}]^{-}\cdot$. Further aerial oxidation resulted in a green solution which was shown to contain $Fe_3(CO)_{12}$ but no paramagnetic species.

Diiron enneacarbonyl is notorious for its insolubility in common organic solvents but it has been found to dissolve with reaction in THF, initially giving an orange solution containing $Fe(CO)_5$ and $Fe(CO)_4(THF)$.[22] If such a solution is reacted with a sodium mirror at ~233 K, a purple coloration becomes evident and paramagnetic species including $[Fe_3(CO)_{12}]^{-}\cdot$ appear. At 293 K, only lines B and C are observed. Once again, aerial oxidation destroys all paramagnetic species and results in a green solution containing $Fe_3(CO)_{12}$. The tetrahydrofuran solutions of $Fe_2(CO)_9$ not subjected to external reduction showed similar behavior to those of $Fe_3(CO)_{12}$. Thus, for aged solutions, the paramagnetic species B and $Fe_3(CO)_{12}^{-}\cdot$ were detected, as was a color change to purple-red. A deep red color has also been observed by Cotton when $Fe_2(CO)_9$ is stirred in THF under a flow of argon gas, but the species responsible was not identified.[22,23] If a similar preparative scale experiment is carried out under vacuum and the tetraethylammonium bromide added to the resultant solution, a purple-red solid can be obtained. This product was identified as $[Et_4N]^+[HFe_3(CO)_{11}]^-$.

Triiron Undecacarbonyl Dianion. It has been suggested[24] that $Fe_3(CO)_{11}^{-}\cdot$ may be the paramagnetic species giving rise to signal B. It was therefore of interest to investigate the redox behavior of its precursor $Fe_3(CO)_{11}^{2-}$. A number of cyclic voltammograms on solutions of $Fe_3(CO)_{11}^{2-}$ were recorded but there was no suggestion of either a reduction or oxidation wave. Similar conclusions were reached from polarographic studies. Moreover, in situ electrolytic oxidation in the ESR cavity did not produce any paramagnetic species in the temperature range 293–203 K. It is therefore unlikely that $Fe_3(CO)_{11}^{-}\cdot$ could be produced from a chemical oxidation of $Fe_3(CO)_{11}^{2-}$ and its lifetime would be less than ~1 s at 203 K.

Monosubstituted Trinuclear Species, $Fe_3(CO)_{11}L$. (a) $Fe_3(CO)_{11}P(OPh)_3$. In THF, the lability of the substituted ligands was so high, especially upon reduction, that the only trinuclear radical anion that could be detected was the parent $[Fe_3(CO)_{12}]^{-}\cdot$. Therefore, reliable information on the substituted trimeric radical anions can only be obtained from electrolytic reductions in dichloromethane. The in situ electrochemical reduction of this compound in dichloromethane at 213 K produced the composite spectrum shown in Figure 4. The set of signals centered about $g = 2.005$ can be analyzed as consisting of two doublets, arising from two phosphite monosubstituted species ($I(^{31}P) = 1/2$) in which the phosphite ligands are in different environments, together with the signal of $[Fe_3(CO)_{12}]^{-}\cdot$. The phosphorus hyperfine coupling constants and g values for the two substituted species are as follows: (i) $\langle a \rangle^P = 23.5$ (2) G, $g = 2.005$ (2); (ii) $\langle a \rangle^P = 42$ (1) G, $g = 2.006$ (2). In view of the cyclic voltammetric data obtained for this compound[7] and the fact that the g values are close to those of $[Fe_3(CO)_{12}]^{-}\cdot$, the paramagnetic species (i) and (ii) can be assigned as two isomers of the radical anion $[Fe_3(CO)_{11}P(OPh)_3]^{-}\cdot$. The $[Fe_3(CO)_{12}]^{-}\cdot$ is a result of ligand dissociation from the substituted radical anion and not from an impurity in the original sample. This enhanced ligand dissociation upon reduction was also observed with the sub-

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[21] We were unable to repeat the observations on aerial stability reported in ref 11.

[22] Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.

[23] Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 3438.

[24] Krusic, P. *Int. Conf. ESR Spectrosc.* **1978**. Krusic, P., personal communication.

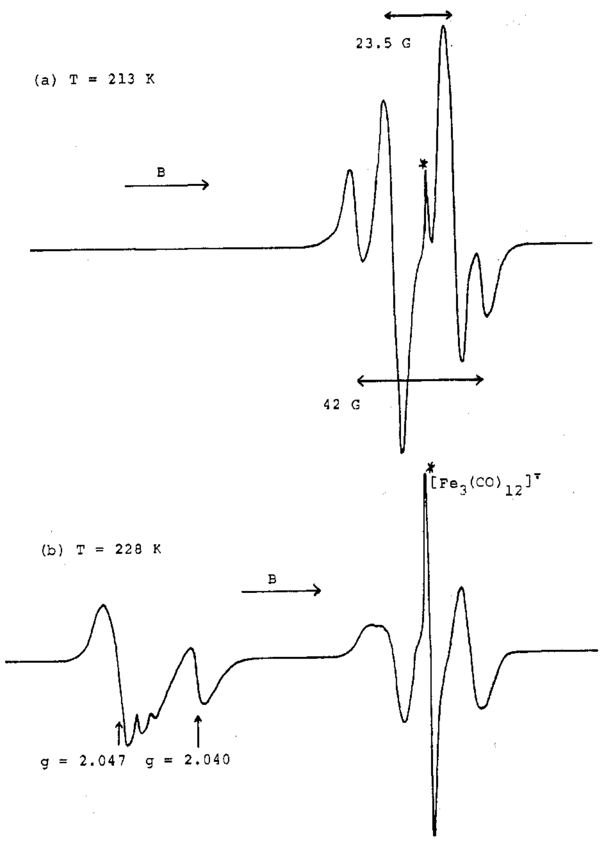

Figure 4. ESR spectra of electrochemically reduced $Fe_3(CO)_{11}P(OPh)_3$ (in CH_2Cl_2).

stituted tricobalt carbon clusters.[4]

When the temperature of the solution is raised, several effects on the ESR spectrum are noted. At 228 K the two doublet signals are less well-resolved while the signal due to $[Fe_3(CO)_{12}]^{-}\cdot$ appears to increase in intensity. The first effect could be due to both the faster exchange between the isomeric forms and the increased lability of the phosphite ligands at the higher temperature. In addition to the large $[Fe_3(CO)_{12}]^{-}\cdot$ signal, this decreased stability is also shown by the appearance of additional paramagnetic species due to decomposition products (Figure 4). These low-field species ($g = 2.047$ and 2.040) are analogous to those observed for $Fe_3(CO)_{12}$. At 233 K the signal of $[Fe_3(CO)_{12}]^{-}\cdot$ is dominant while that of the substituted radical anion is weak with only one pair of lines evident.

(b) $Fe_3(CO)_{11}P(OMe)_3$. Similar behavior was shown upon reduction of this compound, in dichloromethane, in that phosphorus hyperfine coupling was detected for the high-field signal at 203 K. However, only one pair of lines with a separation of 13 G was resolved. Ligand dissociation is apparently more facile with this derivative as the signal due to $[Fe_3(CO)_{12}]^{-}\cdot$ is very pronounced even at this temperature. Also, the appearance of additional signals ($g = 2.044$, 2.034) is indicative of the fragmentation of the substituted cluster radical anion. The only high-field signal present at 223 K is that of $[Fe_3(CO)_{12}]^{-}\cdot$. Several low-field signals are observed at 273 K and two of these ($g = 2.040$, 2.050) are probably due to the same decomposition products as obtained from $[Fe_3(CO)_{12}]^{-}\cdot$.

(c) $Fe_3(CO)_{11}PPh_3$. Ligand dissociation is so rapid upon reduction of this compound that the signal of $[Fe_3(CO)_{12}]^{-}\cdot$ appears immediately upon commencement of electrolysis (CH_2Cl_2, 213 K) and remains the only trinuclear radical anion observed, even at 193 K. Further, the inherent instability of phosphine substituted triiron compounds to cluster fragmentation is shown by the immediate appearance (213 K) of several overlapping low-field signals. At 233 K, these include singlets with $g = 2.044$ and 2.038 and a doublet at $g = 2.046$ ($\langle a \rangle^{P} = 26$ G). The latter signal could be due to the species $[Fe(CO)_4PPh_3]^{+}$ as TLC and infrared analysis of the solution following electrolysis showed the presence of significant amounts of both $Fe(CO)_4PPh_3$[13] and $Fe_3(CO)_{12}$. As the temperature is raised, the above signals collapse and are replaced by others in a complex process. The dominant signal at ambient temperatures is centered at $g = 2.049$.

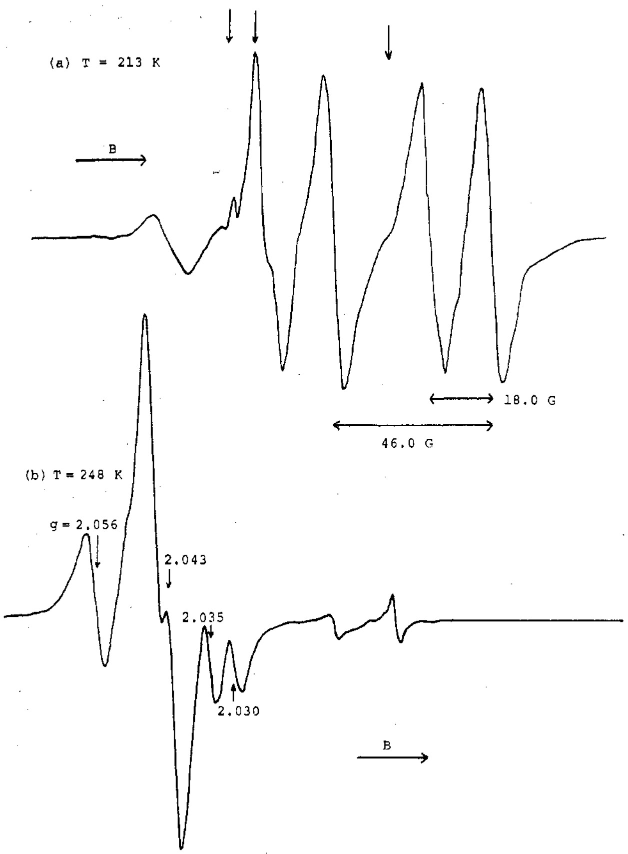

Figure 5. ESR spectra obtained from the electrochemical reduction of $Fe_3(CO)_{10}[P(OPh)_3]_2$ in CH_2Cl_2.

Disubstituted Trinuclear Species, $Fe_3(CO)_{10}L_2$. (a) $Fe_3(CO)_{10}[P(OPh)_3]_2$. Electrolytic reduction in dichloromethane at 213 K gave rise to the spectrum shown in Figure 5. This can be analyzed as a doublet of doublets arising from one species ($[Fe_3(CO)_{10}[P(OPh)_3]_2]^{-}\cdot$) containing two nonequivalent phosphorus nuclei. The hyperfine coupling constants $\langle a \rangle^{P}$ are 18.0 (5) and 46.0 (5) G while the g value is 2.003 (2). The line shapes are not symmetrical owing to the presence of other overlapping signals. At 248 K the original four lines have disappeared, leaving only the signal of $[Fe_3(CO)_{12}]^{-}\cdot$ at high field, together with several species of higher g value (Figure 5). This composite pattern of signals at low field continues to vary as the temperature is raised. Analysis of the final solution by IR and TLC showed that the originally pure sample of $Fe_3(CO)_{10}[P(OPh)_3]_2$ now contained a trace of $Fe_3(CO)_{11}P(OPh)_3$ and a significant amount of $Fe(CO)_4[P(OPh)_3]$. If $Fe_3(CO)_{10}[P(OPh)_3]_2$ is reduced by sodium in THF, the signal of $Fe_3(CO)_{12}^{-}\cdot$ is observed together with a complex pattern of low-field signals similar to that described above. Signals at $g = 2.046$ and 2.033 are the dominant species at all temperatures.

(b) $Fe_3(CO)_{10}[P(OMe)_3]_2$. On reaction with sodium in THF at 233 K the initial deep green solution turned red-brown. The reduced solution showed no high-field ESR signals but a complex pattern centered around $g = 2.040$ was observed. The composite spectrum varied with temperature and at 293 K only one signal, a 1:2:1 triplet, was observed (g = 2.038 (2), $\langle a\rangle^P$ = 20.0 (5) G). This can be assigned to a cluster fragmentation product containing two equivalent phosphorus nuclei. Analysis of the solution following aerial oxidation showed $Fe(CO)_5$ and $Fe(CO)_4[P(OMe)_3]$ to be present.

Trisubstituted Trinuclear Species, $Fe_3(CO)_9L_3$. $Fe_3(CO)_9[P(OMe)_3]_3$. Although the cyclic voltammetric data showed that this species could be reversibly oxidized,[7] no ESR evidence for a radical cation could be obtained, in dichloromethane, at temperatures down to 193 K. Electrolytic reduction (213–253 K), however, produced a 1:2:1 triplet signal which was seen to be the same as that obtained from reduction of the disubstituted species above ($\langle a\rangle^P$ = 21.0 (5) G; g = 2.037 (2)). At 293 K an additional decomposition product with g = 2.050 was detected. Traces of both $Fe(CO)_4P(OMe)_3$ and $Fe(CO)_3[P(OMe)_3]_2$ were detected in solution following electrolysis.

Other Trinuclear Metal Carbonyls. (a) $Fe_2Ru(CO)_{12}$. The in situ electrochemical reduction of this species in dichloromethane, below 233 K, led to the observation of two sharp high-field ESR signals with g values of 2.002 and 1.996. The latter signal was much stronger at all temperatures and, in accord with the electrochemical data, can probably be assigned to $[Fe_2Ru(CO)_{12}]^{-\cdot}$. The other line most likely arises from $[Fe_3(CO)_{12}]^{-\cdot}$ on the basis of its g value. This species must be formed from the decomposition of $[Fe_2Ru(CO)_{12}]^{-\cdot}$ as TLC analysis before the electrolysis experiment showed no $Fe_3(CO)_{12}$ impurity to be present. At temperatures above 233 K neither high-field species is stable and the appearance of a third paramagnetic signal is noted. This species (g = 2.051) undoubtedly arises from the decomposition of the trinuclear radical anion and is probably the same as species B obtained from $Fe_3(CO)_{12}$.

(b) $FeRu_2(CO)_{12}$. Due to the difficulty of separation, the sample of this cluster used for ESR investigation contained some $Fe_3(CO)_{12}$. However, apart from a strong $[Fe_3(CO)_{12}]^{-\cdot}$ signal, a narrow line of g = 1.990 was detected when reduction was carried out on a dichloromethane solution below 213 K. This species was much less stable than either $[Fe_3(CO)_{12}]^{-\cdot}$ or $[Fe_2Ru(CO)_{12}]^{-\cdot}$ and may be assigned to the radical anion $[FeRu_2(CO)_{12}]^{-\cdot}$.

(c) $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. Reduction of $Ru_3(CO)_{12}$ with sodium in THF gave one paramagnetic species (g = 1.982) which was unstable above 233 K. Below 193 K satellite signals due to ruthenium hyperfine coupling (9 G) were discernible.[8] Sodium reduction of $Os_3(CO)_{12}$ in THF produced a broad signal[8] of g = 2.001 over a wide temperature range. No low-field ESR signals were observed for either $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$.

Discussion

There is no doubt that the sharp high-field ESR signals around g = 2.003 are due to the trinuclear radical anions $[Fe_3(CO)_{12-n}L_n]^{-\cdot}$ (n = 0–2); the assignment for $Fe_3(CO)_{12}^{-\cdot}$ is supported by other workers.[9,24] It is interesting that g values of all $[Fe_3(CO)_{12-n}L_n]^{-\cdot}$ species are close to the free-electron value, as are the g values for other metal carbonyl cluster anions.[1,2,4,25] This suggests that there is little mixing of excited or lower levels with the orbital containing the odd electron and that this orbital is delocalized and largely metal in character. Nonetheless, ^{13}C coupling is seen for $[Fe_3(CO)_{12}]^{-\cdot}$ but has not been detected for other cluster radical anions. This could be due to either (a) the ESR spectral lines being too broad in the other species or (b) more "carbonyl" character in the $Fe_3(CO)_{12}$ LUMO. Explanation (a) is more likely since, of the systems studied, only the iron compounds give no hyperfine coupling to the metal nuclei.

The kinetic consequence of Lewis base substitution on $Fe_3(CO)_{12}$ is such that, as the degree of substitution increases, the lifetime of the corresponding radical anion species progressively decreases. At low temperatures the mode of decay is via disproportionation, as for other cluster radical anions[26] and organic radical anions.[27]

$$2[Fe_3(CO)_{12-n}L_n]^{-\cdot} \rightarrow Fe_3(CO)_{12-n}L_n + [Fe_3(CO)_{12-n}L_n]^{2-}$$

With the increased electron density on the iron in the substituted derivatives it is not surprising that this reaction is more facile. Two isomeric forms of $[Fe_3(CO)_{11}P(OPh)_3]^{-\cdot}$ were detected; one with a ^{31}P hyperfine coupling of 23.5 G, the other with $\langle a\rangle^P$ = 42 G. If the unpaired electron occupies an A_2 σ^* orbital (by analogy with a number of radical anions), then the large difference in $\langle a\rangle^P$ suggests that the phosphite ligand is in an equatorial ($\langle a\rangle$ = 42 G) or axial ($\langle a\rangle$ = 23.5 G) conformation rather than the two alternative equatorially substituted positions found[13] in the crystal structure of $Fe_3(CO)_{11}PPh_3$. Against this assignment is the body of evidence which shows that Lewis base ligands normally adopt an equatorial disposition.[28] In $Fe_3(CO)_{10}[P(OPh)_3]_2^{-\cdot}$ the two phosphite ligands are in nonequivalent environments ($\langle a\rangle^P$ = 42 and 18 G, respectively), but there was no evidence for isomers. In contrast, infrared and ^{13}C NMR studies show[30a] that, in solution at temperatures at which the anion is observed, the neutral molecule has a CO-bridged configuration and may exist as both diequatorial and diaxial isomers.

Alternative modes of decomposition to self-disproportionation are clearly accessible to $[Fe_3(CO)_{12-n}L_n]^{-\cdot}$ species at temperatures much above 213 K and in basic solvents. This decomposition gives rise to paramagnetic species, B and C, and diamagnetic species, particularly $Fe(CO)_5$. Before discussing the possible nature of B and C, several crucial points should be noted.

(1) A similar set of signals has been detected[31] at ambient temperatures in THF solutions of $NaHFe_2(CO)_8$ and various substrates such as *trans*-$CH_3CH{=}CHCO_2Et$; in the absence of substrates only C is found. Further, the concentration of C is independent of that of B and $Fe_3(CO)_{12}^{-\cdot}$, but the latter two species are directly related.

(2) B is definitely a product, not an intermediate, in the decomposition of $Fe_3(CO)_{12}^{-\cdot}$. It is not in a temperature-dependent equilibrium with $Fe_3(CO)_{12}^{-\cdot}$.

(3) In any experiment of the type outlined in this work the ESR technique detects the final product(s) in the experiment and the paramagnetic species may be in a low concentration relative to that of the initial reagent. Thus, in an experiment of the type

metal carbonyl + oxidant → paramagnetic products

the species giving the ESR spectra may not come from the primary reaction, particularly in a basic solvent like THF which can induce disproportionation and where paramagnetic species are formed even in the absence of an external reducing agent. Unless there is confirmatory electrochemical or other physical data, "proof" of the existence of a particular radical is suspect.

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(25) Rieger, P. H., unpublished work.

(26) Kirk, C. M.; Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J., manuscript in preparation.

(27) Garst, J. F. "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 503.

(28) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285.

(29) Although isomers of the neutral species are not "frozen out" during low-temperature ^{13}C NMR investigations,[31] it appears that the shorter time scale of the ESR experiment is allowing this observation to be made here.

(30) (a) Mays, M. J., personal communication. (b) Robinson, B. H., unpublished work. (c) Milone, *Inorg. Chem. Symp.* **1978**.

(31) Collman, J. P.; Fink, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 1119.

(4) The g values and temperature-dependent line shapes of B and C are not typical of a cluster where the electron resides in a σ^* orbital[1,2,4,25] or where the electron has been removed from the HOMO orbital, but are reminiscent of those for mononuclear 17-electron radicals[32,34] or Fe(I) compounds.[33]

(5) Hydrido species are rapidly produced in THF but not CH_2Cl_2. Extensive reduction leads ultimately to the elimination of paramagnetic species.

(6) Although thermally more stable than $Fe_3(CO)_{12}^{-}\cdot$, B is much more reactive toward substrates such as O_2, CO, and alkenes. Nonetheless, it did not function as an electron-transfer reagent toward TNN which suggests that it is not a radical anion.

(7) The redox behavior in CH_2Cl_2 is not complicated by reactions with the solvent. For example, hydrido species are not produced, yet B is observed at ambient temperatures and is thus unlikely to result from a base-induced disproportionation of $Fe_3(CO)_{12}^{-}\cdot$. A clue to the mode of decomposition comes from our electrochemical data[7] (confirmed by Vlcek[9]). In the cyclic voltammograms of $Fe_3(CO)_{12}$ recorded at 293 K (see Figure 3, ref 7) there is a significant oxidation wave at ~0.50 V vs. Ag/AgCl which is not found at 203 K nor in scans where the switching potential was insufficiently negative to produce the *dianion* $Fe_3(CO)_{12}^{2-}$. Since the other minor waves on the reverse scan are at potentials typical of couples involving mono- or dinuclear iron species, we attribute this wave at 0.50 V to the irreversible oxidation of B produced from the *dianion*. The absence of B at lower temperatures reflects the increased stability of the dianion at this temperature and the kinetic influence of the reverse reaction of $Fe_3(CO)_{12}^{2-}$ with $Fe_3(CO)_{12}$, as suggested by Vlcek.[9] The cyclic voltammograms in THF are exceedingly complex as many electroactive species are produced after the first reduction to $Fe_3(CO)_{12}^{-}\cdot$, even at 203 K.

(8) The phosphite-substituted trinuclear derivatives gave species corresponding to B which retain the phosphite ligand. This again is inconsistent with a cluster anionic species. Connelly[33a] has investigated several iron(I) phosphine compounds formed by chemical or electrolytic oxidation of Fe(0) derivatives and the g values and $\langle a\rangle^{P}$ are very similar to those found in this work.

An assignment of C to $Fe_2(CO)_8^{-}\cdot$ (or phosphite-substituted species) is consistent with our data, with Collman and coworkers' interpretation,[31] and with the elegant work of Krusic and co-workers.[24] It is interesting that no hyperfine coupling to cesium was observed on signal C in a situation where tight ion-pair formation was anticipated[31] and in a species where there will be considerable spin density on the carbonyl groups participating in a cation–anion interaction.

There must be considerable doubt as to the nature of B. Collman et al.[31] believed it to be $HFe(CO)_4\cdot$ but the absence of proton hyperfine coupling makes this unlikely. Krusic[24] has suggested that it is $Fe_3(CO)_{11}^{-}\cdot$ and, although this explanation is attractive, we find it untenable because of the various points raised above and for the following reasons. There is no electrochemical evidence for an oxidation pathway for $Fe_3(CO)_{11}^{2-}$; in situ oxidation of $Fe_3(CO)_{11}^{2-}$ in the ESR cavity did not produce any paramagnetic species *in the absence of THF*. Furthermore, $[Fe_3(CO)_{11}]^{2-}$ disproportionates slowly in THF but rapidly in the presence of basic phosphines or phosphites to give $Fe_3(CO)_{12-n}L_n$ derivatives.[30b] The reported[24] oxidation of $Fe_3(CO)_{11}^{2-}$ by Ag^+ could be due to a Ag^+-catalyzed disproportionation. Finally, on cooling of a THF solution containing B and $Fe_3(CO)_{12}^{-}\cdot$, the relative concentration of $Fe_3(CO)_{12}^{-}\cdot$ increases without a concomitant increase in B.

In our opinion, B is probably due to an Fe(I) species arising from decomposition of the dianions in CH_2Cl_2 and both the dianions and radical anions in THF.[34] Several sequences of disproportionation reactions can be written; some possibilities for $Fe_3(CO)_{12}$ that are supported by electrochemical synthetic or ESR evidence[24,30b] are shown (similar equations can be written for phosphite-substituted derivatives).

$$2Fe_3(CO)_{12}^{-}\cdot \rightarrow Fe_3(CO)_{12} + Fe_3(CO)_{12}^{2-} \text{ (fast at 293 K)}$$

$$2Fe_3(CO)_{12}^{2-} \rightarrow 3Fe(CO)_4^{2-} + \underset{\textstyle B}{2Fe(I)} + Fe(CO)_5 + 7CO$$

$$Fe(CO)_5 + Fe(CO)_4^{2-} \rightarrow (\underset{\textstyle C}{2Fe(CO)_4^{-}\cdot \rightleftarrows} Fe_2(CO)_8^{2-}) + CO$$

The formation of hydrido species and eventually $[HFe_3(CO)_{11}]^-$ in THF could involve hydrogen abstraction from the solvent either by a radical-induced or photolytic reaction or via proton transfer. Both types of mechanism are known to occur in THF[31,36,37] (see also the discussion in ref 31).

$$[Fe(CO)_4]^{-}\cdot + C_4H_8O \rightarrow [Fe(CO)_4H]^- + [C_4H_7O\cdot]$$

$$Fe_3(CO)_{12}^{-}\cdot + C_4H_8O \xrightarrow{h\nu} [HFe_3(CO)_{11}]^- + [C_4H_7O\cdot] + CO$$

$$HFe(CO)_4^- + 2Fe(CO)_5 \rightarrow HFe_3(CO)_{11}^- + 3CO$$

An alternative route to the $HFe_3(CO)_{11}^-$ anion for $Fe_3(CO)_{12}$ is well-established however, namely, disproportionation of $Fe_3(CO)_{12}$ and hydrogen ion transfer in basic solvents,[38] and while this is a slow reaction under normal conditions it is accelerated under irradiation and by the presence of radical initiators.[30b] The involvement of disproportionation reactions as postulated is entirely consistent with the known chemistry of iron carbonyls and are similar to those recently established in the redox chemistry of dimanganese dodecacarbonyl.[39] There is ample precendent in the chemistry of organic radical anions for the intermediacy of dianions in decomposition and disproportionation reactions,[40] and we consider they will play an important role in the chemistry of organometallic radical anions.

Our ESR work provides further evidence[22,23] that, when $Fe_2(CO)_9$ "dissolves" in THF, the solutions contain $Fe_3(CO)_{12}$ and $Fe(CO)_5$ and that the red color noted by Cotton is probably due to $HFe_3(CO)_{11}^-$ and $Fe_2(CO)_8^{2-}$. If the sequence of disproportionation reactions promulgated above are correct, $Fe(CO)_5$ should not give B upon reduction, as indeed is the case. The reduction of $Fe(CO)_5$ with Na produces $[Fe(CO)_4]^{2-}$ initially, a statement supported by the electrochemical results[7] and earlier chemical redox studies,[10a] while the orange

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(32) Muetterties, E. L.; Sosinsky, B. A.; Zamarev, K. I. *J. Am. Chem. Soc.* **1975**, *97*, 5299.

(33) (a) Connelly, N. G.; Somers, K. R. *J. Organomet. Chem.* **1976**, *113*, C39. (b) Connelly, N. G.; Kelly, R. L. *J. Organomet. Chem.* **1976**, *120*, C16. (c) Lappert, M. F.; Macquitty, J. J.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 411.

(34) The γ irradiation of iron carbonyls in MTHF at 77 K has been studied. One ESR signal was observed for $Fe(CO)_5$ ($g_\perp = 2.079$, $g_\parallel = 2.055$), *no signal* from $Fe_2(CO)_9$, and four signals ($g = 2.003$, intense, 2.070, 2.078, 1.091) from $Fe_3(CO)_{12}$. Apart from the $g = 2.003$ signal ($Fe_3(CO)_{12}^{-}\cdot$) the signals are completely different to those described in this paper. It is believed that they arise from loss of CO from the parent, with concomitant coordination by MTHF, i.e., $Fe(CO)_4MTHF^{-}\cdot$ (cf. ref 35) and $Fe_3(CO)_{12-x}^{-}\cdot$. Details will be published elsewhere. B. M. Peake and M. C. R. Symons, submitted for publication in *Inorg. Chim. Acta*.

(35) Black, J. D.; Braterman, P. S. *J. Organomet. Chem.* **1975**, *85*, C7.

(36) Dobbs, A. J.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc. A* **1971**, 124.

(37) Kirk, C. M., unpublished work in these laboratories.

(38) Landsberg, J. M.; Katz, L.; Olsen, C. *J. Org. Chem.* **1972**, *37*, 930 and references therein.

(39) Huffadine, A.; Peake, B. M.; Robinson, B. H.; Simpson, J. *J. Organomet. Chem.* **1976**, *121*, 391 and references therein.

(40) Szwarc, M. "Ions and Ion Pairs in Organic Reactions"; Wiley: New York, 1974; Vol. 2, Chapter 1.

color subsequently observed is indicative of the formation of $Fe_2(CO)_8^{2-}$. On exposure of these solutions to air $[HFe_3(CO)_{11}]^-$ may be formed via the species $[HFe(CO)_4]^-$.

$$3[Fe(CO)_4H]^- \xrightarrow{O_2} [Fe_3(CO)_{11}H]^- + H_2 + CO_3^{2-}$$

Conclusion

The redox behavior of iron carbonyl compounds in basic solvents such as THF is extremely complex and these solvents should be avoided if definitive results are desired. Although the foregoing discussion gives a reasonable picture of the redox behavior of iron cluster compounds in CH_2Cl_2 and THF, there could be other species that have not been characterized. For example, a weak, sharp signal, $g = 2.013$, on which ^{13}C coupling can be recognized, appears in some spectra, especially in those involving photolytic reactions of $Fe_3(CO)_{12}$. A radical anion of a cluster of higher nuclearity? Paramagnetic species may account for only a small percentage of the total present.[41] Nonetheless, they must be considered as possible intermediates in reactions of iron carbonyl compounds in organic solvents and many of the mechanisms postulated for catalysis by $Fe_3(CO)_{12}$ could be questioned. As a corollary, catalysis using $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ may be more efficient using electrolytically reduced solutions. This concept is currently being explored in these laboratories.

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Registry No. $Fe_3(CO)_{12}$, 17685-52-8; $Fe_3(CO)_{11}P(OPh)_3$, 55787-43-4; $Fe_3(CO)_{10}[P(OPh)_3]_2$, 63104-18-7; $Fe_3(CO)_{11}P(OMe)_3$, 63104-15-4; $Fe_3(CO)_{11}PPh_3$, 12101-59-6; $Fe_3(CO)_{10}[P(OMe)_3]_2$, 63104-16-5; $Fe_3(CO)_9[P(OMe)_3]_3$, 63104-17-6; $Fe_2Ru(CO)_{12}$, 20468-34-2; $FeRu_2(CO)_{12}$, 12388-68-0; $Ru_3(CO)_{12}$, 15243-33-1; $Os_3(CO)_{12}$, 15696-40-9; $Fe_2(CO)_9$, 15321-51-4; $[Et_4N][HFe_3(CO)_{11}]$, 55976-22-2; $[Fe_3(CO)_{12}]^{-\cdot}$, 55787-46-7.

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[41] We have found that the majority of polynuclear iron carbonyls when dissolved in basic or protic solvents, and even CH_2Cl_2, under strictly anaerobic conditions will give signals in an ESR spectrum unless the samples are extremely pure. In some instances the signals appear even though oxygen is present (see also ref 31).

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Ligand Field Studies of Phosphine π Acidity and d–s Mixing in *trans*-Dimesitylbis(diethylphenylphosphine)cobalt(II) and Analogues

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The complete paramagnetic susceptibility tensor of crystals of the planar coordinated system *trans*-dimesitylbis(diethylphenylphosphine)cobalt(II) has been measured by the Faraday technique throughout the temperature range 20–300 K. These single-crystal susceptibility data together with the ESR *g* values and solution electronic spectra of the present complex and its analogues when mesityl is replaced by α-methylnaphthyl or pentafluoro- or pentachlorophenyl (reported earlier) have all been quantitatively reproduced within a common theoretical model. The ligand field is parameterized by the angular overlap model, which is unable to account for the energy of the d_{z^2} orbital (where *z* lies perpendicular to the coordination plane), and by an orbital energy parameterization scheme. The results demonstrate (i) a considerable degree of π acceptance by the phosphine ligands, (ii) a marked Naphelauxetic reduction of F_2 and F_4 values, (iii) a depression by several thousand wavenumbers of the d_{z^2} orbital, ascribed to a d–s configurational mixing process, and (iv) a role, by comparisons throughout the series of four complexes, for the hydrogen atoms of the α-methyl groups in the mesityl (and presumably naphthyl) derivatives, which lie close to the central metal, in the d–s mixing process.

Introduction

This study concerns the ligand-field properties of a series of four low-spin, planar-coordinated complexes of cobalt(II). The only member of the series for which an X-ray structure analysis is available[1,2] is *trans*-dimesitylbis(diethylphenylphosphine)cobalt(II), the molecular structure of which is represented in Figure 1. The four-coordinate ligation of the metal atom appears to result from a steric blocking of the potential fifth and sixth sites of an idealized octahedron by the α-methyl groups of the mesityl ligands. A similar rationalization of the stoichiometry, and closely similar electronic properties, serves for the analogous complex in the series in which the mesityl groups are replaced by α-methylnaphthyl ligands. No doubt steric hindrance is less marked in two further analogues in which mesityls are substituted by pentafluoro- or pentachlorophenyl ligands.

An earlier electron spin resonance study,[3] based on single-crystal measurements on the pure mesityl complex and on the cobalt-doped nickel(II) analogue, revealed a rhombic **g** tensor, with principal directions lying close to the axes of Figure 1, which is highly anisotropic with $g_x = 3.72$, $g_y = 1.96$, and $g_z = 1.74$. These *g* values were quantitatively reproduced within a model spanning the strong field, spin-doublet configurations which result without participation of the, presumed high-lying, $d_{x^2-y^2}$ orbital. Admixtures of these configurations into the ground configuration were calculated by using perturbation theory, the final choice of ground level being made by reference to both **g** and hyperfine **A** tensors. It was ultimately dem-

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(1) P. G. Owston and J. M. Rowe, *J. Chem. Soc.*, 3411 (1963).
(2) L. Falvello and M. Gerloch, *Acta Crystallogr. Sect. B*, **35**, 2547 (1979).
(3) R. B. Bentley, F. E. Mabbs, W. R. Smail, M. Gerloch, and J. Lewis, *J. Chem. Soc. A*, 3003 (1970).