# Chemistry of (Pentabenzylcyclopentadienyl)iron Compounds Including 17-Electron Dithiocarbamate Complexes

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$C_5(CH_2Ph)_5H$, $C_5Bz_5H$, **1**, the precursor of the useful $C_5Bz_5$ ligand that was introduced by Rausch, has been synthesized in 85% yield, a slight improvement over the 62% yield very recently reported by Rausch. $[Fe(C_5Bz_5)(CO)_2]$, **2**, also reported by Rausch, could be obtained in 72% yield as the only product of the reaction between **1** and $[Fe(CO)_5]$ at 90 °C for 4 days. Reaction of **1** with $Br_2$ gives $[Fe(C_5Bz_5)(CO)_2Br]$, **3**, in 84% yield. Photolysis of **3** in THF using visible light in the presence of $Na^+S_2CNMe_2^-$ ($Na^+dtc^-$) gives a 73% yield of $[Fe(C_5Bz_5)(CO)(\eta^2\text{-dtc})]$, **4**, whose oxidation by $[FeCp_2]^+PF_6^-$ gives the 17-electron complex $[Fe^{III}(C_5Bz_5)(\eta^2\text{-dtc})(NCMe)]^+PF_6^-$, **5**, the precursor of $[Fe^{IV}Cp^*(\eta^2\text{-dtc})_2]^+PF_6^-$, **7**. Cyclic voltammetry studies of the $C_5Bz_5$−iron complexes show that the electronic properties of $C_5Bz_5$ are intermediate between those of $C_5H_5$ (Cp) and $C_5Me_5$ (Cp*) and that $C_5Bz_5$ destabilizes paramagnetic iron complexes as opposed to the stabilizing property of Cp*.

## Introduction

Ten years ago, Rausch et al. published the first pentabenzylcyclopentadienyl complexes.[1−3] A paper recently appeared from Rausch's group[4] reporting an improved procedure for the synthesis of pentabenzylcyclopentadiene. In this paper, the reaction of this ligand with iron pentacarbonyl is analyzed and reported to give bis[(pentabenzylcyclopentadienyl)dicarbonyliron] dimer and ($\eta^4$-pentabenzylcyclopentadiene)tricarbonyliron.

We have been interested for some time in cyclopentadienyl-type ligands[5−7] in order to stabilize and crystallize new organometallic complexes,[8] especially paramagnetic ones.[9] Our interest in the pentabenzylcyclopentadienyl ligand started when we tried to obtain crystals from the robust complex $[Fe^{IV}(C_5Me_5)(S_2CNMe_2)_2]^+PF_6^-$. Our frustration was then compensated by success in the case of the pentabenzylcyclopentadienyl derivative $[Fe^{IV}\{C_5(CH_2Ph)_5\}(S_2CNMe_2)_2]^+PF_6^-$, whose crystal structure was recently published.[9] In the course of this work, we improved upon the known synthesis of pentabenzylcyclopentadiene and obtained an 85% yield. The recent report by Rausch[4] urges us to also report these improvements. In the course of our work, we also needed a good-yield synthesis of the starting material bis[(pentabenzylcyclopentadienyl)dicarbonyliron] dimer. Indeed, we have developed a procedure leading to a 72% yield. We have also synthesized the bromo derivative by cleavage of the Fe−Fe bond, and from there, we have synthesized several dithiocarbamate compounds, including paramagnetic ones, which we are also reporting in the present paper.

## Results and Discussion

**Pentabenzylcyclopentadiene, 1.** Pentabenzylcyclopentadiene, first reported by Hirsch and Bailey in 1978,[10] was originally obtained in 19% yield, and its X-ray structure confirmed the proposed assignment of this complex by these authors. Rausch's group improved the yield to 28%[1] and finally to 62%.[4] In our work, at first we followed the original procedure given in ref 1, but found that it could be improved considerably by a slower addition of dicyclopentadiene to the reaction mixture (benzylic alcohol, small pieces of sodium metal, and diisopropyl benzene). We believe this slow rate of addition is crucial to obtain a good yield. We note that our rate of addition is about two times slower than that reported by Rausch et al.,[4] and this must account for our improved yield (eq 1).

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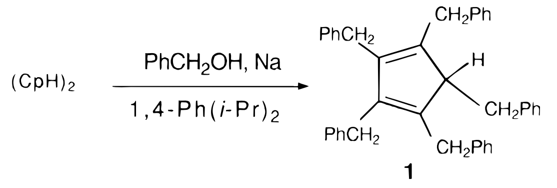
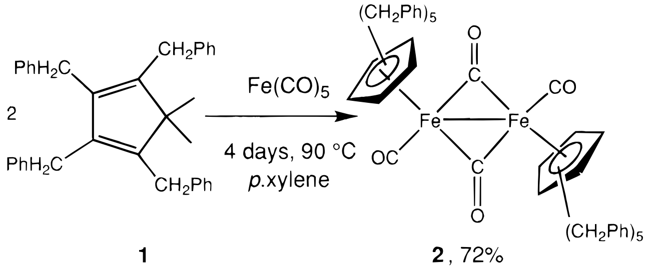


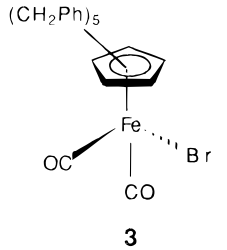
(1)

**Bis[(pentabenzylcyclopentadienyl)dicarbonyliron] Dimer, 2.** The report by Rausch of the stabilization of ($\eta^4$-pentabenzylcyclopentadiene)tricarbonyliron is of interest since the parent Cp ($C_5H_5$) compound is unstable. In their reaction between **1** and [Fe(CO)$_5$], Rausch's group refluxed the reaction mixture for 1 day in toluene (115 °C). Our conditions were different. Since we noted that the conditions used with pentamethylcyclopentadiene, refluxing xylene (145 °C),[12–14] provoked a huge amount of decomplexation, we lowered the reaction temperature to 90 °C and heated the reaction mixture for 4 days at this temperature. Interestingly, we did not obtain any side product (the monometallic tricarbonyl complex shows three carbonyl stretches in the 2000 cm$^{-1}$ region), and the $^1$H and $^{13}$C NMR spectra of the reaction product were clean. The yield under these conditions is 72% of dark-violet crystals (eq 2).



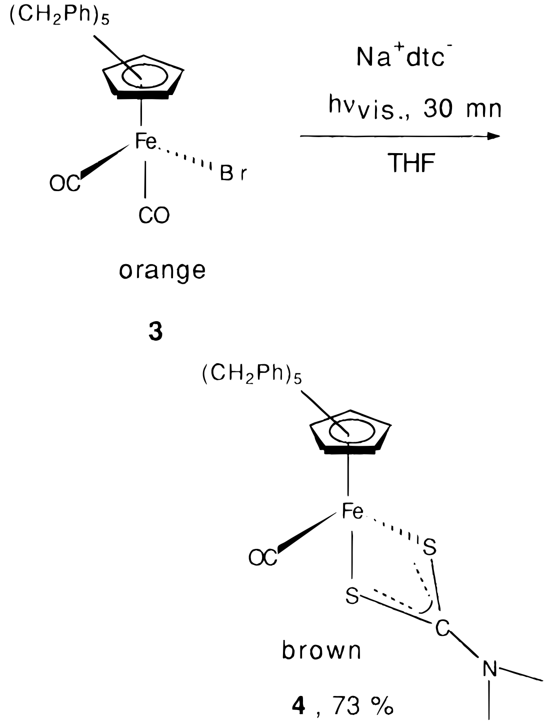
(2)

**Bromodicarbonyl($\eta^5$-pentabenzylcyclopentadienyl)iron(II), 3.** The iron–bromo derivatives [Fe$^{II}$($C_5R_5$)(CO)$_2$Br] are very useful starting materials to synthesize a series of sandwich[15] and piano-stool[16] Fe($C_5R_5$) complexes. In 1981, we reported the synthesis of [FeCp*(CO)$_2$Br] (Cp* = $C_5Me_5$) by clean cleavage of the dimer in $CH_2Cl_2$ using $Br_2$.[15] By applying the same procedure, we synthesized the pentabenzylcyclopentadienyl analogue **3** in 84% yield as orange needles.



**3**

**Versatile Reactivity of the Fe–Br Complex 3 and Synthesis of [Fe{$C_5(CH_2Ph)_5$}(CO)($S_2CNMe_2$)], 4.** We attempted some of the simple reactions known in the previous series [Fe($C_5R_5$)(CO)$_2$Br], R = H or $CH_3$, namely the replacement of the bromine ligand by CO induced by $Al_2Cl_6$[14,16] and the substitution of Br by dimethyldithiocarbamate (dtc$^-$) using its sodium salt[17] (Na$^+$dtc$^-$). Neither of these reactions work for **3**, although they had proved to be efficient for the $C_5H_5$ and $C_5Me_5$ analogues. The reaction of **3** with a 100-bar pressure of CO and $Al_2Cl_6$ failed. Likewise, the reaction of **3** with Na$^+$dtc$^-$ in refluxing DME also failed. Unreacted **3** was recovered almost quantitatively in each case. Either of these reactions would have ultimately led to the dithiocarbamate complexes. We found, however, that photolysis of **3** in the presence of Na$^+$dtc$^-$ gives [Fe{$C_5(CH_2Ph)_5$}(CO)($\eta^2$-dtc)] cleanly in 73% yield of rhombic bright-brown crystals (eq 3).



(3)

**Synthesis and Stability of 17-Electron Dithiocarbamate Complexes [Fe{$C_5(CH_2Ph)_5$}(L)($S_2CNMe_2$)]$^+$$PF_6^-$, L = CO, NCMe.** As in the Cp* series, we attempted to oxidize **4** to the isostructural 17-electron (17e) complex using ferricinium hexafluorophosphate. Although a color change is observed, it is not possible to isolate this 17e product. The solution quickly turns dark, indicating decomposition. In the Cp* series, we had obtained a thermally stable but extremely reactive, thus interesting, 17e complex.[9] It appears that this complex is not stable in the $C_5Bz_5$ series, probably because this ligand is not as electron releasing as Cp*. The agitation of the phenyl substituents (rapid rotation about the Cp–$CH_2$ axes) also may not be compatible with the use of weakly-bound ligands, such as CO, as the legs of the piano-stool, especially in a cationic 17e carbonyl complex.

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[12] King reported the preparation of [FeCp*(CO)$_2$]$_2$, in 48% yield, synthesized from the reaction of Cp*H with [Fe(CO)$_5$] in refluxing 2,2,5-trimethylhexane.[13,14] King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287.

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[14] The reaction was improved to a 65% yield using xylenes at reflux (2 days): Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094.

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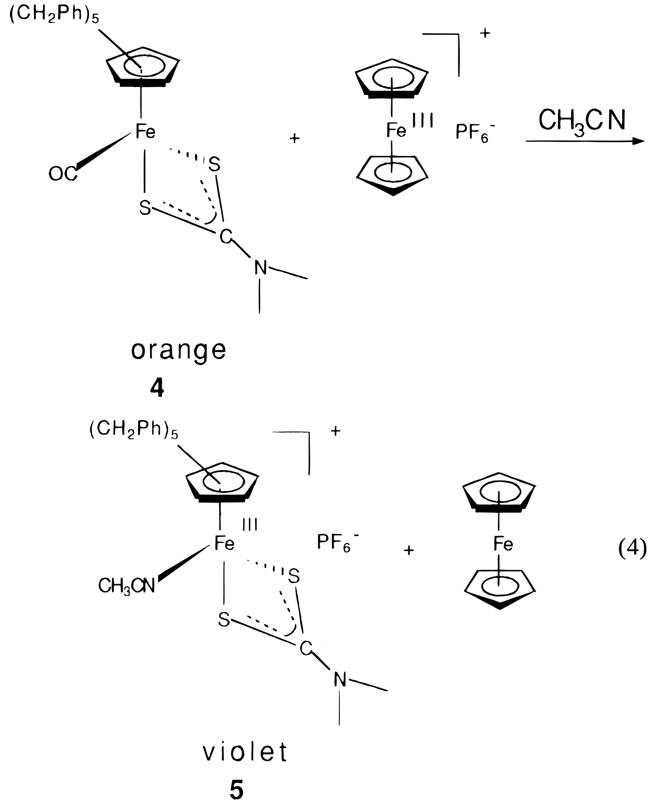
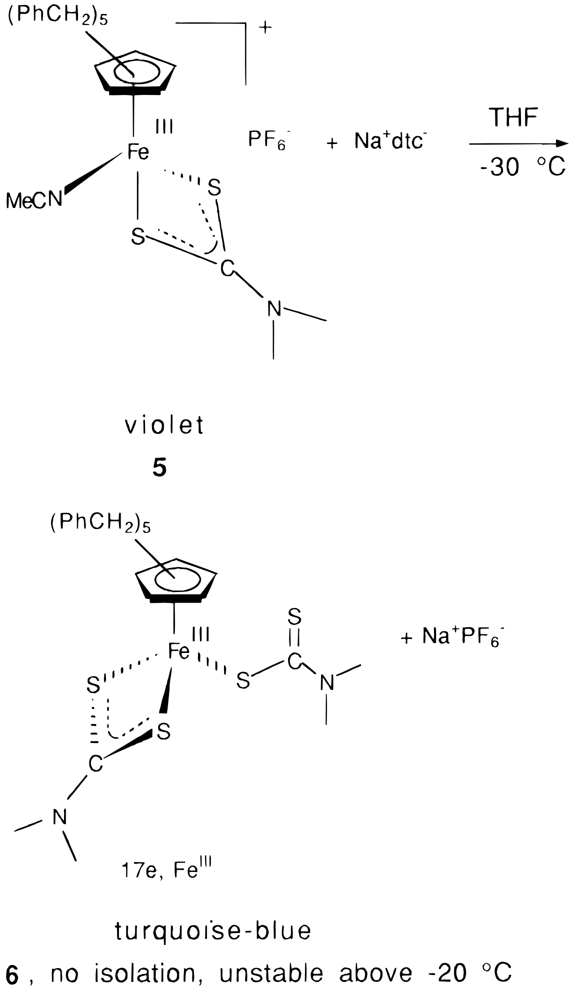
We carried out the same oxidation reaction in acetonitrile with the hope that the electron-releasing acetonitrile ligand would replace CO and stabilize the electron-deficient 17-electron complex. Indeed, in the Cp* series, the 17e carbonyl complex rapidly reacts with $CH_3CN$ with an associative mechanism to give the 17e acetonitrile complex.[9a] The oxidation of **4** in acetonitrile, after a color change from brown to violet, gave a stable paramagnetic dark-violet complex **5** that was characterized by elemental analysis and infrared and ESR spectroscopies. This reaction also produced 1 equiv of ferrocene (eq 4).



(4)

**Synthesis and Stability of Dia- and Paramagnetic Bis(dithiocarbamate) Complexes [Fe{$C_5(CH_2Ph)_5$}(dtc)$_2$]$^{0/+}$, 6/7.** The acetonitrile complex is an ideal substrate for the introduction of a second dithiocarbamate ligand using $Na^+dtc^-$ in THF. In the Cp* series, this led to neutral paramagnetic complexes in which either one (17e complex) or two dtc ligands (19e complex) acted as chelates.[9b] The two forms were interconverting, which led to the first spectroscopic and electrochemical characterization of a paramagnetic complex which was observable under both the 17e and 19e forms. The reaction of **5** with $Na^+dtc^-$ at room temperature led to decomposition, the neutral bis(dtc) complex again being less stable than the Cp* analogue. However, when this reaction was carried out between −35 and −20 °C, a color change from violet to bright turquoise-blue was observed (eq 5).

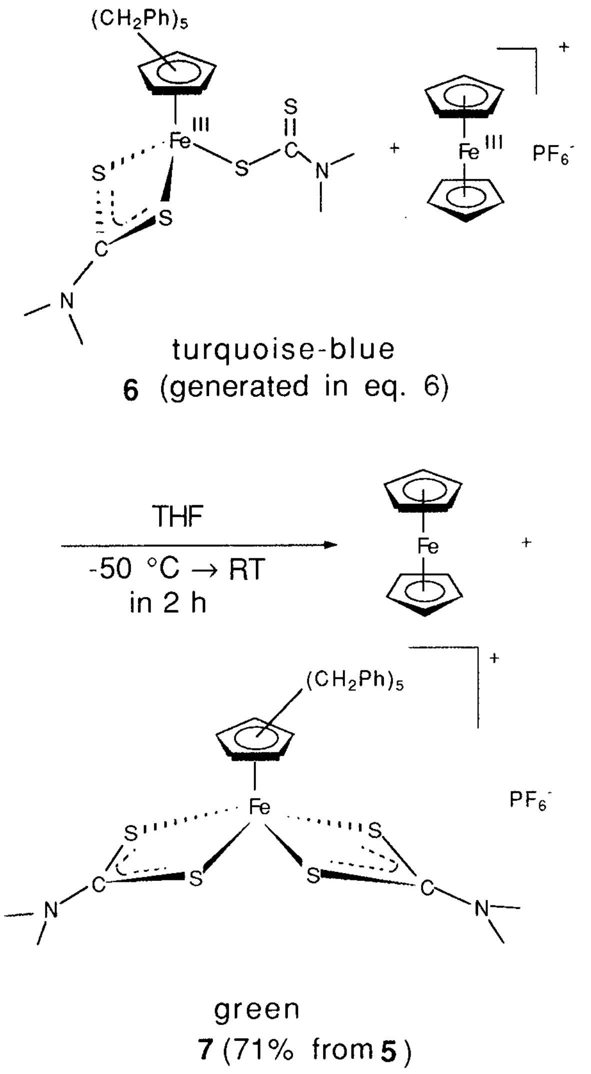


(5)

The bis(dtc) complex could be characterized by ESR spectroscopy. This spectrum shows that the acetonitrile complex **5** has completely disappeared. The new ESR spectrum contained three new *g* values indicating an orthorhombic distortion that is attributed to the 17e form. Table 1 contains the *g* values for the Cp* and $C_5Bz_5$ derivatives of the 17e acetonitrile−dtc and bis(dtc) complexes, and Figure 1 shows the ESR spectrum of **6**. The 17e form is also a necessary intermediate in the thermal decomposition of this complex (see also the electrochemical discussion).

The data on the $C_5Bz_5$ complex **6** taken alone are not as informative as they are for the Cp* analogue since **6** is thermally less stable, and thus it is not possible to observe both the 17e and 19e forms at the same time. This unstability of **6** again seems logical because of the mutual steric constraints that one encountered in the rotation of the phenyl rings about the Cp−$CH_2$ axis, interfering with the rotation of the monodentate dithiocarbamate about the Fe−S axis, especially in a 17e complex. However, taken together with the background knowledge that has been obtained for the Cp* analogue of **6**, the new trends are in accord with the previously established equilibrium between the 17e and 19e forms, decomposition proceeding via the 17e form. It was of interest to verify experimentally that the $C_5Bz_5$ ligand destabilizes paramagnetic complexes contrary to the Cp* ligand.

Although **6** is thermally unstable above −20 °C, its thermal stability up to −20 °C allowed the synthesis of the oxidized $Fe^{IV}$ cationic complex and, ultimately, the resolution of the crystal structure of the latter (Figure 2). Indeed, oxidation of **6**, as shown in eq 5, could be achieved using 1 equiv of ferricinium hexafluorophosphate. Upon addition of solid $[FeCp_2)]^+PF_6^-$ to the THF solution of **6** at −50 °C, the turquoise-blue color progressively disappeared upon warming and **7** precipitated as a green solid which was recrystallized (71.2% yield from **5**, eq 6).



(6)

Complex **7** is robust; thus, the $C_5Bz_5$ ligand is compatible with the coordination of two dtc ligands because the metal now has 18 valence electrons and both dtc ligands are bidentate. Oxidation of the 17e form of **6** generates a 16e fragment to which the free sulfur of the monodentate dtc ligand rapidly coordinates to fill the coordination sphere of the metal. The stabilization of such a high oxidation state results from the strong inorganic nature (four Fe−S bonds) of this complex. Nevertheless, it represents the first family of stable (even robust) $Fe^{IV}$ organometallic complexes.

**Electrochemistry of the $[Fe\{C_5(CH_2Ph)_5\}(dtc)L]$ Complexes.** In order to investigate the stability and behavior of odd-electron pentabenzylcyclopentadienyl dithiocarbamate complexes, we performed cyclic voltammetry experiments for the 18-electron carbonyl complex **4**, the 17-electron acetonitrile complex **5**, and the 18-electron bis(dtc) complex **7**. The results are summarized in Table 2 in which we compare the data of the $C_5Me_5$ and $C_5(CH_2Ph)_5$ ($C_5Bz_5$) complexes.

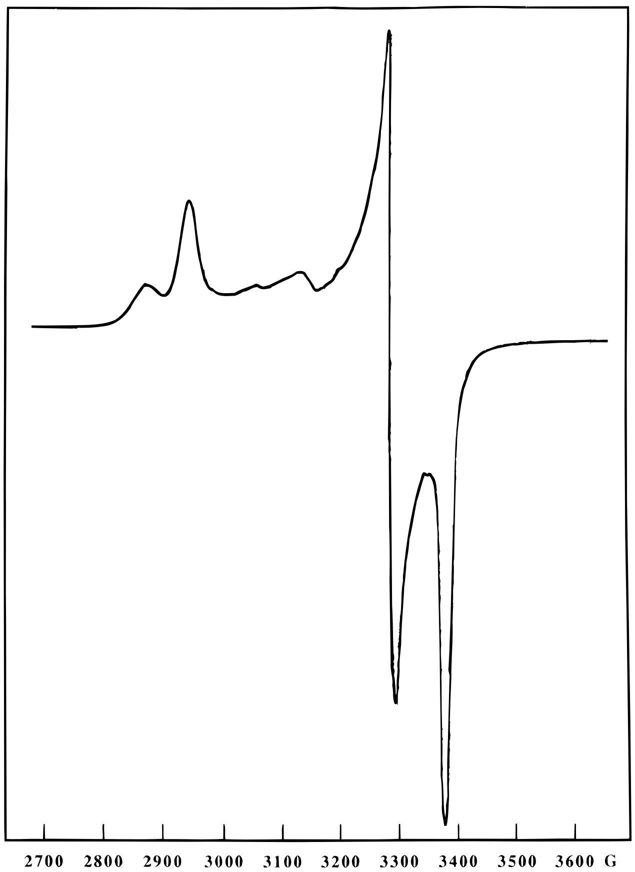
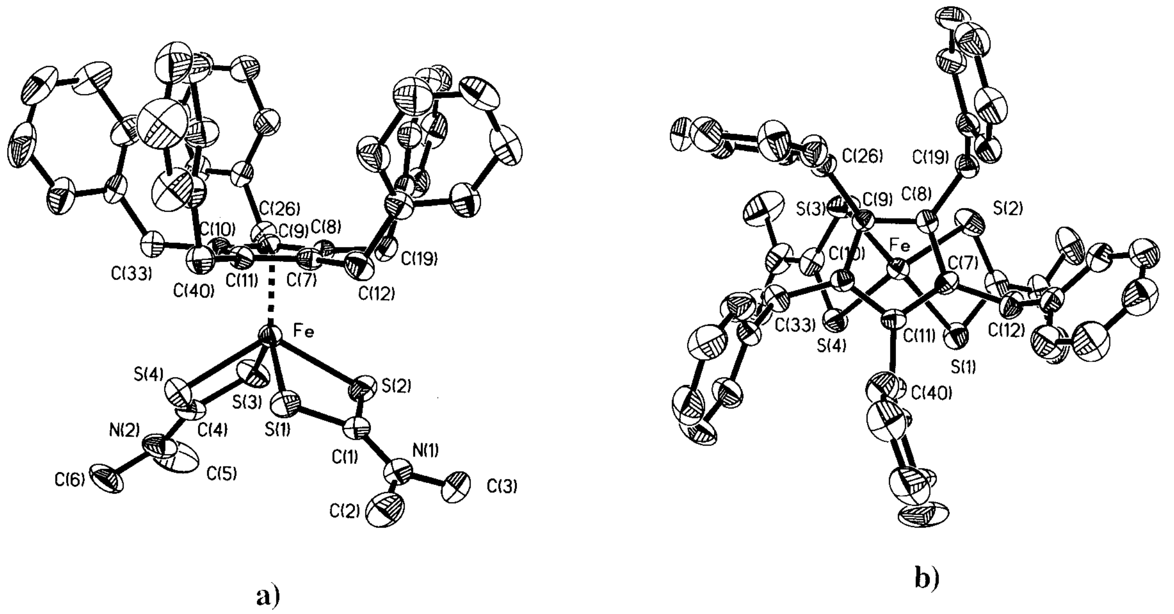


**Figure 1.** ESR spectrum of **6** in frozen THF at 12 K.

**Table 1. ESR Spectra**

| compound | R = $CH_3$ | R = $CH_2Ph$ |
|---|---|---|
| $[Fe(C_5R_5)(dtc)(NCMe)]PF_6$ | solid state (12 K) | solid state (18 K) |
| | $g_1 = 2.6722$ | $g_1 = 2.5736$ |
| | $g_2 = 2.0073$ | $g_2 = 2.0362$ |
| $[Fe(C_5R_5)(dtc)_2]$ | solid state (18 K) | frozen THF (12 K) |
| | $g_1 = 2.2680$ | $g_1 = 2.2707$ |
| | $g_2 = 2.1260$ | $g_2 = 2.0611$ |
| | $g_3 = 2.0350$ | $g_3 = 2.0002$ |

Complexes **4** and **5** give two chemically quasireversible waves corresponding to the $Fe^{II}/Fe^{III}$ and $Fe^{III}/Fe^{IV}$ redox systems at both negative and positive $E°$ values, SCE, respectively. Since these systems are quasireversible, the average between $E_{pa}$ and $E_{pc}$ of each redox system can be taken as the thermodynamic $E°$ value with a good degree of accuracy. The comparison between the $E°$ values of the Cp* and $C_5Bz_5$ complexes can now be done and shows that $C_5Bz_5$ is not as electron releasing as Cp*, the $E°$ being 0.1−0.3 V more positive for the $C_5Bz_5$ compounds than for the Cp* compounds. This tendency also holds for **7**, but at this time, the $E°$ values are not directly accessible from the CVs since the waves are chemically irreversible for the $C_5Bz_5$ compounds even at −80 °C, contrary to the Cp* analogue. For all the compounds examined, it is clear that the chemical reversibility is greatly reduced in the $C_5Bz_5$ complexes as compared to the Cp* analogues. This is related to the failure to isolate some odd-electron $C_5Bz_5$ complexes. It confirms that $C_5Bz_5$ is not a good ligand to stabilize odd-electron complexes, contrary to Cp*. This can be rationalized by the bulk and rotation of the phenyl ring about the Cp−$CH_2$ axis for the five benzyl substituents. There may also be mutual steric constraints between the Cp* ligand and one or several legs of the piano-stool. These constraints increase the energy of the system, which is not often compatible with the removal of one electron from a bonding or partly bonding orbital of the complex. This is particularly true for **6** in which one leg of the piano-stool, the dtc, is itself



a)

b)

**Figure 2.** (a) ORTEP view of the X-ray structure of complex **6**, $[Fe^{IV}(C_5Bz_5)(dtc)_2]$. (b) ORTEP view of **6** showing the clockwise orientation of the benzyl groups, from ref 9b.

**Table 2. Electrochemical Characterizations of the Dimethyldithiocarbamato−Iron Complexes within the Cp* and $C_5Bz_5$ Series in the Solvent Indicated in Parentheses**

| L | | | $C_5Bz_5$ | Cp* |
|---|---|---|---|---|
| CO (THF); **4** | ox[b] | $E$ (V/SCE) | 0.682 | 0.57 |
| | | $\Delta E$ (mV) | 65 | 70 |
| | | $i_a/i_c$ | 0.63 | 1 |
| | | $D°$ (cm$^2$/s) | $1.56 \times 10^{-6}$ | $2.7 \times 10^{-4}$ |
| | red[b] | $E$ (V/SCE) | −1.81 | −1.945 |
| | | $\Delta E_p$ (mV) | 90 | 100 |
| | | $i_a/i_c$ | 0.67 | 0.92 |
| | | $D°$ (cm$^2$/s) | $3.81 \times 10^{-6}$ | $2.4 \times 10^{-4}$ |
| $NCCH_3$ ($NCCH_3$); **5** | ox[c] | $E$ (V/SCE) | 1.165 | 0.835 |
| | | $\Delta E_p$ (mV) | 160 | 120 |
| | | $i_a/i_c$ | 0.30 | 0.81 |
| | | $D°$ (cm$^2$/s) | $7.53 \times 10^{-6}$ | $2.30 \times 10^{-5}$ |
| | | $k°$ (cm/s) | $3.40 \times 10^{-3}$ | $1.30 \times 10^{-2}$ |
| | red[d] | $E$ (V/SCE) | −0.352 | −0.570 |
| | | $\Delta E$ (mV) | 60 | 60 |
| | | $i_a/i_c$ | 0.89 | 0.62 |
| | | $D°$ (cm$^2$/s) | $9.16 \times 10^{-6}$ | $2.30 \times 10^{-5}$ |
| $dtc^-$ ($CH_2Cl_2$); **7** | red$_1$[b] | $E$ (V/SCE) | −0.305 | −0.248 |
| | | $\Delta E_p$ (mV) | irr | 135 |
| | | $i_a/i_c$ | irr | 0.89 |
| | | $D°$ (cm$^2$/s) | $2.16 \times 10^{-5}$ | $1.07 \times 10^{-5}$ |
| | | $k°$ (cm/s) | irr | $4.0 \times 10^{-3}$ |
| | red$_2$[b] | $E$ (V/SCE) | −0.995 | −0.765 |
| | | $\Delta E$ (mV) | irr | 210 |
| | | $i_a/i_c$ | irr | 0.88 |
| | | $D°$ (cm$^2$/s) | $3.60 \times 10^{-6}$ | $1.46 \times 10^{-5}$ |
| | | $k°$ (cm/s) | irr | $2.3 \times 10^{-3}$ |

[a] $n$-$Bu_4NBF_4$ 0.1 M; Pt electrode; $E°$ are given vs SCE. L is the ligand which is bonded to the FeCp($\eta^2$dtc)-moiety. $E$ is the average between $E_{pa}$ and $E_{pc}$ ($\sim E°$ if the wave is at least partly chemically reversible). $\Delta E_p$ is equal to $E_{pa} - E_{pc}$. $D°$ is the diffusion coefficient; k°: heterogeneous electron-transfer rate constant. [b] Scan rate: 0.2 V/s. [c] Scan rate: 0.4 V/s. [d] Scan rate: 0.8 V/s.

nonrigid, but rotating about both the Fe−S and S−C single bonds. Whereas the Cp* analogue of **7** shows reversibility at room temperature and could be isolated and characterized in its old-electron state, **7** is irreversible at −80 °C, which indicates that the odd-electron state is totally unstable even for a fraction of second at -80 °C. This chemical irreversibility of **7** for the redox system $Fe^{IV}/Fe^{III}$ also exists for the $Fe^{III}/Fe^{II}$ system, and two waves are now found on the negative side of the $E$ scale. After the diffusion control is ensured for the first wave by verifying that the peak current is linear to the square root of the scan rate in CV and to $1/t^{1/2}$ in chronoamperometry, the classical criteria are applied for the choice between an electrochemical irreversible wave ($E_{slow}$) and a fast heterogeneous electron transfer followed by a chemical reaction ($E_{fast}C_{fast}$). The shift of the potential for each 10-fold increase in scan rate is 36 mV. Since this is a one-electron system, we conclude that this is the latter ($E_{fast}C_{fast}$) system (theoretical value at 25 °C, 29 mV). For the study of the Cp* series, we know that the neutral 19-electron bis(dtc) complex **6** rapidly decoordinates to give a 17e monodentate complex. Since this complex is not observed in the CV, contrary to the Cp* case, this 17e complex rapidly decomposes, due to the mutual bulk of the $C_5Bz_5$ and $\eta^1$-dtc ligand discussed above (eq 7).

## Conclusion

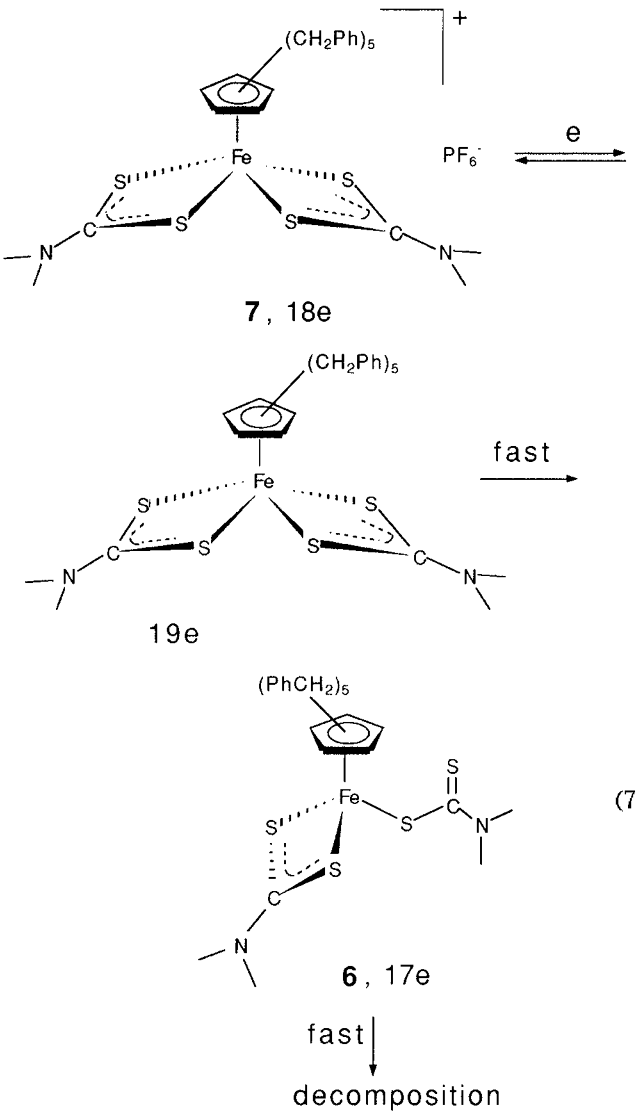
The synthesis of pentabenzylcyclopentadiene has been improved (85% yield) by slowing down the addition of dicyclopentadiene to the reaction mixture.

The yield of bis[(pentabenzylcyclopentadienyl)dicarbonyliron] dimer has been improved to a considerable extent (72% yield) so that this compound can be the only reaction product between iron pentacarbonyl and pentabenzylcyclopentadiene if the reaction is carried out at 90 °C for 4 days.

The new 18-electron complexes $[Fe^{II}(C_5Bz_5)(CO)_2Br]$, **3**, $[Fe^{II}(C_5Bz_5)(CO)(dtc)]$, **4**, and $[Fe^{IV}(C_5Bz_5)(dtc)_2]^+PF_6^-$, **7**, have been synthesized in high yields.

Pentabenzylcyclopentadiene destabilizes odd-electron complexes, this effect being especially dramatic when the metal bears another bulky ligand or an electron-deficient ligand. The only stable 17-electron complex which could be isolated was $[Fe(C_5Bz_5)(\eta^2\text{-dtc})(NCMe)]^+$ $PF_6^-$ in which the acetonitrile ligand is small, rigid, and electron releasing.

Cyclic voltammetry of the complexes of the series $[Fe(C_5Bz_5)(\eta^2\text{-dtc})L]^{0/+}$, L = CO, NCMe or $\eta^2$-dtc, shows



(7)

the two redox couples $Fe^{II}/Fe^{III}$ and $Fe^{III}/Fe^{IV}$ for these three complexes. The $C_5Bz_5$ ligand is found, from the compared $E°$ values, to be less electron releasing than the Cp* ligand. Destabilization of the odd-electron $C_5Bz_5$ complexes is confirmed by the partial chemical reversibility for **4** and **5** and by the total irreversibility for **7**. The destabilizing effect is found to be dramatic for **7** (cathodic reduction irreversible even at −80 °C) and for which the study of the potential variation as a function of scan rate shows an $E_{fast}C_{fast}$ system.

## Experimental Section

**General Data.** Reagent-grade tetrahydrofuran (THF), diethyl ether, and pentane were predried on Na foil and distilled from sodium benzophenone ketyl under argon just before use. Acetonitrile ($CH_3CN$) was stirred under argon overnight with phosphorus pentoxide, distilled from sodium carbonate, and stored under argon. Methylene chloride ($CH_2Cl_2$) was distilled from calcium hydride under argon just before use. All other chemicals were used as received. All manipulations were done by Schlenk technique or in a nitrogen-filled Vacuum Atmosphere drylab. Infrared spectra were recorded with a Perkin-Elmer Model 1420 ratio recording infrared spectrophotometer which was calibrated with polystyrene. Samples were examined in solution (0.1 mm cells with NaCl windows) between NaCl disks in Nujol or in KBr pellet. $^1H$ NMR spectra were recorded with a Bruker AC 200 (200 MHz) spectrometer. $^{13}C$ NMR spectra were obtained in the pulsed FT mode at 50.327 MHz with a Bruker AC 200 spectrometer. All chemical shifts are reported in parts per million (δ, ppm) with reference to the solvent or $Me_4Si$. Cyclic voltammetry data were recorded with a PAR 273 potentiostat galvanostat. In the CV experiments, care was taken to minimize the effects of the solution resistance on the measurements of the peak potentials (the use of positive feedback *iR* compensation and dilute solutions ($<10^{-4}$ mol/L) kept currents around 1 μA). Thermodynamic potentials were recorded with reference to an aqueous SCE in various solvents (0.1M $n$-$Bu_4NBF_4$). The diffusion coefficients were obtained from analysis of the chronoamperometric $i-t$ transient. Elemental analyses were performed by the Center of Microanalytics of the Department of Inorganic Chemistry of the Technische Universität München.

**Preparation. 1,2,3,4,5-Pentabenzylcyclopenta-1,3-diene, [$C_5(CH_2Ph)_5H$], 1.** A 500 mL three-necked flask with a magnetic stirrer was equipped with a Dean−Stark trap with a reflux condenser, a gas inlet valve, and an addition funnel; the system was evacuated and back-flushed with argon three times. In the flask 157 g (1.45 mol) of benzylic alcohol was reacted with 11.7 g (0.5 mol) of sodium metal that was cut into small pieces. This procedure was carried out under stirring and heating to about 120 °C under argon for 12 h. After this time, 125 mL of degassed diisopropylic benzene was added, and the mixture was heated to reflux. When the Dean−Stark trap was filled, 0.8 mL of water was separated. Then 3.45 g (0.025 mol) of dicyclopentadiene (95%) dissolved in 25 mL of degassed diisopropylic benzene was added dropwise to the refluxing mixture for 2.5 h. The reaction mixture continued to reflux for 30 h, and then the reaction solution was cooled to room temperature under argon. The residue consisted of a white solid which was extracted with 1 L of diethyl ether and filtered from sodium benzylate. The organic layer was washed to a neutral pH with 2 L of water, and the organic phase was degassed and dried over $Na_2SO_4$. After evaporation of the solvent, 75 mL of a yellowish residue remained in the flask to which the same volume of degassed $n$-pentane was added. This was cooled to −20 °C, which induced crystallization of 21.7 g (85%, lit.: 28%, ref 1, and 62%, ref 4 of $C_5(CH_2Ph)_5H$ (mp 61−70 °C). A further recrystallization gave 18.2 g (70%) of white crystals (mp 70-72 °C, lit. 69−75 °C). $^1H$ NMR ($CDCl_3$, 20 °C) δ (ppm): 7.44−7.21 (m, $C_6H_5$, 20H), 6.92−6.88 (m, $C_6H_5$, 5H), 4.06, 4.00, 3.78, 3.71 (system AB, $CH_2C_6H_5$, 4H), 3.65 (s, $CH_2C_6H_5$, 4H), 3.40 (t, $CHCH_2C_6H_5$, 1H), 3.266 (d, $CHCH_2C_6H_5$, 2H). $^{13}C$ NMR δ (ppm): 142.98, 141.43, 140.14, 138.66, ($C_q$, $C_6H_5$ + C=C), 129.18−125.78 (9CH, $C_6H_5$), 52.75 ($CH-CH_2C_6H_5$), 34.31, 33.44, 31.84 ($CH_2C_6H_5$) .

**Bis[($\eta^5$-pentabenzylcyclopentadienyl)dicarbonyliron(I)], 2.** 1,2,3,4,5-Pentabenzylcyclopenta-1,3-diene (4.9 g, 0.01 mol) was dissolved in 30 mL of $p$-xylene under stirring. Pentacarbonyliron (2 mL) was added through the reflux condenser, and the mixture was heated to 90 °C for 4 days. After consumption of [$Fe(CO)_5$] (24 h), 2 mL more of this educt was added. Slight traces of an iron mirror were observed. After the solution was cooled to room temperature, the flask was carefully opened in order to avoid the explosion of pyrophoric iron; $o$-xylene was evaporated *in vacuo*, and the solid residue was extracted with $n$-heptane while scratching the surface of the flask. The solids were extracted with dichloromethane in a Kumagawa apparatus in order to separate the metallic iron from the product. The dark-purple solution was concentrated, and absolute alcohol was added. Further evaporation of $CH_2Cl_2$ induced crystallization of 4.3 g (72%) of the dark-violet product. $^1H$ NMR ($CDCl_3$, 20 °C) δ (ppm): 7.050 (m, 20H) 6.795 (m, 20H) 3.680 (s, 10H, $CH_2C_6H_5$). $^{13}C$ NMR δ: 206.74 (C-O), 138.57 ($C_q$, $C_6H_5$), 129.10, 128.07, 126.10 ($C_6H_5$), 102.75 ($C_5Bz_5$), 30.45 ($CH_2$). IR (Nujol, ν $cm^{-1}$): 1930 (CO, terminal), 1740 (CO, bridging). Anal. Calcd for $C_{84}H_{70}Fe_2O_4$: C, 80.38; H, 5.62; Fe, 8.90; O, 5.10. Found: C, 80.03; H, 5.64; Fe, 8.93; O, 5.53.

**Bromodicarbonyl($\eta^5$-pentabenzylcyclopentadienyl)-iron(II), 3.** **2** (1.0018 g, 0.8 mmol) was dissolved in 50 mL of $CH_2Cl_2$ in a dry three-necked flask with a magnetic stirrer and addition funnel under argon; 41.6 $\mu$L (0.8 mmol) of bromine was added within 2 h under protection from the daylight. Thin layer chromatography with a 3:2 mixture of *n*-pentane and $CH_2Cl_2$ indicated that the reaction was finished after this time. The mixture was concentrated and passed through an alumina column with $CH_2Cl_2$ under protection from the daylight. To the deep-red solution absolute ethanol was added. Evaporation of the solvent precipitated 968 mg (84.4%) of bright-orange needles. $^1$H NMR ($CDCl_3$, 20 °C) $\delta$ (ppm): 7.105 (m, 15H), 6.629 (m, 10H), 3.661 (s, 10H). $^{13}$C NMR $\delta$ (ppm): 213.26 (*C*−O), 137.65 ($C_q$, $C_6H_5$), 128.74, 128.44, 126.68 (CH, $C_6H_5$), 100.65 ($C_5Bz_5$), 31.23 ($CH_2$). IR (Nujol, $\nu$ cm$^{-1}$): 2020, 1980 (CO). Anal. Calcd for $C_{42}H_{35}FeO_2Br$: C, 71.30; H, 4.99; Fe, 7.89. Found: C, 71.35; H, 5.02; Fe, 9.1.

**Carbonyl($\eta^2$-dimethyldithiocarbamato)($\eta^5$-pentabenzylcyclopentadienyl)iron(II), 4.** To 500 mg (0.71 mmol) of **3** in a Schlenk flask with a cooling mantle was added 126.6 mg of predried sodium dimethyldithiocarbamate in dry THF under argon. The solution was irradiated with visible light (Philips, 120 W) for 30 min. The color of the reaction mixture changed from red to deep brown-red with precipitation of a white solid. Completion of the reaction was verified by thin layer chromatography on $SiO_2$ with a 7:2 mixture of *n*-pentane and $CH_2Cl_2$. The solution was filtered into a second Schlenk flask over $Al_2O_3$ under argon and then evaporated. The orange crude product was introduced into a glovebox and recrystallized from diethyl ether and *n*-pentane yielding 370 mg (73%) of crystallized substance. $^1$H NMR ($CDCl_3$, 20 °C) $\delta$ (ppm): 7.020 (m, 15H, $C_6H_5$), 6.797 (m, 10H, $C_6H_5$), 3.553 (s, 10H, $CH_2C_6H_5$), 3.247 (s, 6H, $N(CH_3)_2$). $^{13}$C NMR $\delta$ (ppm): 218.11 (*C*−O), 208.38 (*C*−S), 139.29 ($C_q$, $C_6H_5$), 128.76, 127.99, 125.81 (CH, $C_6H_5$), 93.59 ($C_5Bz_5$), 38.40 ($CH_3$), 31.64 ($CH_2$). IR (Nujol, $\nu$ cm$^{-1}$): 1915 (CO). Anal. Calcd for $C_{44}H_{41}FeS_2NO$: C, 73.42; H, 5.74; N, 1.95. Found: C, 72.83; H, 5.90; N, 1.86. Cyclic voltammetry: see text and Table 2.

**Acetonitrile($\eta^2$-dimethyldithiocarbamato)($\eta^5$-pentabenzylcyclopentadienyl)iron(III) Hexafluorophosphate, 5.** In a dry Schlenk flask 242 mg (0.34 mmol) of **4** and 111.4 mg (0.34 mmol) of ferricinium hexafluorophosphate were mixed in the solid state under argon; 20 mL of degassed acetonitrile was transferred to these educts inducing the immediate apparition of a dark-purple color. After this was stirred for 15 min at room temperature, about half of the solvent was removed and the concentrated solution was extracted under argon with small amounts of dry *n*-pentane until no more yellow color was observed in the pentane layer. From the evaporated pentane solution, 62 mg (0.33 mmol) of ferrocene, identified by its $^1$H NMR spectrum was recovered. The reaction solution was evaporated and the solid residue was introduced into a glovebox. Recrystallization from ether/*n*-pentane gave 213 mg (71.4%) of dark-purple product. IR (Nujol, $\nu$ cm$^{-1}$): 1550 (CN), 1030 (CS). ESR (solid state sample, 18 K): $g_1 = 2.574$, $g_2 = 2.036$. Cyclic voltammetry, see text and Table 2. Anal. Calcd for $C_{45}H_{44}FeN_2PS_2F_6$: C, 61.57; H, 5.05; N, 3.19. Found: C, 61.52; H, 5.18; N, 3.10.

**In Situ Preparation of Bis(dimethyldithiocarbamato)-($\eta^5$-pentabenzylcyclopentadienyl)iron(III) in THF Solution, 6.** In a dry Schlenk flask, 228 mg (0.26 mmol) of **5** was dissolved in 20 mL of dry THF at −35 °C. To the cooled solution was added 46.6 mg of predried $Na^+dtc^-$ in 10 mL of THF, prepared under the same conditions, inducing a spontaneous color change from dark purple to blue-turquoise. After 15 min, an ESR sample of this air- and thermally-sensitive complex was taken under argon from the Schlenk flask. ESR (THF frozen solution, 12 K): $g_1 = 2.2707$, $g_2 = 2.0611$, $g_3 = 2.0002$.

**Bis($\eta^2$-dimethyldithiocarbamato)($\eta^5$-pentabenzylcyclopentadienyl)iron(IV) Hexafluorophosphate, 7.** To a solution of **6**, prepared as described above, 86.1 mg (0.26 mmol) of ferricinium hexafluorophosphate was added under a counterstream of argon at −50 °C. The solution was allowed to warm to room temperature for at least 2 h. While the solution was warmed, the blue-turquoise color of **6** disappeared and a green solid precipitated. After evaporation of the THF, the residue was extracted with ether giving a stoichiometric amount of ferrocene, after filtration and removal of the solvent. The solid which remained on the frit was extracted with 10 mL of dichloromethane. The dark-green solution was washed three times with 10 mL of water and dried over sodium sulfate. To the filtered $CH_2Cl_2$ phase was added 10 mL of absolute alcohol, and after partial evaporation of the halogenated solvent, 177.2 mg (71.2%) of crystalline complex **7** was obtained. $^1$H NMR ($CD_3CN$, 20 °C) $\delta$ (ppm): 7.019−6.538 (m, 25H, $C_6H_5$), 3.458 (s, 12H, $N(CH_3)_2$), 3.184 (s, 10H, $CH_2C_6H_5$). $^{13}$C NMR $\delta$ (ppm): 198.67 (*C*−S), 134.62 ($C_q$, $C_6H_5$), 129.20, 128.32, 126.86 ($C_6H_5$), 107.43 ($C_5Bz_5$), 38.35 ($CH_3$), 31.85 ($CH_2$). IR (Nujol, $\nu$ cm$^{-1}$): 1545 (CN), 1020 (CS), 810 ($PF_6^-$). Anal. Calcd for $C_{45}H_{47}FeS_4N_2PF_6$: C, 57.74; H, 4.95; N, 2.93. Found: C, 57.60; H, 5,25; N, 2.76. Cyclic voltammetry: see text and Table 2. MS (FAB/NBA): *m/e* (811, M − $PF_6$, 27), 691 (M − $PF_6$ − dtc, 89), 296 (M − $PF_6$ − $C_5Bz_5$, 100), 91, (M − $(C_5Bz_4)Fe(dtc)_2$ $PF_6$, 49).

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