

bound to three metal atoms in the butterfly interacts strongly with Ru(2) ($Ru(2)-P(av) = 2.369 \text{ \AA}$) and more weakly with Ru(3) ($Ru(3)-P(av) = 2.470 \text{ \AA}$) and Ru(4) ($Ru(4)-P(av) = 2.566 \text{ \AA}$). The new $P-C(14)$ bond length is $1.808(8) \text{ \AA}$. The overall skeletal geometry is that of a nido dodecahedron with the missing vertex being of high coordination number.⁷ The second cluster **3** (Figure 2) has one less carbonyl than **2** and has a closo, pentagonal bipyramidal skeleton with two bridging carbonyl groups between axial (Ru(2) and Ru(4)) and equatorial (Ru(3)) ruthenium atoms as in **2**. Whereas in **2** one of the alkyne carbon atoms was bonded to the phosphorus atom, in **3** the acetylene is attached only to the four ruthenium atoms. The equatorial belt of the pentagonal bipyramid in **3** thus consists of Ru(1), Ru(3), P, and C(12) and C(13) of the alkyne.⁸ The apparent relationship of **2** and **3** evident in their structures was confirmed by warming an authentic sample of **2** in heptane when a smooth conversion to **3** occurred. The transformation of **1** to **3** via intermediate **2** can be best viewed in terms of the SEC rules. Thus **1** a nido octahedron is converted via addition of two three-electron CR fragments and loss of a carbonyl to the seven-vertex nido dodecahedron **2** and subsequently via CO loss and molecular rearrangement to the closo seven-vertex, eight skeletal pair pentagonal bipyramid of **3**. The rearrangement **2** to **3** occurs with P-C and Ru-Ru bond cleavage but not C-C cleavage. These results may have implications for skeletal rearrangement processes in other mixed-cluster systems.

Although the insertion of acetylenes into metal-phosphorus bonds in μ -PR₂-bridged binuclear systems has been reported,⁹ the formation of complexes analogous to **2** and **3** from a phosphinidene has precedent only in the very recent report by Huttner and co-workers¹⁰ of the conversion of $Fe_3(CO)_{10}(\mu_3-PR)$ to $Fe_3(CO)_{10}[PRC(R')C(R'')]$ and $Fe_3(CO)_9(PR)[C(R')C(R'')]$. All of these clusters represent a ternary (M, P, C) structural variety of which the metallocarboranes¹¹ are perhaps the best known examples. There is, in addition, a synthetic analogy between the synthesis of **2** and **3** and the generation of metallocarboranes via reaction of metalboranes with $RC\equiv CR$.¹² We are currently exploring further aspects of the reactivity of μ -PR complexes with ternary cluster formation in mind.

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Note Added in Proof. Following submission of this paper we learned that similar insertion of an acetylene into the framework of the metal-sulfur cluster $Os_4(CO)_{12}(\mu_3-S)$ has been observed (Adams, R. D., personal communication;

see also: Adams, R. D.; Wang, S., Abstract No. 366, XIIth ICOMC, Vienna, Austria, Sept 1985).

Registry No. 1, 81726-80-9; 2, 98586-80-2; 3, 98586-81-3; C_2Ph_2 , 501-65-5.

Supplementary Material Available: Tables of crystal and intensity data, data collection, reduction, and refinement (Table I), atomic positions (Tables IIA-C, VI), anisotropic thermal parameters (Tables IIIA,B, VII), bond lengths and angles (Tables IV, VIII), and structure factors (Tables V, IX) for **2** and **3**, respectively (79 pages). Ordering information is given on any current masthead page.

"Closed", "Half-Open", and "Open" Ferrocenes: Redox Behavior and Electron Spin Resonance of the Radical Cations[†]

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Summary: Successive opening of one or both rings of ferrocene results in a cathodic shift of the redox potential for the couple ferrocene/ferricinium, increased chemical lability, and vastly decreased g anisotropy in the ESR spectra of the respective complex radical cations. As opposed to closed ferricinium, ESR of the open ferricinium ions is observed at room temperature. These findings are discussed on the basis of the electronic structure as suggested by INDO MO calculations.

A characteristic property of ferrocene, **1**, is the reversible one-electron oxidation to the ferricinium radical cation $1^{+\cdot}$.¹ ESR studies of $1^{+\cdot}$, however, are possible only at very low temperatures since the orbital degeneracy of the 2E_g ground state for $1^{+\cdot}$ results in a large g anisotropy and concomitant short relaxation times.^{2,3} Since metallocene chemistry recently experienced a fruitful extension via the class of "open metallocenes",⁴ a comparison of redox and ESR properties of the "closed" ferrocene with its "open" counterpart is warranted. While peripheral substitution^{5,6} (as in **2**) or introduction of heteroatoms into the cyclic ligand (e.g., bis(η^5 -dicarbollide)iron(III)⁷) only brings about small changes in redox and ESR behavior of the closed bis(η^5 -cyclopentadienyl)iron, **1**, we expected that opening one or both rings to form the η^5 -pentadienyl complexes **3** and **4** would constitute a major perturbation resulting in profoundly modified redox potentials and g factor anisotropies. In order to study the consequences of succes-

[†] Dedicated to Professor Karl Dimroth on the occasion of his 75th birthday.

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Table I. Cyclovoltammetric Data (0/+) and ESR Parameters (Radical Cations) for (η^5 -C₅H₅)₂Fe (1), (η^5 -2,4-Me₂C₅H₃)₂Fe (2), (η^5 -2,4-Me₂C₅H₃)₂Fe (3), and (η^5 -2,4-Me₂C₅H₃)₂Fe (4)

compd	couple	potential ^a	characteristics	<i>g</i> factors (radical cation)
1	0/+	$E^\circ = 0.490$	rev, 20 °C all sr	$\langle g \rangle^b$ not observed $g_{\parallel} = 4.36^c$ $g_{\perp} = 1.28$
2	0/+	$E^\circ = 0.304^d$	rev, 20 °C all sr	$\langle g \rangle^b$ not observed $g_{\parallel} = 4.51^e$ $g_{\perp} = 1.40$
3	0/+	$E^\circ = 0.292$	rev, 20 °C sr ≥ 100 mV/s	$\langle g \rangle^b = 2.1163^f$ $g_1 = 2.2255$ $g_2 = 2.1033$ $g_3 = 2.0020^f$
4	(+/2+)	$E_{pa} = 1.320$	irrev, 20 °C	$\langle g \rangle^b = 2.0860^f$
	0/+	$E^\circ = 0.114^g$	irrev, 20 °C all sr rev, -15 °C sr ≥ 400 mV/s rev, -45 °C all sr	$g_1 = 2.1822$ $g_2 = 2.0689$ $g_3 = 2.0155^f$

^aV vs. SCE, solvent dimethoxyethane/tetrabutylammonium perchlorate, glassy carbon electrode, sr = sweep rate. ^bFluid solution, 20 °C. ^cSolvent dimethylformamid, 4 K.¹¹ ^dExtrapolated value using an increment of -47 mV per methyl group.¹⁰ ^ePolycrystalline sample, 15 K.⁶ ^fElectrochemical in situ generation, dimethoxyethane/tetrabutylammonium perchlorate, -70 °C (fluid solution), -160 °C (rigid solution). ^gValue for E° obtained via extrapolation of low-temperature E° data, $\Delta E^\circ = +1.55$ mV/°C.

sively opening the two η^5 -cyclopentadienyl ligands, we have therefore also prepared and completely characterized the "half-open" sandwich complex 3.^{8,9}

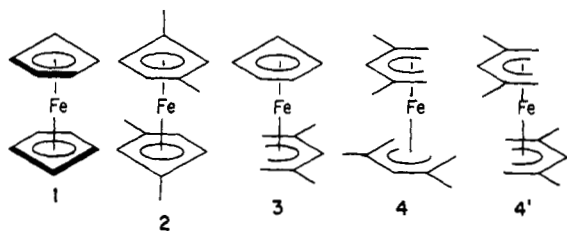


Table I lists electrochemical data obtained by cyclic voltammetry, for which some representative traces are depicted in Figure 1. Like the closed ferrocenes, half-open 3 and open 4 also undergo one electron oxidations to the respective radical cations. The redox potentials are shifted in the cathodic direction, paralleling the effect of peripheral methylation. A comparison of the E° value for 2, 3, and 4 suggests that opening one ring is tantamount to the introduction of two methyl groups,¹⁰ either transformation

(8) $\text{Fe}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})$ can be prepared by the slow addition of a 1:1 mixture of NaC_5H_5 and $\text{K}(2,4\text{-C}_7\text{H}_{11})$ in THF to a slurry of FeCl_2 in THF at -78 °C under nitrogen. After the addition is complete, the mixture is slowly warmed to room temperature and stirred for ca. 1 h. The THF is then removed in vacuo, and the product is extracted into pentane or hexane and filtered. After removal of solvent in vacuo, one is left with a nearly 1:1:2 mixture of $\text{Fe}(\text{C}_5\text{H}_5)_2$, $\text{Fe}(2,4\text{-C}_7\text{H}_{11})_2$, and $\text{Fe}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})$. To remove the "open ferrocene" component, the product is dissolved in a minimum volume of pentane and cooled to -20 or -40 °C, resulting in crystallization of nearly all the $\text{Fe}(\text{C}_5\text{H}_5)_2$ and $\text{Fe}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})$. After removal of the supernatant, the remaining product is dissolved in ca. 5–8 times the minimum volume of pentane required for dissolution and cooled as slowly as possible to ca. -20 °C. If the cooling rate is slow enough, deep red rods of $\text{Fe}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})$ will form, occasionally as large as $0.5 \times 1.5 \times 50$ mm, which may readily be separated from any orange $\text{Fe}(\text{C}_5\text{H}_5)_2$ which crystallizes. Further product may be isolated by concentrating the supernatant and repeating the crystallization procedure. The product has been completely characterized by IR, ¹H and ¹³C NMR, mass spectroscopy, elemental analysis (C, H), and an X-ray structural determination.⁹

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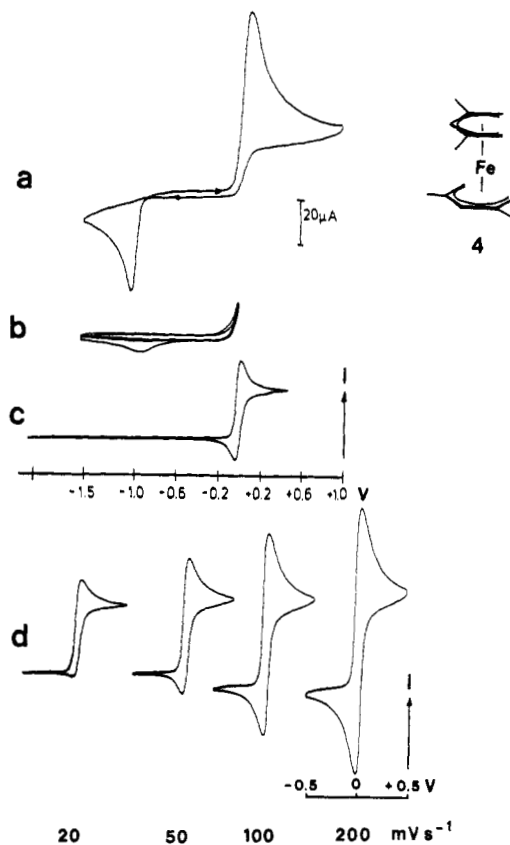


Figure 1. Cyclovoltammograms of the couple (η^5 -2,4-Me₂C₅H₃)₂Fe^{0/+} (medium dimethoxyethane/tetrabutylammonium perchlorate): (a) 25 °C, -1.5 < E < +1.0 V, 100 mV s⁻¹; (b) 25 °C, -1.5 < E < 0 V, 100 mV s⁻¹; (c) -35 °C, -2.0 < E < +1.0 V, 100 mV s⁻¹; (d) -25 °C. Variation of scan rate: 20, 50, 100, and 200 mV s⁻¹.

favoring the oxidation process. Since vertical ionization potentials in the gas-phase He I PE spectra^{12,13} are practically identical for 4 and 2, it is tempting to suggest that the greater ease of oxidation of the open ferrocene in solution is due to more effective solvation of the corresponding cation. However, the fact that the "open metallocenes" seem in general to be extremely crowded molecules^{4b} suggests that other factors are probably also important.

The redox couples 2 (0/+), 3 (0/+), and 4 (0/+) differ noticeably in the degree of reversibility. Whereas electrochemical oxidation of the closed 2 is reversible at room temperature at all scan rates, the half-open sandwich complex 3 displays reversibility at room temperature only for scan rates ≥ 100 mV s⁻¹, while oxidation of the open ferrocene 4 is irreversible under these conditions (Figure 1a).¹⁴ However, reversibility of the redox process 4 (0/+) even at slow scan rates can be achieved by recording the cyclovoltammogram at $T \leq -45$ °C (Figure 1c, $i_a/i_c = 1$,

(10) For the polarographic potentials of ferrocene derivatives additivity of substituent effects has been established. $\Delta E^\circ = -47$ mV per methyl group: Sabbatini, M. M.; Cesarotti, E. *Inorg. Chim. Acta* 1977, 24, L9. However, in the case of the "open metallocenes" the actual site of methylation may well play a role, leading to deviations from simple additivity, due to the uneven charge distribution over the ligand carbon atoms.

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(14) Although a cathodic peak at $E_{pc} = -1.028$ V can be seen at room temperature for 4 with a wide scan range (Figure 1a), if a smaller scan range is used this peak is absent (Figure 1c), demonstrating that it originates from a secondary product, possibly a ligand dimer.

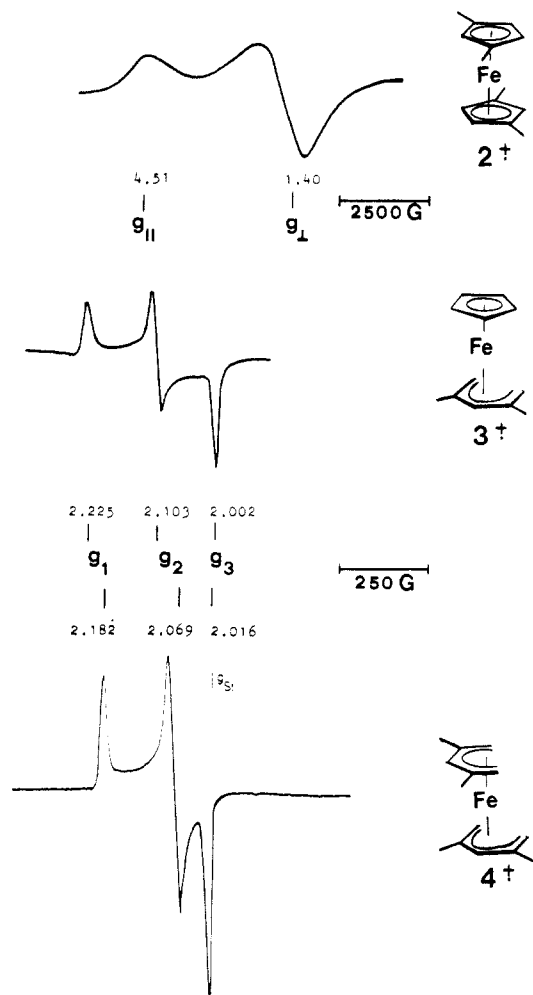


Figure 2. ESR spectra of the radical cations $(\eta^5\text{-}2,4\text{-Me}_2\text{C}_5\text{H}_3)_2\text{Fe}^+$ (2^+), $(\eta^5\text{-}2,4\text{-Me}_2\text{C}_5\text{H}_3)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^+$ (3^+), and $(\eta^5\text{-}2,4\text{-Me}_2\text{C}_5\text{H}_3)_2\text{Fe}^+$ (4^+). 2^+ : polycrystalline sample, 15 K.⁶ 3^+ and 4^+ : rigid solution after electrochemical in situ oxidation, dimethoxyethane/tetrabutylammoniumperchlorate, 113 K. Note the difference in field scale.

$\Delta E = 70$ mV). At intermediate temperatures, this couple demonstrates a dependence of the degree of electrochemical reversibility on the scan rate (Figure 1d), as inferred from the i_a/i_c values of ≤ 1 . We therefore conclude that the chemical lability of ferricinium ions increases in the sequence closed < half-open < open.¹⁵ Quite possibly this sequence may be due to the greater tendency of pentadienyl ligands to undergo coupling reactions, either intramolecular^{16a,b} or intermolecularly.^{16c,d}

Whereas the variation in redox behavior during the transition from closed via half-open to open ferrocene is continuous and of moderate extent only, the changes in the ESR spectra of the radical cations are discontinuous and spectacular. As Figure 2 demonstrates, transition from 2^+ (closed) to 3^+ (half-open) is accompanied by an immense decrease in g anisotropy; in contrast, on passing from 3^+ (half-open) to 4^+ (open), only marginal changes in the g tensor components are encountered (Table I). As

a result, whereas observation of the ESR spectra for 2^+ requires $T \leq 20$ K, ESR of 3^+ can even be observed at room temperature in fluid solution. The fact that the ESR detectability of 4^+ does require low temperatures is the result of the lability of this ion in solution rather than of relaxational line broadening. At -50 °C the isotropic ESR spectrum of 4^+ , electrochemically generated in situ, consists of a single envelope (width ≈ 20 G). Since the ESR characteristics of ferricinium ions are altered only to a small extent by peripheral alkylation,^{2,6} this type of perturbation does not perceptibly raise the degeneracy of the $^2E_{2g}$ ground state of parent 1^+ (see Figure 2A). Instead, it must be the effect of ring opening on electronic structure which is primarily responsible for the observed variation of the g tensor in going from 2^+ to 3^+ and 4^+ . INDO-type calculations in conjugation with He I photoelectron (PE) spectra demonstrate that a simple correlation of the MO's of closed and open ferrocenes is not possible because extensive conformation-dependent inter Fe(3d) and metal-ligand orbital mixings pertain in the latter two systems.^{12,17} Therefore in order to calculate numerical values for the g tensor components from INDO results, a definite conformation must be ascribed to 3^+ and 4^+ in rigid solution.¹⁷ Even if this is done, however, an assignment of $g_{1,2,3}$ to a fixed molecular coordinate system would still be ambiguous in the absence of single-crystal ESR data.

In order to offer at least a qualitative rationalization of the strongly reduced g anisotropy in the half-open and open ferricinium ions, we will assume a gauche-eclipsed conformation for the ground state of 4^+ in both fluid and rigid solutions.¹⁸ This assumption is supported by the fact that $\langle g \rangle$ measured in fluid solution closely matches the average value of g_1 , g_2 , and g_3 , measured in rigid solution. INDO calculations and the subsequent consideration of Koopmans' defects^{12,17} indicate that the singly occupied orbital 14a in 4^+ is almost exclusively Fe(3d_{z²}).¹⁷ This is in accord with one g tensor component being close to the free spin value, and it appears legitimate to assign g_3 (3^+ , 4^+) to the molecular z axis. It should be mentioned that the single occupancy of a Fe(3d_{z²}) orbital in 4^+ , as suggested by INDO calculations, contrasts with the HOMO in the neutral complex 4, which is mainly localized on the ligands. As to this conversion from a ligand-centered HOMO to a metal-centered HOMO upon oxidation, however, theoretical and experimental data are mutually consistent. Concerning g_1 and g_2 , deviations from $g = 2.0023$ may be assumed to stem from mixing via spin-orbit coupling of the singly occupied MO (14a, 96% Fe(3d_{z²}) with the various filled MO's, MO_{occ}. Since INDO results indicate a large SOMO/LUMO energy gap and only small metal coefficients in the subsequent virtual orbitals, contributions $\Delta g < 0$ are probably negligible. The first-order relationships¹⁹

$$g_1 = 2.0023 + 6\lambda c_z^2(\text{SOMO}) \sum_{\text{MO}_{\text{occ}}} \frac{c_{zz}^2(\text{MO}_{\text{occ}})}{\Delta E(\text{SOMO}, \text{MO}_{\text{occ}})}$$

$$g_2 = 2.0023 + 6\lambda c_z^2(\text{SOMO}) \sum_{\text{MO}_{\text{occ}}} \frac{c_{yz}^2(\text{MO}_{\text{occ}})}{\Delta E(\text{SOMO}, \text{MO}_{\text{occ}})}$$

$$g_3 = 2.0023$$

(15) The generally less robust nature of $(\eta^5\text{-C}_5\text{H}_7)\text{M}$ complexes relative to $(\eta^5\text{-C}_5\text{H}_5)\text{M}$ complexes has been observed before also for open vs. closed cymantrene: Seyferth, D.; Goldman, E. W.; Pornet, J. *J. Organomet. Chem.* 1981, 208, 189.

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(18) (a) From variable-temperature ¹H NMR (toluene-*d*₆, +26 °C > $T > -105$ °C) a gauche-eclipsed ground configuration was inferred for 4^+ :^{18b} coalescence temperature ~ -60 °C, ΔG^\ddagger (ligand oscillation) = 38 kJ/mol. Conformational considerations based on orbital populations suggest a nearly gauche-eclipsed configuration for the cation.⁴ (b) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Organometallics* 1983, 2, 1220.

together with energy differences ΔE and MO coefficients c_x^2 , c_{xz} , and c_y^2 from INDO calculations^{17b} lead to the estimates $g_1 = 2.085$, $g_2 = 2.074$, and $g_3 = 2.0023$, if for the spin-orbit coupling constant somewhat intuitively the value of $\lambda[\text{Fe(I)}] = 356 \text{ cm}^{-1}$ is adopted.¹⁹ While quantitative agreement is not to be expected for this crude treatment,²⁰ there is reasonable accord in that one g value is predicted to be close to the free spin value, while the other two are predicted to be substantially larger. In addition, this treatment illustrates the sources of the widely divergent ESR properties of closed and open ferrocenes. In particular, the totally different orbital compositions and energetic sequences for the open ferrocene MO's, a consequence of lower molecular symmetry, lead to orbitally nondegenerate 2A ground states for the open cations 3^+ and 4^+ . Furthermore, the more extensive metal-ligand mixing in the open ferrocenes reduces the impact of spin-orbital coupling on $g_{1,2,3}$. Ironically, ESR spectra of the open ferricinium ions bear more resemblance to octahedral complexes of low-spin $\text{Fe}^{3+}(\text{d}^5)$ ²¹ than to closed ferricinium species, thereby justifying a description of the open ferrocenes in terms of two eclipsed pentadienyl ligands which provide a distorted octahedral ligand field on iron(II) by means of the charged centers at $\text{C}_{1,3,5}$. Further experimental and theoretical studies on these and related molecules are in progress.

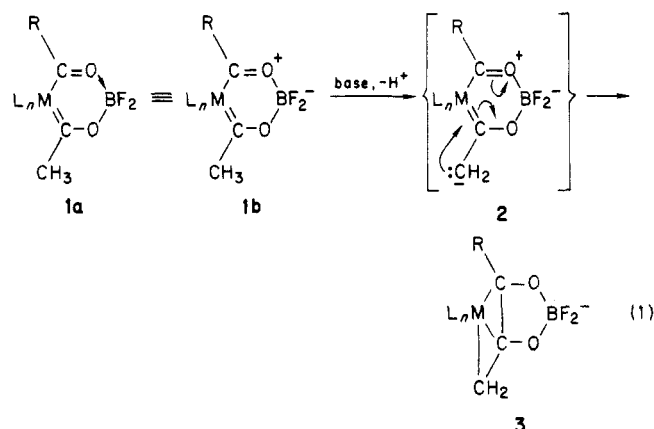


Acknowledgment. We are grateful to Professor Rolf Gleiter for providing results of INDO calculations on the open ferrocene cations. This work was supported by Deutsche Forschungsgemeinschaft (Grant E1 62/4-2 to C.E.) and by grants from the National Science Foundation (CHE-8120683 and CHE-8419271 to R.D.E.) and from the donors of the Petroleum Research Fund, administered by the American Chemical Society (to R.D.E.).

removal of the Fe and BF_2 moieties gives pivaloin in yields ranging from 26 to 58%. A formal mechanism for this reductive coupling of two adjacent acyl carbon donor atoms is proposed.

We have reported previously that the α -enolate anions of (metalla- β -diketonato) BF_2 complexes,^{1,2} metalla- β -diketonate anions,³ and (triacylrhenato)BX complexes⁴ undergo reductive coupling of two acyl carbon donor atoms to give η^3 -allyl complexes. One representation of this C-C coupling reaction for a (metalla- β -diketonato) BF_2 complex is shown in eq 1. Deprotonation of the methyl substituent of **1b** generates the α -enolate anion **2** which apparently rearranges spontaneously to give the η^3 -allyl complex **3**. An isolobal analysis of this type of rearrangement has been published earlier.⁵

Within the formal representation shown in eq 1, the crucial C-C bond coupling is initiated by formal reduction at M by the lone pair of electrons on the exo-methylene carbon atom. The metal undergoes a concomitant formal oxidation when the C-C bond is formed. The electron count of M in going from **1b** to **3**, therefore, remains the same.



We have examined the intriguing possibility that C-C coupling in these molecules might be initiated by external reduction of the metal atom rather than by an intramolecular electronic rearrangement as shown in eq 1. We now report that either chemical or electrochemical reduction of the complex $[(\eta\text{-C}_5\text{H}_5)(\text{OC})\text{Fe}(\text{Me}_3\text{CCO})_2]\text{BF}_2$,⁶ **4**, occurs to give C-C coupling. This coupling is verified by the isolation of pivaloin (the organic coupling product).

When 0.8-4.1-g samples of **4** are treated with an excess of chemical reducing agent (Na/Hg in THF, or sodium naphthalenide, NaNp, in THF, or sodium benzophenone ketyl, NaBZK, in dioxane) for 2 h at 25 °C, the reaction solution changes color from red-orange to black. The reaction residue then is refluxed with 50 mL of 0.5 M NaOH for 2 h to remove the BF_2 and Fe moieties. Following neutralization with aqueous HCl, the neutral reaction products are extracted into methylene chloride. Pivaloin is isolated by sublimation from the extraction residue or

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Reactions of Coordinated Molecules. 46. Formation of Pivaloin by the Reductive Coupling of Two Pivaloyl Ligands

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Summary: Chemical or electrochemical reduction of the complex $[(\eta\text{-C}_5\text{H}_5)(\text{OC})\text{Fe}(\text{Me}_3\text{CCO})_2]\text{BF}_2$ followed by re-