filtration. IR (KBr): 1456, 1406, 1105, 997, 905, 826, 475 cm^{-1}. Anal. Calcd for $C_{24}H_{26}Fe_2I_5N$: C, 26.82; H, 2.44; Fe, 10.39; I, 59.04; N, 1.30. Found: C, 26.83; H, 2.47; Fe, 10.42; I, 59.00; N, 1.26. Crystals suitable for X-ray diffraction were obtained by layering a CH_2Cl_2 solution of **17** with benzene that contained a small amount of iodine.

Reaction of *N*-Methyl-2,5″-(2-azapropane-1,3-diyl)biferrocene (13) with Iodine. To a solution of 85 mg (0.20 mmol) of **13** in 20 mL of benzene was added dropwise 76 mg (0.30 mmol) of iodine in 10 mL of benzene. A dark brown crystalline compound was obtained (121 mg, 75%). Anal. Calcd for $C_{23}H_{23}Fe_2I_3N$: C, 34.28; H, 2.88; Fe, 13.86; I, 47.24; N, 1.74. Found: C, 34.55; H, 2.88; Fe, 13.77; I, 47.05; N, 1.73.

Reaction of *N*-Methyl-2,5″-(2-azapropane-1,3-diyl)biferrocene (13) with DDQ. A solution of 45 mg of 2,3-dichloro-5,6-dicyanoquinone (DDQ) in 10 mL of benzene was added dropwise to a stirred solution of 85 mg (0.20 mmol) of **13** in 20 mL of benzene. A dark brown crystalline compound which has the formula **13**$\cdot$DDQ$\cdot H_2O\cdot{}^1/_2C_6H_6$, was obtained. Anal. Calcd for $C_{34}H_{28}Cl_2Fe_2N_3O_3$: C, 57.58; H, 3.98; Cl, 10.00; Fe, 15.75; N, 5.92. Found: C, 57.15; H, 4.07; Cl, 10.28; Fe, 15.66; N, 6.01.

Reaction of *N*-Methyl-2,5″-(2-azapropane-1,3-diyl)biferrocene (13) with Ferrocenium Hexafluorophosphate. To a suspension of 50 mg (0.15 mmol) of ferrocenium hexafluorophosphate in 30 mL of benzene was added 85 mg (0.20 mmol) of **13**. The mixture was stirred for 24 h and then filtered. The solid was washed with benzene and air dried. A 87-mg amount (93%) of reaction product, which has the formula [**13**]$PF_6\cdot H_2O\cdot{}^1/_2C_6H_6$, was obtained. Anal. Calcd for $C_{26}H_{28}F_6Fe_{20}P$: C, 49.79; H, 4.50; Fe, 17.81; N, 2.23. Found: C, 50.38; H, 4.60; Fe, 17.52; N, 2.10.

Crystal Measurements and Structure Determination for Complex 17. The dark, opaque, prismatic crystal used for data collection had well-developed faces (0.2 × 0.4 × 0.4 mm). The crystal was mounted by using epoxy to a thin glass fiber with the (230) scattering planes roughly normal to the spindle axis. A Syntex P2_1 automated four-circle diffractometer was used to collect intensities at 299 K. Corrections were made for Lorentz and polarization effects, anomalous dispersion, and crystal decomposition (total decay, 53%). A numerical correction for absorption was applied where the maximum and minimum transmission factors were 0.210 and 0.065, respectively. Additional experimental details are given in Table I.

The structure was solved by direct methods (SHELXS-86). Correct positions for the iodine iron atoms were deduced from an *E* map. Subsequent least-squares difference Fourier calculations gave positions for the remaining non-hydrogen atoms. Hydrogen atoms were included as fixed contributors in "idealized" positions. In the final cycle of least squares, anisotropic thermal coefficients were refined for the non-hydrogen atoms and a group isotropic thermal parameters was varied for the hydrogen atoms. Successful convergence was ndicated by the maximum shift/error for the last cycle. The highest residual electron density in the final difference Fourier map was found in the vicinity of the iodine atoms. A final analysis of variance between observed and calculated structure factors showed a slight inverse dependence on sin *θ*. The final atomic positional parameters are given in Table II.

Acknowledgment. We are grateful for partial funding from National Institutes of Health Grant HL 13652 (D.N.H.).

Supplementary Material Available: Tables of calculated hydrogen positions, planes, and thermal parameters (4 pages); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Contribution from the Institut für Anorganische Chemie
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Reactivity of $(i\text{-}C_3H_7)_2GaBr$ with C_2H_5SH and C_2H_5SeH. Synthesis of $i\text{-}C_3H_7(Br)GaEC_2H_5$ (E = S, Se)

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The synthesis of the Lewis acid–base adducts $(i\text{-}C_3H_7)_2GaBr\cdot HEC_2H_5$ (E = S, Se) is reported. The thermal treatment of these adducts to give isopropyl(ethylchalcogenolato)gallium bromides was demonstrated. All new compounds were characterized by physical methods (^{1}H NMR, ^{13}C NMR, and IR spectroscopy and DTA).

In comparison with the trialkylgallanes, the reactivity of dialkylgallium halides toward H-acidic compounds has received scant attention. With the exception of the well-investigated chemistry of the $(CH_3)_2Ga^+$ moiety in aqueous solution,[1] there is not much information available on the chemistry in organic solvents of compounds containing this fragment.[2] This fact may be due to the enormously reduced reactivity of the gallium–carbon bond in such dialkylgallium compounds in general.[3] In this connection it has been elucidated very clearly that reactions of $(CH_3)_2GaSR$ with HSR′ result in an exchange of the thiolate group and thus in the formation of $(CH_3)_2GaSR'$ if HSR is more volatile than HSR′.[4] Therefore, it seems worthwhile to us to investigate the reactions of $(i\text{-}C_3H_7)_2GaBr$ with chalcogenols, such as HSC_2H_5 and $HSeC_2H_5$, respectively, with respect to the reactivity of the gallium–carbon, gallium–bromine, and gallium–chalcogen bonds.

Experimental Section

All experiments were performed under an atmosphere of dry nitrogen or, if necessary, argon in freshly distilled solvents. $GaBr_3$,[5] $(i\text{-}C_3H_7)_3Ga$,[6] and $i\text{-}C_3H_7Li$[7] were prepared by published procedures. ^{1}H NMR spectra were recorded on a JEOL FX 90Q spectrometer. Benzene-d_6 ($\delta = 7.75$) was used as solvent, and all chemical shifts are reported with respect to Me_4Si. ^{13}C NMR spectra were obtained on a JEOL FX 90Q instrument and are reported in ppm. IR spectra were recorded as Nujol mulls or films between CsI plates on a Perkin-Elmer 283 instrument, osmometric molecular weight determinations in benzene solution on a Knauer vapor-phase osmometer; melting- and decomposition points are uncorrected and obtained on a Du Pont 990 thermal analyzer. C and H microanalyses were performed on a Carlo Erba 1106 instrument; Ga[8] and Br[9]

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were analyzed according to well-known analytical methods.

$(i\text{-C}_3\text{H}_7)_2\text{GaBr}$ (1). (i). To a solution of GaBr_3 (6.00 g, 19.4 mmol) in benzene (15 mL) was added 20.4 mL of a benzene solution of $i\text{-C}_3\text{H}_7\text{Li}$ (1.9 M) within 30 min. A white precipitate formed, and after the reaction mixture was stirred for 15 min, it was filtered. The residue was washed twice with 5-mL portions of benzene. The filtrates were combined, and the solvent was removed under vacuum. The resulting light yellow liquid (yield 3.70 g (81 %)) was purified by fractional distillation under reduced pressure (bp 95–97 °C (0.1 mm)).

(ii). To a solution of GaBr_3 (0.93 g, 3.01 mmol) in benzene (10 mL) was added a solution of $(i\text{-C}_3\text{H}_7)_3\text{Ga}$ (1.20 g, 6.03 mmol) in benzene (10 mL). The resulting solution was heated at reflux for 3 h after which time the solvent was removed under vacuum. The resulting liquid (yield 1.85 g (87 %)) was purified by fractional distillation (bp 95–96 °C (0.1 mm)). Anal. Calcd for $\text{C}_6\text{H}_{14}\text{BrGa}$: C, 30.6; H, 6.00; Br, 33.9; Ga, 29.6. Found: C, 30.2; H, 5.80; Br, 32.5; Ga, 30.5. ^{1}H NMR: δ 1.16 (d, asym,[10] CH_3 and GaCH). ^{13}C NMR (C_7D_8): δ 20.06 (s, CH_3), 22.11 (s, CH). IR (1500–200 cm^{-1}, CsI, film): 1464 (b), 1385 (s), 1372 (s), 1365 (sh), 1339 (m), 1297 (w), 1259 (m), 1206 (b), 1158 (m), 1140 (m), 1112 (b), 1077 (s), 989 (s), 949 (b), 916 (m), 872 (s), 822 (b), 795 (sh), 782 (m), 688 (w), 609 (b), 543 (b), 505 (m), 414 (m), 400 (s), 350 (w), 290 (b), 279 (s), 261 (s), 219 (m) cm^{-1}.

$(i\text{-C}_3\text{H}_7)_2\text{GaBr}\cdot\text{HSC}_2\text{H}_5$. To a solution of $(i\text{-C}_3\text{H}_7)_2\text{GaBr}$ (3.89 g, 16.5 mmol) in benzene (20 mL) was added $\text{C}_2\text{H}_5\text{SH}$ (1.03 g ≅ 1.23 mL, 16.5 mmol). The resulting solution was stirred for 10 min at room temperature. The solvent was removed under vacuum, and the remaining oil was dried under reduced pressure for several hours. Yield: 3.86 g (79 %) DTA: 183 °C (exotherm). Anal. Calcd for $\text{C}_8\text{H}_{20}\text{BrGaS}$: C, 32.25; H, 6.77; Br, 26.8; Ga, 23.4. Found: C, 33.1; H, 7.01; Br, 25.8; Ga, 23.3. ^{1}H NMR: δ 0.70–1.65 (m, 18, CH_3, GaCH, SH), 2.20–3.13 (m,[11] 2, SCH_2). IR (1500–200 cm^{-1}, CsI, film): 1463 (b), 1385 (s), 1380 (sh), 1370 (w), 1262 (s), 1204 (s), 1154 (m), 1140 (w), 1110 (b), 1072 (m), 1053 (m), 984 (s), 967 (s), 945 (b), 915 (m), 871 (s), 823 (s), 805 (m), 765 (m), 675 (w), 645 (b), 609 (b), 540 (b), 505 (w), 393 (m), 375 (m), 289 (b) cm^{-1}.

Thermal Treatment of $(i\text{-C}_3\text{H}_7)_2\text{GaBr}\cdot\text{HSC}_2\text{H}_5$. (i). An attempt to distill the adduct under reduced pressure (200 °C, 0.01 mm) resulted in partial decomposition by loss of $\text{C}_2\text{H}_5\text{SH}$, which condensed in a −78 °C trap. To the distillation product, $(i\text{-C}_3\text{H}_7)_2\text{GaBr}$ containing small amounts of $\text{C}_2\text{H}_5\text{SH}$, was added excess $\text{C}_2\text{H}_5\text{SH}$. The resulting mixture was treated for several hours at room temperature under vacuum. An oily liquid remained, which was found to be the adduct $(i\text{-C}_3\text{H}_7)_2\text{GaBr}\cdot\text{HSC}_2\text{H}_5$.

(ii). To the adduct (1.25 g, 4.20 mmol) was added excess $\text{C}_2\text{H}_5\text{SH}$; the resulting solution was heated at reflux for 3 days. The solution was treated under reduced pressure to remove all volatiles. An oil remained. Yield: 0.88 g (82 %). Anal. Calcd for $\text{C}_5\text{H}_{12}\text{BrGaS}$: C, 23.66; H, 4.77; Br, 31.48; Ga, 27.47. Found: C, 23.37; H, 4.39; Br, 32.0; Ga, 27.9. ^{1}H NMR: δ 0.68–1.57 (m, 10, CH_3, GaCH), 2.58–3.18 (q, 2, $J = 8$ Hz, SCH_2). IR (1500–200 cm^{-1}, CsI, film): 1463 (b), 1379 (s), 1367 (s), 1260 (b), 1204 (m), 1155 (m), 1106 (w), 1075 (s), 1055 (s), 986 (s), 967 (s), 941 (m), 917 (w), 871 (s), 825 (w), 805 (m), 764 (m), 665 (b), 643 (b), 537 (m), 395 (m), 380 (m), 293 (b), 270 (sh) cm^{-1}. Mol wt: 253.83n (772, n = 3.0). Vapor pressure osmometric: 0.057 g in 10 mL of benzene.

$(i\text{-C}_3\text{H}_7)_2\text{GaBr}\cdot\text{HSeC}_2\text{H}_5$. To a stirred solution of $(i\text{-C}_3\text{H}_7)_2\text{GaBr}$ (3.54 g, 15 mmol) in benzene (30 mL) was added $\text{C}_2\text{H}_5\text{SeH}$ (1.64 g ≅ 1.12 mL, 15 mmol). The resulting solution was stirred for 10 min at room temperature, after which time the solvent was removed under vacuum. The remaining oily liquid was treated under reduced pressure for several hours. Yield: 4.29 g (81%). DTA: 170 °C (exotherm). Anal. Calcd for $\text{C}_8\text{H}_{20}\text{BrGaSe}$: Br, 23.17; Ga, 20.22. Found: Br, 22.8; Ga, 19.8. ^{1}H NMR: δ 0.73–1.68 (m, 18, CH_3, GaCH, SeH), 2.23–3.18 (m,[11] 2, SeCH_2). IR (1500–200 cm^{-1}, CsI, film): 1464 (b), 1450 (sh), 1378 (s), 1366 (s), 1259 (m), 1227 (s), 1200 (s), 1152 (m), 1073 (m), 1046 (m), 981 (s), 960 (s), 915 (m), 869 (s), 801 (m), 748 (s), 673 (w), 546 (b), 540 (sh), 503 (w), 394 (m), 270 (sh), 259 (b) cm^{-1}.

Thermal Decomposition of $(i\text{-C}_3\text{H}_7)_2\text{GaBr}\cdot\text{HSeC}_2\text{H}_5$ to $i\text{-C}_3\text{H}_7(\text{Br})\text{GaSeC}_2\text{H}_5$. The adduct (3.00 g, 8.70 mmol) was heated at atmospheric pressure to 200 °C for 60 min. After the reaction was cooled to room temperature, the remaining white solid was treated for several hours under reduced pressure to remove all volatiles. Yield: 2.57 g (98 %). DTA: 129 °C. Anal. Calcd for $\text{C}_5\text{H}_{12}\text{BrGaSe}$: C, 19.97; H, 4.03; Br, 26.57; Ga, 23.18. Found: C, 20.23; H, 4.35; Br, 26.8; Ga, 23.6. ^{1}H NMR: δ 0.67–1.58 (m, 10, CH_3, GaCH), 2.32 (q, 2, $J = 8$ Hz, SeCH_2). ^{13}C NMR: (C_6D_6): δ 14.82 (s, CH_3), 19.96 (s, CH_2CH_3), 20.32 (s, GaCH), 24.41 (s, SCH_2). IR (1400–200 cm^{-1}, CsI, Nujol mull): 1382 (s), 1366 (s), 1260 (m), 1224 (s), 1197 (s), 1152 (s), 1106 (m), 1076 (s), 981 (s), 940 (m), 914 (w), 869 (s), 805 (m), 755 (w), 676 (m), 648 (m), 612 (m), 526 (b), 392 (s), 279 (b), 205 (b) cm^{-1}. Mol wt: 300.73n (998, n = 3.3). Vapor pressure osmometric: 0.106 g in 10 mL of benzene.

Results and Discussion

The reactions of both $\text{C}_2\text{H}_5\text{SH}$ and $\text{C}_2\text{H}_5\text{SeH}$ with $(i\text{-C}_3\text{H}_7)_2\text{GaBr}$ in benzene solutions at ambient temperatures lead to formation of the 1:1 Lewis acid–base adducts (eq 1), which

$$(i\text{-C}_3\text{H}_7)_2\text{GaBr} + \text{C}_2\text{H}_5\text{EH} \underset{\text{high temp}}{\overset{\text{low temp to room temp}}{\rightleftarrows}} (i\text{-C}_3\text{H}_7)_2\text{GaBr}\cdot\text{HEC}_2\text{H}_5 \quad (1)$$

$$\text{E} = \text{S, Se}$$

can be isolated at room temperature in high yields as oily liquids. The adducts are identified by conventional physical measurements. The IR spectrum of the thiol adduct shows additional absorption signals at 645 and 393 cm^{-1} compared with the IR spectrum of $(i\text{-C}_3\text{H}_7)_2\text{GaBr}$. These signals can be assigned to the carbon–sulfur and gallium–sulfur stretching frequencies, whereas the carbon–selenium as well as the gallium–selenium stretching frequencies in the IR spectrum of the selenol adduct may be assigned to the absorption signals at 540 and 259 cm^{-1}. Both signals, however, are superposed, the first one by the asymmetric gallium–carbon stretching frequency and the second one by a gallium–bromine stretching frequency. The ^{1}H NMR spectra of both adducts show several quartets for the methylene protons of the $\text{CH}_3\text{CH}_2\text{S}$ as well as $\text{CH}_3\text{CH}_2\text{Se}$ groups that superpose each other. This phenomenon may be due to different isomers and/or a dissociation–association mechanism of the adducts in solution. Further investigations concerning this interesting phenomenon are still in hand. The differential thermal analysis (DTA) of the two adducts show that these compounds are not stable at higher temperatures. The decomposition of the adducts may follow at least three reaction pathways under formation of (i) C_3H_8 (eq 2), (ii) HBr (eq 3), and (iii) HEC_2H_5 (eq 1, high temperature) (E = S, Se). It

$$(i\text{-C}_3\text{H}_7)_2\text{GaBr}\cdot\text{HEC}_2\text{H}_5 \xrightarrow{\text{room temp}} \text{C}_3\text{H}_8 + i\text{-C}_3\text{H}_7(\text{Br})\text{GaEC}_2\text{H}_5 \quad (2)$$

$$(i\text{-C}_3\text{H}_7)_2\text{GaBr}\cdot\text{HEC}_2\text{H}_5 \xrightarrow{\text{room temp}} \text{HBr} + (i\text{-C}_3\text{H}_7)_2\text{GaEC}_2\text{H}_5 \quad (3)$$

$$\text{E} = \text{S, Se}$$

could be shown that the decomposition reaction of the two compounds leads to the elimination of propane under the formation of the three times differently substituted isopropylbromo(ethylchalcogeno)gallanes, hence following eq 2. However, to form equivalent products, the reaction conditions for the decomposition of the two adducts have to be changed completely. Without a solvent, the thermal treatment of the selenol adduct easily leads to the loss of propane and thus results in the formation of the new compound $i\text{-C}_3\text{H}_7(\text{Br})\text{GaSeC}_2\text{H}_5$, whereas in the case of the thiol adduct the same procedure leads to the partial loss of $\text{C}_2\text{H}_5\text{SH}$, following the back-reaction in eq 1. Obviously, the acidic strength of the selenol is only just sufficient to enforce the cleavage of the gallium–carbon bond of the adduct at elevated temperatures, whereas under the same conditions the acidic strength of the thiol is too small. However, if the thiol adduct is treated for several days in an excess of refluxing $\text{C}_2\text{H}_5\text{SH}$, the only product observed in this case is the gallium thiolate $i\text{-C}_3\text{H}_7(\text{Br})\text{GaSC}_2\text{H}_5$, which for its part could be prepared independently via the reaction of $i\text{-C}_3\text{H}_7\text{GaBr}_2$ with $(\text{CH}_3)_3\text{SiSC}_2\text{H}_5$ in benzene solution.[12] Using an excess of thiol allows the reaction according to eq 1 to be shifted to the right side even at higher temperatures. This consequently

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(10) AB_6 spin system. This fact is not unusual for such compounds; see, for example: Weidenbruch, M.; Schiffer, W.; Hägele, G.; Peters, W. *J. Organomet. Chem.* **1975**, *90*, 145.

(11) Quartets, superposing each other.

(12) Hoffmann, G. G.; Fischer, R. *Z. Anorg. Allg. Chem.*, submitted for publication.

enables the decomposition reaction with the formation of propane (eq 2).

On the other hand, however, there is no evidence for the cleavage of the gallium–bromine bond with formation of HBr (eq 3). These results indicate that the bond strengths of the gallium–heteroatom bonds are decreasing in the order of GaBr[13] >GaSe > GaC[14] ~ GaS.

The compounds $i\text{-}C_3H_7(Br)GaEC_2H_5$ (E = S, Se) were identified by conventional physical measurements as well as microanalyses. The most striking difference in the IR spectra of the chalcogenolates to those of the adducts is the lack of one gallium–carbon stretching frequency. This is, of course, due to the fact that there is only one isopropyl group attached to the gallium atom. An osmometric molecular weight determination in benzene solution reveals a trimeric arrangement of $i\text{-}C_3H_7(Br)GaSeC_2H_5$ in solution.

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Registry No. 1, 122648-93-5; $\mathbf{1}\cdot HSC_2H_5$, 122700-89-4; $\mathbf{1}\cdot HSeC_2H_5$, 122700-90-7; $GaBr_3$, 13450-88-9; $(i\text{-}C_3H_7)_3Ga$, 54514-59-9; C_2H_5SH, 75-08-1; $i\text{-}C_3H_7(Br)GaSC_2H_5$, 122648-94-6; C_2H_5SeH, 593-69-1; $i\text{-}C_3H_7(Br)GaSeC_2H_5$, 122648-95-7.

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Redox Kinetics of Metal Complexes in Nonaqueous Solutions: Oxidation of Methyl-Substituted Tris(1,10-phenanthroline)iron(II) Complexes by Hexakis(*N*,*N*-dimethylformamide)iron(III) in Acetonitrile

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Of the methyl-substituted tris(1,10-phenanthroline)iron(II) perchlorates ($Fe(X\text{-}phen)_3^{2+}$), the tetra- and hexamethyl derivatives are quantitatively oxidized by iron(III) in acetonitrile (MeCN) solution, introduced as $Fe(dmf)_6(ClO_4)_3$ (dmf = *N*,*N*-dimethylformamide). For the latter, evidence involving NMR studies is presented for the occurrence of three fast solvation equilibria (L = dmf; coordinated MeCN is omitted), $FeL_6^{3+} \rightleftharpoons FeL_3^{3+} + 3L$. In line with the respective redox potentials, FeL_3^{3+} and FeL_4^{3+} are the redox-active species. At higher [L] only equilibrium positions are reached that are adequately described by the equilibrium $FeL_4^{3+} + Fe(X\text{-}phen)_3^{2+} \rightleftharpoons FeL_4^{2+} + Fe(X\text{-}phen)_3^{3+}$. Coupled with the redox equilibrium are the solvation equilibria $FeL_4^{3+} + e^- \rightleftharpoons FeL_4^{2+} \rightleftharpoons FeL_3^{2+} \rightleftharpoons FeL_2^{2+}$, giving rise to reversible product inhibition at a low concentration level of L. The dependences of the pseudo-first-order redox rate constants are successfully accommodated by a rate law embodying both ion pairing between both reactants and ClO_4^- and ionic strength dependences through work terms for both the free-ion and ion-paired paths. For the iron(III) species also appreciable formation of ion triplets is required. The relationship between the rate constants with no electrostatic interaction and the driving force is shown.

Introduction

In the preceding article[2] we reported the kinetics of the reduction of $Fe(phen)_3^{3+}$ by $Fe(dmf)_6^{2+}$ in acetonitrile (MeCN) with both salts added as the perchlorates. This study faced the problem of a substitutionally labile system complicating an outer-sphere redox process as well as the problem of electrostatic interaction between highly charged reactants in a solvent of moderate dielectric constant and finally the related problem of ion pairing. The analysis of such data represents an awkward problem at the moment owing to the lack of particularly reliable theoretical approaches.

If now methyl groups are introduced into the phenanthroline rings, the redox potential of the iron complex is shifted to more negative values so that the reaction proceeds in the reverse direction, again in MeCN. Thus, upon mixing of an excess of $Fe(dmf)_6^{3+}$ with tetramethylferroin, quantitative oxidation of the latter is observed.[3] The analysis in this earlier paper proved to be erroneous. The correction and the completion of these studies is the purpose of the present paper. In addition, some other methylferroins have been used.

Table I. Redox Potentials[a] for $Fe^{3+/2+}$ in Acetonitrile at 25 °C

complex	$E_{1/2}$,[b] V
$Fe(dmf)_6^{3+/2+}$ [c]	1.06_8 (100)
$Fe(dmf)_5(MeCN)^{3+/2+}$	1.27[e]
$Fe(dmf)_4(MeCN)_2^{3+/2+}$	1.48[d]
$Fe(Me_6phen)_3^{3+/2+}$	1.52_0 (173)
$Fe(3,4,7,8\text{-}Me_4phen)_3^{3+/2+}$	1.57_5 (85)
$Fe(4,7\text{-}Me_2phen)_3^{3+/2+}$	1.66_7 (74)
$Fe(dmf)_3(MeCN)_3^{3+/2+}$	1.70[e]
$Fe(5,6\text{-}Me_2phen)_3^{3+/2+}$	1.76_9 (75)
$Fe(phen)_3^{3+/2+}$	1.83_6 (105)
$Fe(MeCN)_6^{3+/2+}$ [c]	2.56_4 (365)

[a] The potentials are referenced to BCr (−1.118 V vs ferrocene/ferrocenium). [b] $E_{1/2}$ taken as $(E_p^{red} + E_p^{ox})/2$. Numbers in parentheses are peak separations in millivolts. Scan rate = 100 mV/s, 0.1 M $Bu_4N(PF_6)$ was present, and reactant concentrations were ca. 1 mM. [c] Reference 2. [d] Calculated from the redox equilibrium constant described in the text. [e] Interpolated.

Experimental Section

The ligands 5,6-dimethyl- and 3,4,5,6,7,8-hexamethyl-1,10-phenanthroline ($5,6\text{-}Me_2phen$ and Me_6phen) were prepared by Skraup reactions using a literature method.[4] 4,7-Dimethyl- and 3,4,7,8-tetramethyl-1,10-phenanthroline ($4,7\text{-}Me_2phen$) (Baker) and Me_4phen

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