Fe$_3$-Triangle Opening and Closing by a Single Two-Electron Process in the Bicapped Triiron Clusters Fe$_3$(CO)$_9$(μ_3-PML$_n$)$_2$ (ML$_n$ = CpFe(CO)$_2$, CpMn(CO)$_2$)

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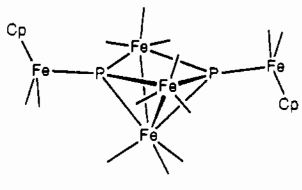
Received December 20, 1991

The structure of a metal cluster can often be rationalized by the total number of valence electrons it possesses.[1] The pathways for interconversion between structural types can be studied by electrochemical manipulation of the number of valence electrons.[2] Upon reduction of a saturated multimetal cluster, the M–M-bonded framework can undergo distortions along a variety of coordinates to minimize the antibonding interactions,[3] one possibility of which is a localized distortion resulting in cleavage of a single M–M bond[3a,4] analogous to what occurs in the case of a metal–metal-bonded dinuclear complex.[5] We report here the first definitive example of a multimetal cluster that undergoes *localized* bond cleavage and bond formation by a quasi-reversible, single 2-e$^-$ process relating the closed and open[6] Fe$_3$ cluster frames in complexes of formulation Fe$_3$(CO)$_9$(μ_3-PML$_n$)$_2$ (**1**, ML$_n$ = CpFe(CO)$_2$; **2**, ML$_n$ = CpMn(CO)$_2$). For the case of **2**, the reduction reaction to **2**$^{2-}$ was characterized by an X-ray structure determination of the 2-e$^-$ reduced product as well as an infrared spectroelectrochemical experiment that permitted observation of the 1-e$^-$ reduced intermediate.

The cluster Fe$_3$(CO)$_9$[μ_3-PFe(CO)$_2$Cp]$_2$ (**1**)[7] possesses an *open*-Fe$_3$(μ_3-P)$_2$ core (with two Fe–Fe bonds) and can be viewed as a 50-electron metallophosphine ligand, [Fe$_3$(CO)$_9$(μ_3-P)$_2$]$^{2-}$, that is coordinated to two CpFe(CO)$_2$$^+$ groups. The Fe$_3$(μ_3-P)$_2$ cluster core in **1** is isostructural with that in the bicapped phosphinidene clusters Fe$_3$(CO)$_9$(μ_3-PR)$_2$ (I).[8] A related cluster, Fe$_3$(CO)$_9$[μ_3-PMnCp(CO)$_2$]$_2$ (**2**), prepared by Huttner and co-workers,[9] has a neutral *closed*-Fe$_3$(μ_3-P)$_2$ core and can be viewed as a 48-electron metallophosphine ligand, Fe$_3$(CO)$_9$(μ_3-P)$_2$, that is coordinated to two neutral CpMn(CO)$_2$ groups. This study was initiated to explore the relationship between clusters with closed and open triangular cores.



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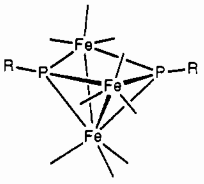

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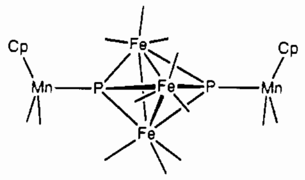

2

The cyclic voltammograms of **1** and **2** are shown in Figure 1;[10] the results for **2** will be discussed first. The 48-electron closed cluster **2** shows an electrochemically quasi-reversible *reduction* wave in CH$_3$CN solution at $E_{1/2}$ = –0.861 V vs Ag/0.1 M AgNO$_3$. The separation between the cathodic and anodic peaks, ΔE_p, is 36 mV at scan speeds of 25 mV s^{-1} or less,[11] suggesting that more than one electron is involved in the electrochemical process.[12] The bulk reduction[13] of **2** at –1.0 V proceeds with n_{app} = 2.0 faradays mol^{-1}, and the intensely brown-purple solution of **2** is replaced by a red-orange solution of **2**$^{2-}$ that is very similar in color to **1**.[14] The CO stretching frequencies of the two-electron reduced product are shifted by approximately 60 cm^{-1} to lower

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(1) See, for example: (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976,** *18,* 1. (b) Lauher, J. W. *J. Am. Chem. Soc.* **1978,** *100,* 5305. (c) Mingos, D. M. P. *Acc. Chem. Res.* **1984,** *17,* 311.

(2) For reviews, see: (a) Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985,** *24,* 87. (b) Geiger, W. E. *Prog. Inorg. Chem.* **1985,** *33,* 275. (c) Lemoine, P. *Coord. Chem. Rev.* **1988,** *83,* 169. (d) Drake, S. R. *Polyhedron* **1990,** *9,* 455. (e) Lemoine, P. *Coord. Chem. Rev.* **1982,** *47,* 55.

(3) In the 49-electron bicapped tricobalt clusters of formulation [Co$_3$(η^5-Cp)$_3$(μ_3-L)$_2$]$^+$, examples of uniform elongation of the three Co–Co edges, elongation of a single Co–Co edge, and elongation of two Co–Co edges with shortening of the third have been observed. (a) Pulliam, C. R.; Thoden, J. B.; Stacy, A. M.; Spencer, B.; Englert, M. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1991,** *113,* 7398. (b) Olson, W. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1986,** *108,* 7657. (c) Bedard, R. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1986,** *108,* 5942.

(4) There are very few clusters where an overall 2-e$^-$ process has been definitively associated with bond formation or bond breaking localized on a single M–M edge. See ref 3a and: (a) Lockemeyer, J. R.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989,** *111,* 5733. (b) Whitmire, K. H.; Shieh, M.; Lagrone, C. B.; Robinson, B. H.; Churchill, M. R.; Fettinger, J. C.; See, R. F. *Inorg. Chem.* **1987,** *26,* 2798.

(5) Reversible M–M bond cleavage occurs in many examples of bridged dinuclear complexes by either two sequential 1-e$^-$ steps or apparent 2-e$^-$ processes (see reviews in ref 2). For well-characterized examples of single 2-e$^-$ processes associated with M–M bond cleavage in dinuclear complexes see: (a) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982,** *21,* 146. (b) Connelly, N. G.; Lucy, A. R.; Payne, J. D.; Galas, A. M. R.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1983,** 1879. Freeman, M. J.; Orpen, A. G.; Connelly, N. G.; Manners, I.; Raven, S. J. *J. Chem. Soc., Dalton Trans.* **1985,** 2283. (c) Feng, D.; Schultz, F. A. *Inorg. Chem.* **1988,** *27,* 2144. Fernandes, J. B.; Zhang, L. Q.; Schultz, F. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1991,** *297,* 145. (d) Moran, M.; Cuadrado, I.; Masaguer, J. R.; Losada, J. *J. Chem. Soc., Dalton Trans.* **1988,** 833. (e) Moulton, R.; Weidman, T. W.; Vollhardt, K. P. C.; Bard, A. J. *Inorg. Chem.* **1986,** *25,* 1846. (f) Gaudiello, J. G.; Wright, T. C.; Jones, R. A.; Bard, A. J. *J. Am. Chem. Soc.* **1985,** *107,* 888. (g) Mann, K. R.; Rhodes, M. R. *Inorg. Chem.* **1984,** *23,* 2053. Hill, M. G.; Mann, K. R. *Inorg. Chem.* **1991,** *30,* 1431.

(6) In this paper the simplified terms open and closed will be used to represent nido and closo, respectively.

(7) Bautista, M. T.; White, P. S.; Schauer, C. K. *J. Am. Chem. Soc.* **1991,** *113,* 8963.

(8) Cook, S. L.; Evans, J.; Gray, L. R.; Webster, M. *J. Organomet. Chem.* **1982,** *236,* 367.

(9) Lang, H.; Huttner, G.; Zsolani, L.; Mohr, G.; Sigwarth, B.; Weber, U.; Orama, O.; Jibril, I. *J. Organomet. Chem.* **1986,** *304,* 157.

(10) Cyclic voltammograms were recorded in a single-compartment airtight three-electrode cell under nitrogen at room temperature. All potentials reported in this paper are converted to the Ag/AgNO$_3$ (0.1 M in CH$_3$CN) reference using the potential for the Cp$_2$Fe/(Cp$_2$Fe)$^+$ standard ($E_{1/2}$ = 0.042 V). In acetonitrile solution, a Ag/AgNO$_3$ reference electrode, which was separated from the analyte solution by placement in a vycor-tipped compartment, was employed. Electrochemical measurements in CH$_2$Cl$_2$ solution employed a Ag/AgCl reference electrode immersed in a 3 M aqueous sodium chloride solution in a separate vycor-tipped compartment.

(11) Experiments to obtain peak-to-peak separations were performed in acetonitrile solution utilizing a silver wire reference electrode. All cyclic voltammetry data were corrected for uncompensated resistance by the positive-feedback *iR* compensation method or by correcting the ΔE_p values using the peak-to-peak separation (ΔE_p (mV)) and anodic peak current (i_{pa}(μA)) observed for the Cp$_2$Fe/(Cp$_2$Fe)$^+$ standard couple.

(12) Polcyn, D. S.; Shain, I. *Anal. Chem.* **1966,** *38,* 370.

(13) Bulk electrolyses were performed at a Pt-mesh electrode in tetrahydrofuran solution with an electrolyte concentration ([n-Bu$_4$N][BF$_4$]) of 0.1 M and a sample concentration of 5 mM.

(14) The UV-vis spectra are available as supplementary material.

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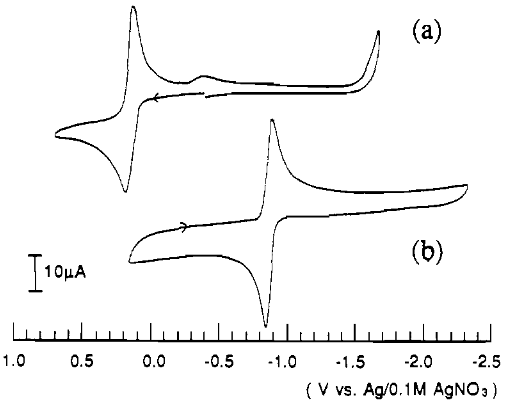

Figure 1. (a) Cyclic voltammograms (scan speed = 100 mV s^{-1}) of a ca. 1 mM solution of $Fe_3(CO)_9[\mu_3\text{-}PFe(CO)_2Cp]_2$ (**1**) in 0.1 M $[n\text{-}Bu_4N][BF_4]/CH_2Cl_2$ at a platinum working electrode. (b) Cyclic voltammogram (scan speed = 50 mV s^{-1}) of a ca. 1 mM solution of $Fe_3(CO)_9[\mu_3\text{-}PMn(CO)_2Cp]_2$ (**2**) in 0.1 M $[n\text{-}Bu_4N][BF_4]/CH_3CN$ at a glassy carbon working electrode.

energy.[15] The dianion $\mathbf{2}^{2-}$ is quite stable, and reoxidation back to **2** passes charge corresponding to n_{app} = 2.0 faradays mol^{-1}.

The reduction of **2** is one of a growing number of examples of apparent 2-e^- behavior in dinuclear complexes and metal clusters.[2,3c,4a,5,16] As opposed to the unlikely simultaneous addition of two electrons, an apparent 2-e^- reduction wave is typically attributed to two consecutive 1-e^- reductions where addition of the second electron occurs with nearly equal or greater facility than addition of the first.[17] The difference between the 1-e^- potentials is reflected in ΔE_p for the 2-e^- wave[17] and in the value of the disproportionation constant, K_{disp}, governing the equilibrium shown in eq 1 for the 1-e^- reduced species, $\mathbf{2}^-$. For cases where

$$2\,\mathbf{2}^- \overset{K_{disp}}{\rightleftharpoons} \mathbf{2}^{2-} + \mathbf{2} \tag{1}$$

the 1-e^- reduced product is observable, measurement of K_{disp} enables extraction of the individual one-electron potentials.[18] The strong carbonyl stretches in the infrared spectrum for **2** provide a sensitive spectroscopic tool for characterization of the electrochemical reduction reaction. Electrolysis of **2** in an infrared-transparent electrochemical cell reveals the strongest CO stretch for the mononegatively charged cluster radical at 1996 cm^{-1} (Figure 2), intermediate in energy between the stretches for **2** and $\mathbf{2}^{2-}$ as expected.[19] From analysis of the infrared data taken over the course of the electrolysis, the value $K_{disp} \approx 10$ is estimated,[20] implying that the second reduction occurs at a potential approximately 60 mV more positive than the first.[17] This value of $\Delta E_{1/2}$ predicts a value of ΔE_p equal to 34 mV,[17] which is in good agreement with the experimentally observed value of 36 mV.

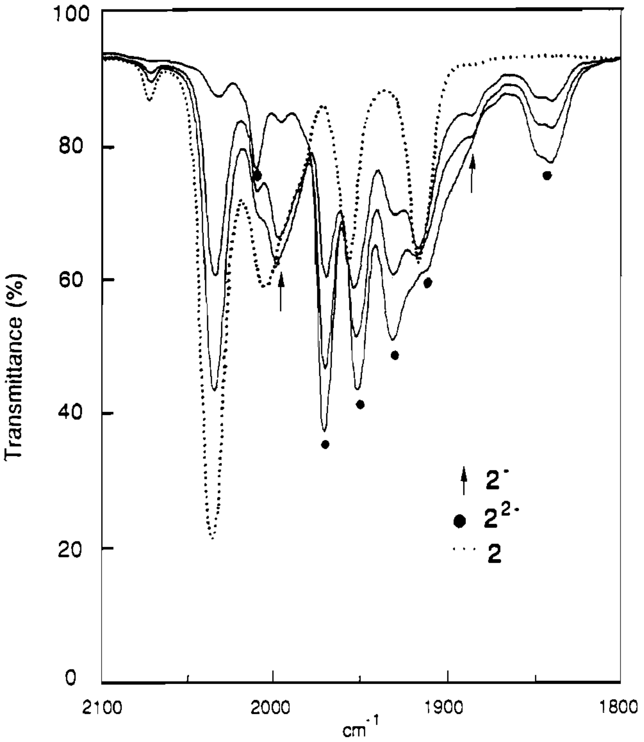

Figure 2. Plot of the infrared spectral changes as a function of time during the bulk electrolysis of $Fe_3(CO)_9[\mu_3\text{-}PMn(CO)_2Cp]_2$ (**2**) in an infrared-transparent electrochemical cell (0.1 M $[n\text{-}Bu_4N][BF_4]$/tetrahydrofuran).

Typically, the potentials for sequential addition of two electrons are well separated due to electrostatic repulsion between the first and second electrons. The fact that addition of the second electron to **2** is more favorable than addition of the first presumably results from a structural change that is coupled with the reduction.[21] A chemical reduction of **2** was performed,[22] and a single-crystal X-ray diffraction study of $[(Ph_3P)_2N]_2[\mathbf{2}^{2-}]$[23] (Figure 3) clearly shows that the closed Fe_3 frame in **2** has been transformed to an open Fe_3 frame isostructural with **1** (eq 4). The bonding Fe–Fe distances (2.660 (9) and 2.660 (9) Å) are much shorter than the

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(15) IR (ν_{CO}, THF, cm^{-1}) for $\mathbf{2}^{2-}$: 2011 (w), 1971 (vs), 1952 (s), 1931 (m), 1844 (w).

(16) (a) Tulyathan, B.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5960. (b) Barley, M. H.; Drake, S. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1657. (c) van der Linden, J. G. M.; Paulissen, M. L. H.; Schmitz, J. E. J. *J. Am. Chem. Soc.* **1983**, *105*, 1903. (d) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 14. (e) Hinkelmann, K.; Heinze, J.; Schacht, H. T.; Field, J. S.; Vahrenkamp, H. *J. Am. Chem. Soc.* **1989**, *111*, 5078. (f) Nembra, G.; Lemoine, P.; Gross, M.; Braunstein, P.; de Méric de Bellefon, C.; Ries, M. *Electrochim. Acta* **1986**, *31*, 1205. (g) Gourdon, A.; Jeannin, Y. *J. Organomet. Chem.* **1985**, *290*, 199. (h) Nemra, G.; Lemoine, P.; Braunstein, P.; de Méric de Bellefon, C.; Ries, M. *J. Organomet. Chem.* **1986**, *304*, 245.

(17) (a) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278. (b) Myers, R. L.; Shain, I. *Anal. Chem.* **1969**, *41*, 980. (c) Hinkelmann, K.; Heinze, J. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 243.

(18) The observed $E_{1/2}$ for an apparent 2-e^- wave for the reaction defined in eq 2 is an average of the potentials for the individual 1-e^- couples: $E_{1/2} \approx E^{0'} = (E^{0'}{}_1 + E^{0'}{}_2)/2$. Equation 3 relates the disproportionation constant to the difference between the 1-e^- potentials. These two expressions together enable extraction of $E^{0'}{}_1$ and $E^{0'}{}_2$.

$$A \overset{e^-,\,E^{0'}{}_1}{\rightleftharpoons} A^- \overset{e^-,\,E^{0'}{}_2}{\rightleftharpoons} A^{2-} \tag{2}$$

$$\Delta E_{1/2} \approx \Delta E^{0'} = E^{0'}{}_2 - E^{0'}{}_1 = \frac{RT}{F} \ln K_{disp} \tag{3}$$

(19) IR (ν_{CO}, THF, cm^{-1}, by spectral subtraction) for $\mathbf{2}^-$: 2040 (w), 1996 (vs), 1967 (m), 1958 (w sh), 1946 (w sh), 1930 (w sh), 1885 (w). A room-temperature EPR spectrum of $\mathbf{2}^-$ in tetrahydrofuran solution showed a broad singlet at g = 2.014. No well-resolved phosphorus coupling was observed (see supplementary material). The EPR sample was prepared by partial reduction (~70%) of a 7.6 mM solution of **2** by stirring over 4% Na/Hg amalgam.

(20) Because the spectra of **2**, $\mathbf{2}^-$, and $\mathbf{2}^{2-}$ severely overlap, it is necessary to estimate the concentration of $\mathbf{2}^-$ by spectral subtraction.

(21) Large heterogeneous electron-transfer rate constants (0.2 cm s^{-1}) were found for a series of dimers that exhibit significant structural changes as a result of the electron transfer. Several explanations are offered for this fact, including the possibility that the electron transfer is not kinetically coupled to the structural change. Gennett, T.; Geiger, W. E.; Willett, B.; Anson, F. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *222*, 151.

(22) A tetrahydrofuran solution of **2** was reduced by titration with a Na/benzophenone solution in tetrahydrofuran while the IR spectrum of the solution was periodically monitored. A color change from brown-purple to red-orange accompanies the reduction. When the reduction was complete, the solution was cannulated into a flask containing 2 equiv of $[(Ph_3P)_2N]Cl$ and stirred overnight. The solvent was removed under vacuum, the residue was washed with MeOH and then dissolved in CH_2Cl_2. Layering the CH_2Cl_2 solution with Et_2O yielded crystalline $[PPN]_2[\mathbf{2}^{2-}]$. A single ^{31}P NMR resonance attributable to $\mathbf{2}^{2-}$ was observed at δ 590 ppm in CH_2Cl_2 solution.

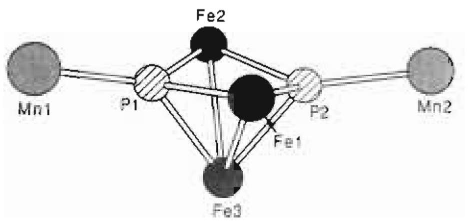
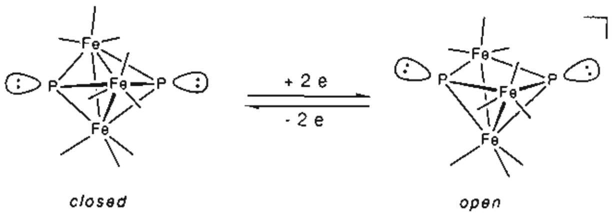


Figure 3. Ball and stick diagram of the metal–phosphorus core from the crystal structure of $[PPN]_2[Fe_3(CO)_9(\mu_3\text{-}PMn(CO)_2Cp)_2]\cdot 0.6CH_2Cl_2$. Selected distances (Å): Fe1–Fe3 = 2.660 (9), Fe2–Fe3 = 2.660 (9), Fe1···Fe2 = 3.532 (10), P1···P2 = 2.768 (17), Fe1–P1 = 2.301 (14), Fe1–P2 = 2.247 (14), Fe2–P1 = 2.232 (14), Fe2–P2 = 2.251 (14), Fe3–P1 = 2.239 (12), Fe3–P2 = 2.204 (14), Mn1–P1 = 2.245 (14), Mn2–P2 = 2.282 (14).

nonbonding interaction (3.532 (10) Å). Extended Hückel calculations[24] were performed on **2** to examine the character of the orbitals involved in the electrochemistry. The picture that emerges from these calculations is quite similar to that found in Fenske–Hall calculations performed on the triangular cluster $Fe_3(CO)_9(\mu_3\text{-}S)_2$ in both a symmetrical geometry with three equivalent Fe–Fe bonds and a distorted geometry with one elongated Fe–Fe edge.[25] The LUMO is an in-plane antibonding a′ symmetry orbital (in C_{3h} symmetry) of primarily d_{xz} character. Upon distortion of the structure by elongation of a single Fe–Fe edge, a more stable *localized* Fe–Fe antibonding orbital is produced by mixing the a′ LUMO with the next higher lying orbital of a′ symmetry (derived from an e′ set of orbitals in C_{3h} symmetry based on d_{xz} orbitals). The energetic consequences of the Fe–Fe bond elongation and other coupled structural changes that take place along the two-step electron-transfer reaction coordinate must result in the second electron transfer being thermodynamically favored over the first, despite the unfavorable electrostatic considerations.

The 50-electron open cluster **1** is electrochemically less well-behaved than **2** (see Figure 1). A chemically and electrochemically quasi-reversible *oxidation* wave is observed in CH_2Cl_2 solution at $E_{1/2}$ = 0.160 V (ΔE_p = 48 mV at scan speeds of 50 mV s^{-1} or less) presumably the reverse of the process observed in the reduction wave for **2** (see eq 4). The lack of complete chemical reversibility is evidenced by the peak on the reverse scan at E_{pc} = –0.4 V, which is more pronounced at slower scan speeds and in the more coordinating solvents tetrahydrofuran and acetonitrile. A cyclic voltammogram was obtained of a solution containing equimolar amounts of **1** and **2**, and the calculated ratio, $i_{pa}(\mathbf{1})/i_{pc}(\mathbf{2})$ = 1.0, confirms the involvement of



(4)

two electrons in the wave for **1**. Although the instability of the oxidized product $\mathbf{1}^{2+}$ precludes a detailed characterization of the disproportionation equilibrium, the ΔE_p value observed in the cyclic voltammogram suggests it is slightly less thermodynamically favorable to remove the second electron than the first.[26] On the basis of the analogy of the behavior for **2** reported above, the unstable oxidized product, $\mathbf{1}^{2+}$, is suggested to have a closed structure like **2**.

The phenylphosphinidene cluster $Fe_3(CO)_9(\mu_3\text{-}PPh)_2$,[27] which is isostructural with **1**, displays very different electrochemical behavior. Two chemically reversible 1-e$^-$ reductions ($E_{1/2}$ = –1.18 and –1.67 V) and an irreversible ca. three-electron oxidation ($E_p{}^a$ = 0.99 V) are observed. Consistent with the view that the cluster core in **1** is formally dinegatively charged (see above), the oxidation of **1** is more facile and the reduction of **1** more difficult than for $Fe_3(CO)_9(\mu_3\text{-}PPh)_2$.

In the cases of **1** and **2**, the opening and closing of the Fe_3 triangle occurs by an apparent 2-e$^-$ process. Dahl and co-workers recently reported conversion of the open cluster $[Co_3(C_5H_4Me)_3(\mu_3\text{-}S)_2]$ (**3**) to the closed cluster, $\mathbf{3}^{2+}$, in two 1-e$^-$ steps separated by 0.8 V.[3a] The structures of **3** and each of the oxidized products show that the successive oxidations are accompanied by shortening of the Co–Co nonbonding distance (3.19 Å for **3**, 2.87 Å for $\mathbf{3}^{+}$, and 2.52 Å for the equilateral triangle in $\mathbf{3}^{2+}$), similar to the net structural changes involved in interconverting $\mathbf{2}^{2-}$ and **2**. In a related system, the open cluster $Ru_3(arene)_3(\mu_3\text{-}S)_2$ is converted to *closed*-$[Ru_3(arene)_3(\mu_3\text{-}S)_2]^{2+}$ by two 1-e$^-$ waves separated by only 0.14 V.[4a] Clearly, the influence of very similar net structural changes on the thermodynamics of the first and second electron transfer in a 2-e$^-$ process is quite variable. We are exploring the electrochemistry of other clusters related to **1** and **2** to see if the factors favoring 2-e$^-$ behavior in this series of Fe_3P_2 clusters can be clearly determined.

Acknowledgment. Professor W. E. Geiger, Jr. (University of Vermont) and Professor R. W. Murray (UNC-CH) are acknowledged for enlightening discussions. Partial financial support provided by a Presidential Young Investigator Award from the National Science Foundation (CHEM-8958027) and the Petroleum Research Fund is gratefully acknowledged. Partial funds for equipping the single-crystal X-ray diffraction facility at UNC-CH were provided by a grant from the National Science Foundation (CHE-8919288).

Supplementary Material Available: UV–vis spectra of **1**, **2**, and $\mathbf{2}^{2-}$, an EPR spectrum of $\mathbf{2}^{-}$, and text and tables giving complete crystallographic data and results for $[PPN]_2[\mathbf{2}^{2-}]\cdot 0.6CH_2Cl_2$ (13 pages). Ordering information is given on any current masthead page.

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(23) $[(Ph_3P)_2N]_2[\mathbf{2}^{2-}]\cdot 0.6CH_2Cl_2$ ($C_{95.6}H_{71.2}Cl_{1.2}Fe_3Mn_2N_2O_{13}P_6$): a = 16.246 (10) Å, b = 17.844 (6) Å, c = 17.991 (7) Å, α = 81.38 (3)°, β = 69.62 (4)°, γ = 71.34 (4)°. Data collection on a Rigaku AFC6S diffractometer yielded 2479 unique observed ($I \geq 2.5\sigma(I)$) reflections. A disordered CH_2Cl_2 present in the lattice was modeled by three chlorine atom positions with appropriate refined occupancies. Due to the very low number of reflections observed for the best crystal in a series of marginally diffracting crystals, the phenyl groups on the cations and the Cp groups on the anion were modeled as rigid groups. Least-squares refinement of 393 parameters converged at R (R_w) = 0.11 (0.11), and GOF = 2.48.

(24) The calculations were performed within the extended Hückel formalism with use of the weighted H_{ij} formula using program No. QCMP 011 (Quantum Chemistry Program Exchange, Indiana University). The atomic parameters were adopted from: Halet, J. F.; Hoffmann, R.; Saillard, J. Y. *Inorg. Chem.* **1985**, *24*, 1695.

(25) Rives, A. B.; Xiao-Zeng, Y.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2286.

(26) When the potentials for removing the first and second electrons are equal, a ΔE_p value of 42 mV is predicted. The observed value ΔE_p = 48 mV predicts that the potential for removal of the second electron lies 10 mV more positive than the potential for removal of the first.

(27) (a) Ohst, H. H.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 2066. (b) Ohst, H. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2897.