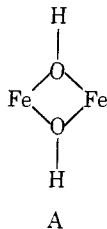


Figure 5. The proposed structure of the  $\mu$ -dihydroxo-octaaquodiiron(III) dimer in a 0.023 M perchloric acid solution.

oxygen distances described above. In Figure 4 both  $F(k)$  and  $\chi(k)$  have been multiplied by  $k^2$  to better illustrate the fit at high  $k$ .

The nonlinear least-squares fitting techniques were not applied to the peak in  $|\phi(r)|$  at 2.42 (4) Å because of significant contributions to this peak from its neighbors.<sup>12</sup> However, assuming this peak is due to iron backscattering, we find an iron-iron distance of 2.91 (6) Å. We have used an empirical phase shift (linear in the  $k$  dependent term) of 0.49 (4) Å determined from an iron metal standard in making this assignment. Additional uncertainty in  $E_0$  between standard and sample does not appreciably change the stated uncertainty in the iron-iron distance.

These results lead to the structure model for the iron(III) dimer, **1**, as that shown in Figure 5, where each iron(III) is octahedrally coordinated to two  $\text{OH}^-$  ligands and to four  $\text{H}_2\text{O}$  molecules. A planar ring, A, is postulated resulting in Fe-



$\text{OH-Fe}$  bond angles of  $101^\circ$  and  $\text{HO-Fe-OH}$  bond angles of  $79^\circ$ . These angles compare well with the  $103.2^\circ$   $\text{Fe-OH-Fe}$  and  $76.4^\circ$   $\text{HO-Fe-OH}$  bond angles reported for the crystalline model compounds mentioned above.<sup>11</sup> The structural data for **1** is similar to the published structure of  $[(\text{H}_2\text{O})_4\text{AlOH}]_2^{4+}$ ,<sup>13</sup> where the Al-Al distance is 2.86 Å and the Al-OH-Al angle is  $100.4^\circ$ . The Fe-Fe distance which we have observed allows for the ionic radii increase from  $\text{Al}^{3+}$  to  $\text{Fe}^{3+}$ . This iron(III) dimer model is consistent with a paramagnetic dimer with weakly coupled electron spins due to the relatively short 2.91 (6) Å Fe-Fe interaction.<sup>3b</sup>

The radial distribution function  $|\phi(r)|$  shows peaks above the Fe-Fe dimer distance. Rather than attributing these peaks to additional ordering of molecules about the dimer in solution, which may be a possibility, we feel that they are primarily due to high frequency noise in the data and the formation of a high molecular weight oxo- and hydroxo-bridged iron(III) polymer.<sup>4,12</sup> This polymer is currently the subject of an EXAFS study in our laboratory.

We are encouraged by the present EXAFS results which show that structural data for light elements in solutions may be obtained. These results attest further to the sensitivity and subsequent value of EXAFS studies as a structural tool performed on laboratory instrumentation.

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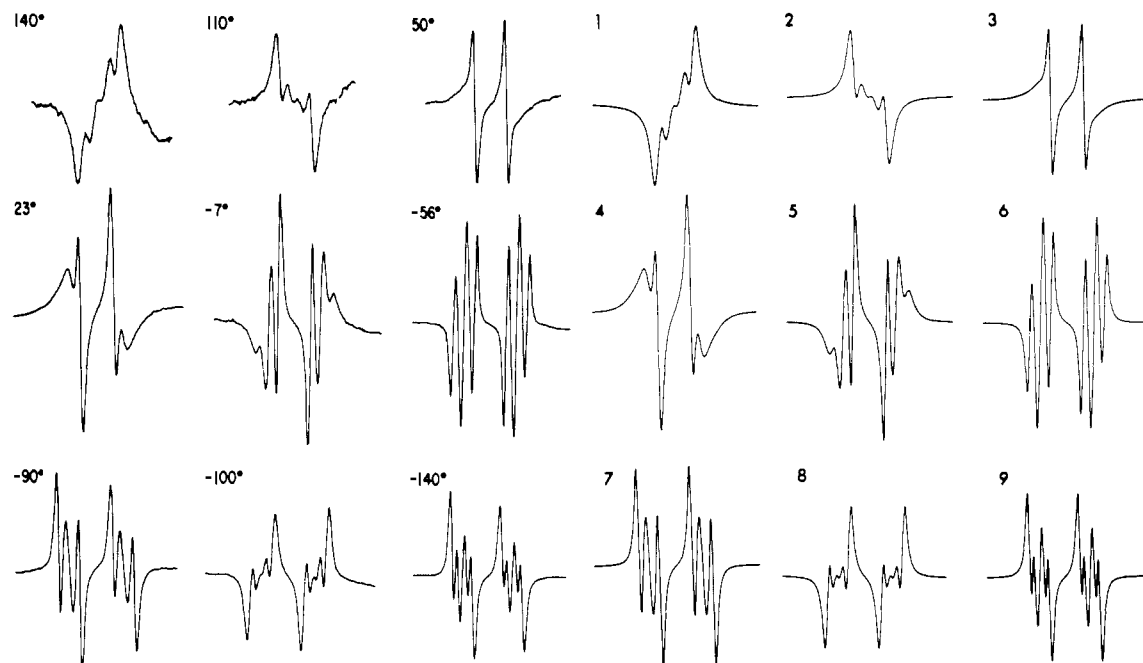
## An Electron Spin Resonance Study of the Fluxional Nature of Paramagnetic ( $\pi$ -Alkenyl)tris(trimethyl phosphite)iron Complexes

Sir:

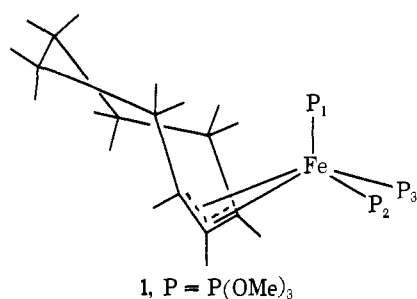
We wish to report the first examples of a new class of paramagnetic compounds,  $\text{Fe}[\text{P}(\text{OMe})_3]_3(\eta^3\text{-alkenyl})$ , which are fluxional on the ESR time scale as revealed by characteristic ESR line-shape changes as a function of the temperature. For organic radicals there exist extensive studies of temperature-dependent line-width effects.<sup>1</sup> This is the first example, however, of a transition-metal organometallic radical displaying such behavior as a result of the high mobility of its ligands in a pentacoordinate structure.<sup>2,3</sup>

It has been recognized for some time that the diamagnetic dimer  $[(\pi\text{-allyl})\text{Fe}(\text{CO})_3]_2$  exists in equilibrium with its paramagnetic monomer.<sup>4</sup> The latter can be considered as the progenitor of the organoiron radicals of this work. Addition of substituents to the allyl group as well as substitution of a carbonyl ligand with triphenylphosphine and other phosphine ligands inhibits the dimerization ostensibly for steric reasons. The tris(trimethyl phosphite) analogues of this study similarly show no tendency toward dimerization.<sup>5</sup>

Recently we reported the unusual 16-electron species  $[\text{Fe}[\text{P}(\text{OMe})_3]_3(\eta^3\text{-cyclooctenyl})][\text{BF}_4]$  prepared by protonation of  $\text{Fe}[\text{P}(\text{OMe})_3]_3(\eta^4\text{-1,3-cyclooctadiene})$ .<sup>6</sup> This compound undergoes a facile one-electron reduction in tetrahydrofuran (THF) with sodium amalgam to yield an isolable, air-sensitive, but thermally quite stable, dark blue-green paramagnetic species **1**, shown in a possible pseudo-square-pyramidal structure. Dilute solutions of this compound in hydrocarbon solvents are emerald green and afford ESR



**Figure 1.** ESR spectra of **1** at nine different temperatures. The rates ( $k_2, k_1$ ) used in the simulated spectra 1-9 follow: 1 ( $7 \times 10^{10}, 2.3 \times 10^9$ ), 2 ( $5 \times 10^{10}, 1.6 \times 10^9$ ), 3 ( $2 \times 10^{10}, 4 \times 10^8$ ), 4 ( $1 \times 10^{10}, 2 \times 10^8$ ), 5 ( $5 \times 10^9, 7.5 \times 10^7$ ), 6 ( $9 \times 10^8, 8.5 \times 10^6$ ), 7 ( $1.5 \times 10^8, 9.4 \times 10^5$ ), 8 ( $6.1 \times 10^7, 4.2 \times 10^5$ ), 9 ( $9.5 \times 10^6, 1 \times 10^5$ ).



spectra which change markedly as a function of the temperature (Figure 1).

At 140 °C, in tridecane as solvent,<sup>7</sup> a partially resolved quartet of  $20 \pm 1$  G is observed appropriate for a hyperfine interaction with three equivalent phosphorus nuclei. As the temperature is lowered, the two inner lines of the quartet first broaden at 110 °C and then disappear completely at 50 °C. With further lowering of the temperature, in pentane, two new lines develop gradually at each end of the spectrum resulting in two approximately binomial triplets at -56 °C which indicate the presence of a unique phosphorus nucleus with a hyperfine splitting of 100.5 G and a pair of phosphorus nuclei, equivalent on the ESR time scale, with an average splitting of 19.6 G. These changes are caused by a process which exchanges the unique phosphite and the two equivalent phosphite ligands of **1**. Opposite signs for the phosphorus coupling constants must be taken for the average  $|(a_1 + a_2 + a_3)|/3$  to be 20.4 G in close agreement with the observed quartet splitting at 140 °C. Further cooling to -90 °C results in the broadening of the central lines of each triplet which disappear completely at ca. -100 °C. A solvent of very low freezing point and viscosity, such as a 1:1 v/v mixture of cyclopropane and ethane, was required to maintain sufficiently narrow line widths (~10 G) to allow the resolution at -140 °C of the slow exchange limit of three inequivalent phosphite ligands with phosphorus coupling constants of 99.6, -27.9, and -10.5 G.<sup>8</sup> The  $g$  factor at this temperature is  $2.057 \pm 0.002$ . The line-width effect below -56 °C is caused by a second intramolecular rate process which modulates the phosphorus hyperfine interactions

of the two phosphite ligands with smaller couplings.

The available data are insufficient to define the mechanisms of the two rate processes which cause the observed line-shape effects. What is clear is that the lowest energy configuration of the molecule cannot have the plane of symmetry implied in structure **1**; all three phosphorus nuclei are in different environments. The low energy process which exchanges two nuclei but not the third cannot involve a conformational effect in the ring because we observe two analogous processes in the related allyl complex which is acyclic.<sup>9</sup>

The ESR spectra of **1** at 14 different temperatures were calculated as a function of two rates using a general ESR line-shape computer program<sup>11</sup> which takes into account two simultaneous exchange processes (Figure 1). The resulting Arrhenius plots led to the following expressions for the two rates:

$$k_1 = 1.1 \times 10^{12} \exp[-5.1(\text{kcal/mol})/RT]$$

$$k_2 = 9.1 \times 10^{12} \exp[-4.0(\text{kcal/mol})/RT]$$

Thus, the activation energy for the process which permutes all three phosphite ligands is 5.1 kcal/mol; this should be compared with 14.4 kcal/mol for the similar process in the related cationic precursor.<sup>6</sup> The activation energy for the faster, low energy process is 4.0 kcal/mol. The fluxional processes in this paramagnetic species are indeed quite fast since they proceed at rates of  $\sim 2 \times 10^8 \text{ s}^{-1}$  and  $10^{10} \text{ s}^{-1}$ , respectively, at room temperature.

The cycloheptenyl analogue of **1**, prepared by a similar technique, displays an almost identical fluxional behavior. The ESR parameters in the slow exchange limit (ethane solvent, -140 °C) follow:  $a_1^p = 100.9$ ,  $a_2^p = -28.0$ ,  $a_3^p = -12.4$  G;  $g = 2.056$ .

The simplest member of this family of 17-electron species,  $\text{Fe}[\text{P}(\text{OMe})_3]_3(\pi\text{-allyl})$ , can be formed in THF solution by sodium amalgam reduction of the 18-electron cationic species  $[\text{Fe}[\text{P}(\text{OMe})_3]_4(\pi\text{-allyl})]^+$  prepared by reaction of  $\text{Fe}[\text{P}(\text{OMe})_3]_5$  with allyl bromide in THF<sup>12</sup> and isolated as the  $\text{BPh}_4^-$  salt. In butane at room temperature, the spectrum is a partially resolved quartet (~17 G) which indicates that the permutation of the three phosphite ligands is much faster in



Figure 2. ESR spectrum of  $(\pi\text{-allyl})\text{Fe}[\text{P}(\text{OMe})_3]_3$  at  $-110^\circ\text{C}$  in ethane.

this species than in **1**, for which a temperature of  $140^\circ\text{C}$  was necessary for the complete averaging of the phosphorus couplings. At  $-80^\circ\text{C}$  in ethane the spectrum is analogous to that for **1** at  $50^\circ\text{C}$  (Figure 1) with an additional partially resolved triplet structure of  $\sim 5\text{ G}$  which must be assigned to the syn protons, i.e., the pair of protons of the allyl ligand which are replaced by carbons in the cycloalkenyl analogues. From this we estimate ( $\Delta E_a \sim T_a \Delta E_b / T_b$ ) that the activation energy for the process of higher activation energy ( $k_1$ ) is  $\sim 3\text{ kcal/mol}$ . At lower temperatures, complex spectra are observed (Figure 2) since the two processes are now proceeding at comparable rates. The slow exchange limit is not reached even at  $-140^\circ\text{C}$  where the spectrum has the appearance of a doublet of doublets (81.5 and 29 G) with the small triplet structure mentioned above being just discernible. The smaller of the two doublet splittings should correspond to  $a_2 + a_3$  giving a fast-exchange phosphorus splitting of  $17.5\text{ G}$ <sup>8</sup> in agreement with the observed quartet splitting at room temperature. Below  $-140^\circ\text{C}$  all lines broaden presumably by the slowing down of the tumbling motion of the molecule as a whole. Although the spectra have not yet been simulated, it is clear that the activation energy for the faster process ( $k_2$ ) must be less than the corresponding energy for **1**. Furthermore, it also follows that the lowest energy configuration of this species cannot have a plane of symmetry.

By extrapolation, it can be concluded that the progenitor of these species,  $(\pi\text{-allyl})\text{Fe}(\text{CO})_3$ , and its monophosphine derivatives<sup>4</sup> should also be viewed as highly fluxional molecules isostructural with their tris(trimethyl phosphite) analogues. Indeed, the observation<sup>4</sup> of a 17.5-G phosphorus doublet in  $(\pi\text{-allyl})\text{Fe}(\text{PPh}_3)(\text{CO})_2$  is entirely consistent with this view,

and it indicates that the phosphine ligand spends, on the average, equal time at the three sites available to it. Furthermore, this fluxionality may well be related to the ease with which the  $\pi$ -allylic ligand can be induced to form a  $\sigma$ -propenyl bond to iron in the presence of olefins,<sup>4b</sup> and it is thus of fundamental importance to a thorough understanding of the catalytic properties of these compounds.

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- (8) It is assumed arbitrarily that the largest coupling is positive.
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