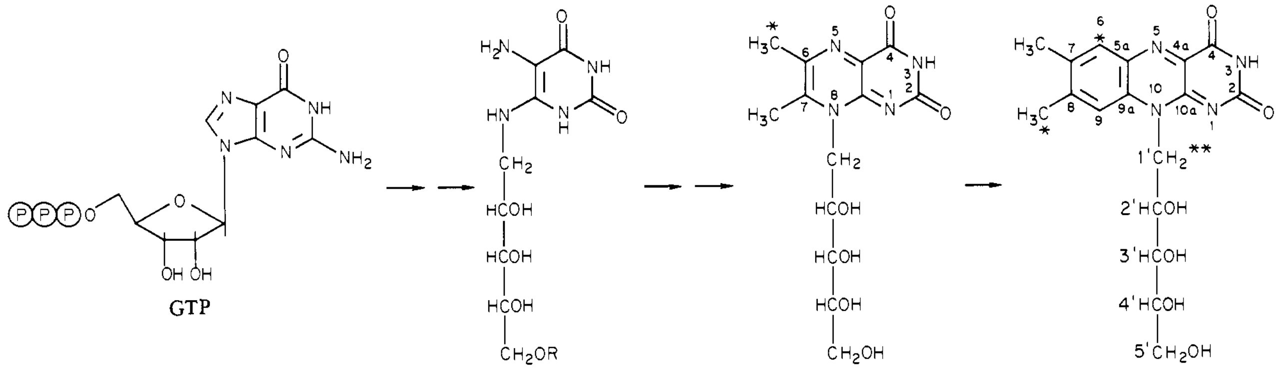
Scheme I. Biosynthesis of Riboflavin[a]



1 (R = Ⓟ) 2 3

[a] The single asterisks illustrate the regiochemistry of the riboflavin synthase reaction. They also coincide with the major sites of labeling of the xylene moiety of 3 from [1-^{13}C]ribose. The double asterisk indicates the major site of labeling in the ribitol moiety of 3.

^{13}C NMR spectra of [2′-^{2}H]- and [3′-^{2}H]riboflavin[19] obtained from Dr. William M. Moore, Utah State University, and a determination of carbon–carbon connectivities by analysis of the two-dimensional double-quantum coherence ^{13}C NMR spectrum[20] of **4** biosynthesized from [U-^{13}C$_6$]glucose.

The ^{13}C distribution in **4** derived from [1-^{13}C]ribose is shown in Table I. The majority of the ^{13}C is found in three positions, with secondary labeling evident in three additional carbon atoms. The isotope is efficiently incorporated into position 1′ of the ribityl side chain. This is expected since it has been shown that the ribitol moiety of riboflavin is derived from the ribose moiety of GTP.[3,21] In the heterocyclic moiety, carbon atom 6 and the 8-methyl group show the same ^{13}C abundance within experimental error. However, the enrichment at these positions is significantly lower than that at C-1′.

These results lead to the following conclusions: (i) In the last biosynthetic step catalyzed by riboflavin synthase, the 6-methyl group of **2** gives rise to carbon atom 6 and the 8-methyl group of **3**. This is in agreement with the regioselectivity of the enzyme as suggested earlier on the basis of in vitro studies with deuterium-labeled **2**.[22]

(ii) The isotope from [1-^{13}C]ribose is efficiently incorporated into the 6-methyl group but not into the 7-methyl group of the lumazine **2**. It follows that symmetrical molecules such as diacetyl are ruled out as intermediates in the generation of the four-carbon unit, because any symmetrical intermediate would lead to an even distribution of the label between the two methyl groups.

(iii) Since carbon 1′ of the ribitol moiety is labeled significantly more heavily than any atom in the aromatic ring, it appears that although a pentose does contribute to the generation of the four-carbon moiety, the ribitol moiety of **1** may not be a direct precursor of this four-carbon unit as has been suggested.[11,12] If two molecules of **1** were to react to give one molecule of **2** in a manner similar to the conversion of two molecules of **2** into one molecule of **3**, the final product **3** would have to contain equal amounts of ^{13}C at C-1′, C-6, and the 8-methyl group. The finding that this is not the case is in line with earlier results on the incorporation of guanosine into riboflavin by a purine mutant, which indicated that the ribose moiety of GTP contributes to the ribitol moiety but not to the isoalloxazine ring of **3**.[21]

Studies with other ^{13}C-labeled precursors are underway in order to further delineate the specific origin of this four-carbon moiety.

Acknowledgment. We are indebted to the Los Alamos Stable Isotope Resource (supported by NIH Grant RR 00962) for providing the [1-^{13}C]ribose and to Professor William M. Moore, Logan, UT, for copies of the unpublished ^{13}C NMR spectra of [2′-^{2}H]- and [3′-^{2}H]riboflavin. Financial support from the Deutsche Forschungsgemeinschaft (Grant Ba 574/5-6 to A.B.) and the U.S. Public Health Service (NIH Grant AI 11728 to H.G.F.) is gratefully acknowledged. This project was initiated while one of the senior authors (H.G.F.) was a guest at the Technical University München under a Hümboldt US Senior Scientist Award; he thanks the Hümboldt Foündation for its support and Professor Helmüt Simon for his kind hospitality.

Registry No. 3, 83-88-5; 4, 752-13-6; D-[1-^{13}C]ribose, 70849-24-0.

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Electron-Transfer Pathways in the Reduction of d^{6} and d^{7} Organoiron Cations by LiAlH$_4$ and NaBH$_4$

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The activation by transition metals of unsaturated ligands toward reduction by main-group hydrides has been used extensively during the last two decades.[1,2] Recently, attention has focused on the homogeneous reduction of coordinated CO by borohydrides[3]

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[‡] CNRS Fellowship Recipient 1978-1982.

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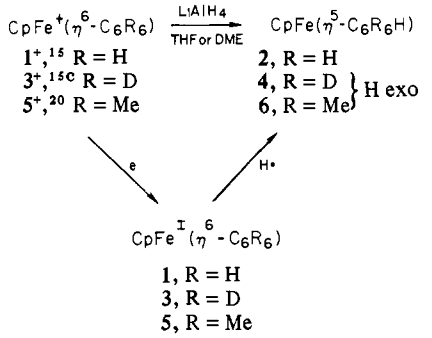
Scheme I



as a model for Fischer–Tropsch synthesis.[4,5] In 1978, Green et al. elegantly rationalized the chemoselectivity of the attack of most nucleophiles on transition-metal cations in terms of charge control, including many examples of metal hydride reduction of CpFe$^+$(arene) cations.[2] In both experimental and theoretical works,[6,7] the reduction of organometallic complexes by main-group hydrides was always considered as a nucleophilic attack of H$^-$.[8] This belief parallels the well-documented polar mechanism known in organic chemistry for the reduction of ketones and other functions by main-group hydrides.[9] A few recent reports, however, have focused on electron-transfer (ET) paths in reactions of electron-rich metal hydrides.[8,10-12] We have reexamined the reduction of d^6 and d^7 organoiron complexes by LiAlH$_4$ and NaBH$_4$, with the aim of investigating the feasibility of electron-transfer paths. For this purpose we have chosen substrates for which the antibonding LUMO is energetically accessible so that the ET intermediates,[13] potentially 19- or 20-electron species, are relatively stable or, if not, characterizable by EPR in reactions at −80 °C. We find that the reduction by LiAlH$_4$ and/or NaBH$_4$ in DME and THF of a variety of monocationic organoiron complexes proceeds via single ET, although these complexes are electron rich, being electrochemically reduced at very negative redox potentials[14] (−1.4 to −1.8 V vs. SCE).

Typically, the yellow salt CpFe$^+$(η^6-C$_6$H$_6$)PF$_6^-$ (**1$^+$**) (Cp = η^5-C$_5$H$_5$) reacts rapidly with LiAlH$_4$ (mol ratio 1/10) at 20 °C in THF, giving orange CpFe(η^5-C$_6$H$_7$)[6a] (**2**) (Scheme I). When this reaction is carried out at −60 °C, a forest green color develops rapidly. The EPR spectrum of this solution frozen to 77 K allows observation of the characteristic features of the unstable d^7 complex CpFe$^{\rm I}$(η^6-C$_6$H$_6$)[14c,d] (**1**). This ET step is complete in $^1/_2$ h, and **1** can be extracted at low temperature. Concentration of the THF solution followed by precipitation by pentane gives 80% yield of **1**, the purity of which is deduced from its temperature-dependent Mössbauer doublet.[14c] Alternatively, if this forest-green solution is allowed to warm up, a color change to orange proceeds at −33 °C in 2 min. The formation of the ET intermediate is highly solvent dependent: it is also observed in DME (ET complete in 20 min at −35 °C; H atom transfer in 1 min at −20 °C) but not in ether[16] (H$^-$ transfer in 30 min at 15 °C). Reaction rates decrease when the concentration of LiAlH$_4$ is reduced. If only stoichiometric amounts of cation and LiAlH$_4$ are reacted, the reaction still proceeds to completion, indicating that AlH$_3$ (arising from AlH$_4$• → AlH$_3$ → $^1/_2$H$_2$) can also transfer a H atom as LiAlH$_4$ in the second step, but the reaction rate is much lower ($t_{1/2}$ = 3 h at 17 °C). A similar rate is observed when a sample of **5** is reduced stoichiometrically with LiAlH$_4$.

The ET mechanism could be demonstrated even when very unstable d^7 complexes are intermediates. When LiAlH$_4$ is reacted with CpFe$^+$C$_6$H$_5$F PF$_6^-$ (**7$^+$**),[17] the reaction is fast at −95 °C in THF, owing to the lower reduction potential of this cation. The EPR spectrum at 77 K of the frozen forest-green solution (Figure 1) fits nicely in the spectral series of the nonsubstituted complex **1** diluted in various molecular hosts and frozen solutions,[14d] giving the three g values characteristic of the Jahn–Teller-active d^7 species **7**, despite its instability.

Whereas Na/Hg reduction of CpFe$^+$(η^5-C$_4$Me$_4$S)PF$_6^-$ (**11$^+$**)[18] in THF at −21 °C leads to decomposition within a few seconds (as for **7$^+$**), the reaction of **11$^+$** with LiAlH$_4$ in THF provides a virtually complete reduction to a new unstable deep-purple complex (**11**) at −50 °C. Its EPR spectrum at 77 K in frozen THF (g_x = 2.0275, g_y = 2.0642, g_z = 1.9968) indicates a strongly distorted d^7 or d^6 L system, but the Mössbauer parameters at 77 K in frozen THF (IS = 0.58 mm s^{-1} vs. Fe, QS = 0.92 mm s^{-1}) are typical of the d^7 Fe(I) series[14c,19] (Scheme II). The reaction between LiAlH$_4$ and CpFe$^+$C$_6$Et$_6$PF$_6^-$ (**12$^+$** [14c]) in DME gives (η^4-C$_5$H$_6$)Fe^0(η^6-C$_6$Et$_6$) (**13**[21,22]) via **12**.[14c] The reactions of NaBH$_4$

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(16) The opposite trend is observed in reactions of carbanions with these cations. For example CH$_3$Li reacts with CpFe$^+$(η^6-C$_6$Et$_6$) PF$_6^-$ (**12$^+$**) in 4 h at 20 °C in ether to give the ET product **12**, whereas the same reaction in THF gives (η^4-CH$_3$C$_5$H$_5$)Fe^0(η^6-C$_6$Et$_6$) in 5 min at −20 °C. See also ref 6b,d.

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(19) (a) The color shift from forest green (**5**) to purple (**11**) is also consistent with both complexes belonging to the d^7 series. The e$_1$*(d$_{xz,yz}$) → e$_2$*(arene) transition responsible for the color is more energetic for **11**, e$_2$*(C$_4$Me$_4$S) being higher in energy than e$_2$*(C$_6$Me$_6$). (b) Although **11** is unstable in the solid state, addition of excess cold pentane to the reaction mixture at −50 °C followed by filtration gave solutions that were stable at 20 °C for a few hours; addition of a THF solution of I$_2$ gave back **11$^+$**: Guerchais V., unpublished observations.

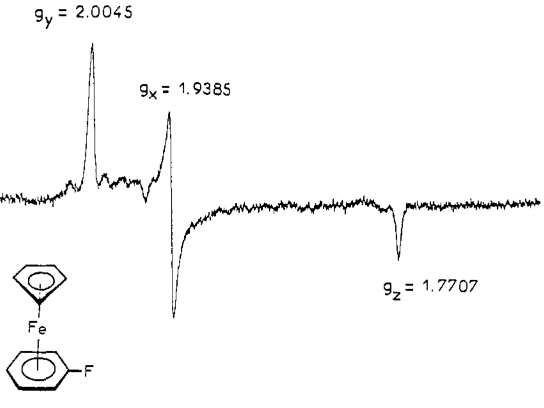


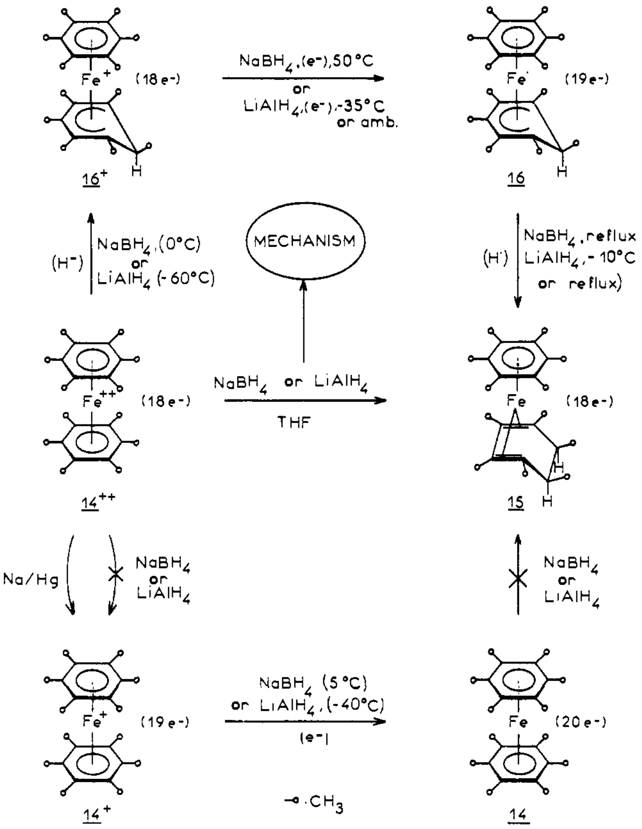
Figure 1.

Scheme II

$$\mathrm{CpFe^{+}(\eta^{5}\text{-}C_4Me_4S)} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{CpFe^{I}(\eta^{5}\text{-}C_4Me_4S)}$$

($\mathbf{11}^+$: d^6, 18e^-) (**11**: d^7, 19e^-)

Scheme III



and $\mathrm{LiAlH_4}$ with $(\eta^6\text{-}\mathrm{C_6Me_6})_2\mathrm{Fe^{2+}(PF_6^-)_2}$ ($\mathbf{14}^{2+\,23a}$) in THF give orange $(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{Fe}(\eta^4\text{-}\mathrm{C_6Me_6H_2})$ (**15**[24]) in which both incoming hydrogens are exo, rather than $(\eta^5\text{-}\mathrm{C_6Me_6H})_2\mathrm{Fe}$, the reaction product expected from Green's rule.[2] The reactions start at −60 °C with $\mathrm{LiAlH_4}$ or 0 °C with $\mathrm{NaBH_4}$, giving high yields of the new dark red complex $(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{Fe^+}(\eta^5\text{-}\mathrm{C_6Me_6H})\mathrm{PF_6^-}$ ($\mathbf{16}^{+\,25}$), the $\mathrm{H^-}$ transfer product. Further reaction proceeds at −35 °C in $^1/_2$ h with $\mathrm{LiAlH_4}$ or at 50 °C in 10 min with $\mathrm{NaBH_4}$ to give the thermally stable air-sensitive ET product **16** in quantitative spectroscopic yield. **16** can also be synthesized by Na/Hg reduction of $\mathbf{16}^+$ in DME (1 h, 20 °C); recrystallization from pentane gives 77% ivory-brown crystals.[26] The Mössbauer parameters are in the range known for d^7 Fe(I), but the variation of QS with T is less marked: IS (mm $\mathrm{s^{-1}}$ vs. Fe) 0.46 (293 K), 0.58 (77 K); QS (mm $\mathrm{s^{-1}}$) 0.91 (293 K), 1.04 (77 K). Finally continuation of the reductions by $\mathrm{LiAlH_4}$ (−10 °C, 2 min, 73% isolated yield) or by $\mathrm{NaBH_4}$ (reflux, 20 min, 55% isolated yield) gives **15**, the H atom transfer product (Scheme III). Note that, despite the large steric bulk in the dication $\mathbf{14}^{2+}$ and its low reduction potential (−0.5 V vs. SCE), $\mathrm{H^-}$ transfer is always preferred to ET. Demonstration that ET with $\mathbf{14}^{2+}$ does not occur upon reaction with hydrides is provided by reactions of $\mathrm{NaBH_4}$ and $\mathrm{LiAlH_4}$ with $(\mathrm{C_6Me_6})_2\mathrm{Fe^+PF_6^-}$ ($\mathbf{14}^{+\,22a,b}$). The reactions of $\mathbf{14}^+$ with $\mathrm{LiAlH_4}$ at −40 °C and with $\mathrm{NaBH_4}$ at 5 °C give the known d^8 20-electron sandwich **14**,[23a,c] characterized by Mössbauer[27] and UV[23a] spectroscopies; further reactions at reflux lead to decomposition rather than to **15**. Thus, the $\mathrm{H^-}$ transfer and ET paths are totally different (Scheme III). It is thus clear that the ET mechanism becomes favored over $\mathrm{H^-}$ transfer as the cationic charge of the sandwiches decreases from 2 to 1. This suggests that reactions of metal hydrides with many neutral complexes may proceed by ET, a mechanism most of the time hidden by the high reactivity of the intermediate 19-electron species.

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(20) The hydride reduction of $\mathrm{CpFe^+}(\eta^6\text{-}\mathrm{C_6Me_6})$ was erroneously referred to as an attack on the Cp ring[2] although the original formulation, attack onto the $\mathrm{C_6Me_6}$ ring, was correct.[6b] More bulk is necessary (reaction of $\mathrm{CH_3Li}$ with $\mathrm{CpFe^+}(\eta^6\text{-}\mathrm{C_6Me_6})$[6b] or $\mathrm{H^-}$ with $\mathrm{CpFe^+}(\eta^6\text{-}\mathrm{C_6Et_6})$) to provide exceptions to the rule, according to which an even ligand is preferred to an odd one.[2]

(21) $(\eta^4\text{-}\mathrm{C_5H_6})\mathrm{Fe^0}(\eta^6\text{-}\mathrm{C_6Et_6})$: ^{1}H NMR ($\mathrm{Me_4Si}$, $\mathrm{C_6D_6}$) δ 3.83 (m, Hα, 2 H), 3.16 (m, Hβ, 2 H), 1.90 (d, H endo, 1 H), 0.30 (d, H exo, 1 H), 2.70 (q, $\mathrm{CH_2}$, 12 H), 1.16 (t, $\mathrm{CH_3}$, 18 H); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{Me_4Si}$, $\mathrm{C_6D_6}$) δ 97.3 ($\mathrm{C_6}$), 23.3 ($\mathrm{CH_2}$, ethyl), 16.9 ($\mathrm{CH_3}$), 26.1 (ring $\mathrm{CH_2}$), 38.9 (Cα), 76.9 (Cβ); Mössbauer QS = 2 mm $\mathrm{s^{-1}}$, IS = 0.40 mm $\mathrm{s^{-1}}$; MS *m/e* $\mathrm{M^+}$ calcd 368.216, found 368.217; IR (pentane) $\nu_{\mathrm{CH\,exo}}$ 2742 $\mathrm{cm^{-1}}$.

(22) Note that the H atom is transferred onto the Cp ring in **12** and onto the $\mathrm{C_6Me_6}$ ring in **5**. To our knowledge, single H atom transfers to arenes or Cp are unprecedented. (a) For a double H atom transfer by a transition-metal hydride, see: Sweany, R.; Butler, S. C.; Halpern, J. *J. Organomet. Chem.* **1981**, *213*, 487–492. (b) For catalytic hydrogenation of arenes, see: Blecke, J. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 556–564. (c) For a stoichiometric hydrogenation of coordinated $\mathrm{C_6H_6}$, see ref 23c.

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(24) $(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{Fe^0}(\eta^4\text{-}\mathrm{C_6Me_4H_2})$ (**15**). MS M calcd 382.4162, found 382.4161; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 2.16 (s, β $\mathrm{CH_3}$, 6 H), 1.96 (s, $\mathrm{CH_3}$, 18 H), 1.80 (s, α $\mathrm{CH_3}$, 6 H), 1.00 (exo $\mathrm{CH_3}$, endo H, 8 H); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 91.3 ($\mathrm{C_6}$ ring), 83.8 (β ring C), 59.0 (α ring C), 21.7 (β $\mathrm{CH_3}$), 16.7 (6$\mathrm{CH_3}$), 15.7 (ortho ring C), 13.5 (endo $\mathrm{CH_3}$); Mössbauer parameters (mm $\mathrm{s^{-1}}$) IS (vs. Fe) 0.33 (298 K), 0.44 (77 K), QS 0.98 (298 and 77 K). Anal. Calcd. for $\mathrm{C_{24}H_{38}Fe}$: C, 75.39; H, 9.95; Fe, 14.66. Found: C, 75.64; H, 9.80; Fe, 14.56. **15** gives $\mathbf{16}^+$ upon reaction with $\mathrm{Ph_3C^+}$ in $\mathrm{CH_2Cl_2}$. This, together with the location of the δ values in the ^{1}H NMR spectra of **15** and $\mathbf{16}^+$, indicates the stereochemistry of the incoming hydrogens are exo, consistent with the $\mathrm{H^-}$ transfer mechanism.

(25) $(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{Fe^+}(\eta^5\text{-}\mathrm{C_6Me_6H})\mathrm{PF_6^-}$ ($\mathbf{16}^+$): ^{1}H NMR ($\mathrm{CD_3COCD_3}$) δ 2.60 (s, *p*-$\mathrm{CH_3}$, 3 H), 2.33 (s, $\mathrm{CH_3}$, 18 H), 1.90 (s, *m*-$\mathrm{CH_3}$, 6 H), 1.23 (m, endo and ortho $\mathrm{CH_3}$, exo H, 10 H); ^{13}C NMR ($\mathrm{CD_3CN}$) δ 100.8 ($\mathrm{C_6}$ ring), 95.1 (*m* ring C), 92.3 (*p* ring C), 50.6 (*o*-ring C), 39.1 ($\mathrm{sp^3}$ ring C), 16.6 (endo $\mathrm{CH_3}$), 15.1 (*p*-$\mathrm{CH_3}$), 15.6 (*m*-$\mathrm{CH_3}$), 14.0 (*o*-$\mathrm{CH_3}$), 16.1 ($\mathrm{CH_3}$); Mössbauer parameters (mm $\mathrm{s^{-1}}$) IS (vs. Fe) 0.51 (293 K), 0.62 (77 K), QS 1.38 (293 and 77 K). Anal. Calcd for $\mathrm{C_{24}H_{37}Fe}$: C, 54.75; H, 7.03; Fe, 10.64. Found: C, 54.64; H, 6.90; Fe, 10.66. Electrochemical data (polarography and cyclic voltammetry in DMF + $\mathrm{Bu_4N^+ClO_4^-}$ at 20 °C on Hg) −1.45 V vs. SCE ($16/16^+$, reversible), −2.20 V vs. SCE (irreversible reduction to the 20-electron complex), +0.75 V vs. SCE on Pt (irreversible oxidation of $\mathbf{16}^+$ to $\mathbf{14}^{2+}$).

(26) $(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{Fe^I}(\eta^5\text{-}\mathrm{C_6Me_6H})$ (**16**): UV (pentane) λ 428 nm (ϵ 434 L $\mathrm{mol^{-1}\,cm^{-1}}$), 348 nm ($\epsilon$ 2080 L $\mathrm{mol^{-1}\,cm^{-1}}$); calcd 381.4081, found 381.4082. Anal. Calcd for $\mathrm{C_{24}H_{37}Fe}$: C, 75.60; H, 9.70; Fe, 14.70. Found: C, 75.10; H, 9.73; Fe, 15.17.

(27) $(\mathrm{C_6Me_6})_2\mathrm{Fe^0}$: QS = −1.47 mm $\mathrm{s^{-1}}$, IS = 1.02 mm $\mathrm{s^{-1}}$: Michaud, P.; Mariot, J. P.; Varret, F.; Astruc, D. "Mössbauer Discussion Group of the Chemical Society", Canterbury, July 1979, abstr, p 2.