Table I. Chemical Shifts[a] and DF Coupling Constants[b] for the Monodeuteriofluorobenzenes

Solvent	Fluorobenzene-2-*d* $\int_\mathrm{H}^\mathrm{D}$	Fluorobenzene-2-*d* J_{DF}	Fluorobenzene-3-*d* $\int_\mathrm{H}^\mathrm{D}$	Fluorobenzene-3-*d* J_{DF}	Fluorobenzene-4-*d* $\int_\mathrm{H}^\mathrm{D}$	Fluorobenzene-4-*d* J_{DF}
Cyclohexane	0.285 ± 0.003	1.4 ± 0.08	0.008 ± 0.003	0.8 ± 0.08	0.011 ± 0.002	<0.2
Methanol-O-*d*	0.285 ± 0.003	1.3 ± 0.08	0.011 ± 0.003	0.9 ± 0.08	0.011 ± 0.002	<0.2
Trifluoroacetic acid-*d*	0.285 ± 0.003	1.3 ± 0.08	0.005 ± 0.003	0.9 ± 0.08	0.012 ± 0.002	<0.2

[a] Parts per million relative to fluorobenzene-d_0 [b] In hertz.

O-*d*, and trifluoroacetic acid-*d*. Concentrations of 5% or less are considered justifiable approximations to infinite dilution.[3]

Figure 1, top trace, shows the ^{19}F spectrum (recorded at 56.4 MHz on a Varian HA-60-IL spectrometer) of a mixture of fluorobenzene-2-*d* and fluorobenzene in methanol-O-*d*. The lock signal from TCTFCB is seen downfield from the complex pattern of the aromatic materials. In order to determine precise chemical shifts, it was decided to simplify the spectrum by eliminating all H–F coupling. This was accomplished by simultaneous irradiation at the proton magnetic resonance frequency. The resulting spectrum (bottom trace) contains a 1:1:1 triplet ($|J_{\mathrm{DF}}|$ = 1.3 Hz) for fluorobenzene-2-*d*; this multiplet is 0.285 ppm upfield from the single sharp resonance of fluorobenzene-d_0. Analogous results were obtained for the *meta* and *para* compounds, although the isotope shifts were significantly smaller and the resonance of fluorobenzene-4-*d* appeared as a singlet, implying that $|J_{\mathrm{DF}}| < 0.2$ Hz. The results are summarized in Table I.

The proton–fluorine coupling constants in fluorobenzene have been determined previously.[7] Using these data, we have calculated the corresponding deuterium–fluorine coupling constants ($J_{\mathrm{DF}} = 0.15 J_{\mathrm{HF}}$)[8] and have obtained 1.41, 0.91, and 0.02 Hz for the *ortho*, *meta*, and *para* positions, respectively. These results agree with the coupling constants observed directly (Table I).

Within experimental error, the isotope effect on the ^{19}F chemical shifts and D–F coupling constants for the three deuterated fluorobenzenes are invariant to the solvents employed. These solvents were chosen since they produce significant variations in the relative chemical shifts of substituted fluorobenzenes.[3,9] Furthermore, no change in the isotopic chemical shift of fluorobenzene-4-*d* was noted, despite a 40% decrease in its concentration. This over-all invariance suggests that the observed shifts are a reflection of intramolecular interactions rather than medium effects.

The upfield direction of the isotopic shift is expected because the net shielding on fluorine should be increased by the deuterium. This effect has ample precedence from nmr studies[10] as well as chemical investigations.[2]

The magnitudes of the isotopic shifts vary markedly with deuterium position. The effect of an *ortho* deuterium is 25 and 35 times that of a *para* and *meta* deuterium, respectively. This contrasts sharply to deuterium kinetic effects in solvolytic reactions[2c] and carbanion formation,[2a] where smaller variations have been found.

Using Taft's equations relating ^{19}F chemical shifts of *meta*- and *para*-substituted fluorobenzenes to the substituent parameters σ_{I} and σ_{R}^0,[3] our results demonstrate that the parameters for deuterium (relative to protium) are $\Delta\sigma_{\mathrm{I}} = -0.0011$[11] and $\Delta\sigma_{\mathrm{R}}^0 = -0.0001$. It can be inferred from these data that deuterium in the *meta* or *para* position interacts with a group in the 1 position primarily *via* an inductive mechanism rather than a mesomeric perturbation of the π system.[12]

It appears that an *ortho* deuterium creates an abnormally large isotope effect on the ^{19}F chemical shift. This may be the result of some direct F–D nonbonded interaction. In this regard, the difference between the lengths as well as the vibrational amplitudes of the C–H and C–D bonds may play a significant role. Additional discussion must await results from our investigations of polydeuterated fluorobenzenes and theoretical calculations concerning the effects of vibrational levels on chemical shifts.

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(7) (a) T. F. Page, Jr., *Mol. Phys.*, **13**, 523 (1967); (b) L. C. Snyder, *J. Chem. Phys.*, **43**, 4041 (1965).

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 188.

(9) In fact, the TCTFCB signal was 1.5 ppm upfield from the fluorobenzene-d_0 resonance in cyclohexane, but 0.1 to 0.4 ppm downfield in the polar media.

(10) (a) G. V. D. Tiers, *J. Am. Chem. Soc.*, **79**, 5585 (1957); (b) H. S. Gutowsky, *J. Chem. Phys.*, **31**, 1683 (1959); (c) M. Saunders, J. Plostnieks, P. S. Wharton, and H. H. Wasserman, *ibid.*, **32**, 317 (1960); (d) K. Schaumburg and C. Deverell, *J. Am. Chem. Soc.*, **90**, 2495 (1968).

(11) From the experimental pK_a of acetic acid-d_3, Streitwieser and Klein have calculated $\Delta\sigma_{\mathrm{I}} = -0.0012$ (see ref 2c).

(12) Corroborating evidence can be found in ref 2a and 2c.

William R. Young, Costantino S. Yannoni
IBM Thomas J. Watson Research Center
Yorktown Heights, New York 10598

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Diselenocyanatobis(2,2′-bipyridyl)iron(II), a Possible Iron(II) Analog of the Yellow Lifschitz Nickel(II) Complexes[1]

Sir:

Recently, it was demonstrated[2] that the compound *cis*-dithiocyanatobis(2,2′-bipyridyl)iron(II), [Fe(bipy)$_2$(NCS)$_2$], undergoes a transition between spin quintet and spin singlet electronic ground states at temperatures of 210–216°K, depending on the polymorph studied. X-Ray structural investigations[3] show that the transition is accompanied by a change of the Fe–N(bipy) bond length from 2.17 ± 0.02 to 2.03 ± 0.02 Å,[4] corresponding to the $t_{2g}^4e_g^2$ and t_{2g}^6 configurations of octahedral iron(II), respectively. Analogous transitions are encountered in the bis(1,10-phenanthroline) complexes [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$].[5,6]

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(1) This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

(2) E. König, K. Madeja, and K. J. Watson, *J. Am. Chem. Soc.*, **90**, 1146 (1968).

(3) K. J. Watson and E. König, to be submitted for publication.

(4) The bond lengths quoted are preliminary results characterized by R = 0.19. The data are in the process of refinement.

(5) E. König and K. Madeja, *Chem. Commun.*, 61 (1966).

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However, all our attempts to isolate a similarly behaving compound of composition [$Fe(bipy)_2(NCSe)_2$] were so far unsuccessful.

The only well-defined product which was obtained by thermal decomposition of [$Fe(bipy)_3$]$(NCSe)_2$ analyzes as $Fe(bipy)_{2.33}(NCSe)_2$. The preparation was effected using the extraction method[7] in an inert gas atmosphere and anhydrous acetone as solvent. The crystals of the product formed as dark brown rhombic plates. A sample analysis is represented as follows. *Anal.* Calcd for $Fe(C_{25.30}H_{18.64}N_{6.66}Se_{2.00})$: C, 48.25, H, 2.98; N, 14.82; Se, 25.08; Fe, 8.87. Found: C, 48.56; H, 3.19; N, 14.89; Se, 24.30; Fe, 8.57. The lowest multiple resulting in an integral ratio of the constituents is three, *viz.*, $Fe_3(bipy)_7(NCSe)_6$, mol wt 1890.73 amu. Attempts at determination of the molecular weight by vapor osmometry failed since no solvents other than those causing decomposition were found.

The magnetic susceptibility of the substance was studied between 293 and 77°K by the Gouy method. Assuming a molecular weight of 1890.73 amu, the magnetic moment amounts to $\mu_{eff} = 3.42$ BM per iron atom at 293°K and decreases to 3.01 BM at 77°K. These values are intermediate between those encountered in normal spin-free and spin-paired bis(diimine)iron(II) complexes, whereas spin triplet ground states produce $\mu_{eff} \sim 3.90$ BM.[8]

An investigation of the ^{57}Fe Mössbauer effect yields two overlapping spectra having an intensity ratio of roughly 2:1 (*cf.* Figure 1). The more intense spectrum is characterized, at 293°K, by the isomer shift $\delta = 0.30 \pm 0.05$ mm/sec and the quadrupole splitting $\Delta E_Q = 0.32 \pm 0.05$ mm/sec.[9] From the lower intensity spectrum, we obtained $\delta \sim 1.02$ mm/sec and $\Delta E_Q \sim 1.23$ mm/sec.[10] Comparing these results with Mössbauer spectra of various bis(diimine)iron(II) complexes[11] as well as with abundant data from the literature,[12] we conclude that the more intense spectrum is due to spin-paired and the less intense spectrum due to spin-free iron(II). Down to 77°K no unusual changes other than a pronounced temperature dependence of ΔE_Q in the spin-free iron(II) spectrum (*cf.* Figure 1) is observed. Within the range 298–77°K, spin-state equilibria may thus be ruled out.

It is conceivable that there are almost equal recoil-free fractions of iron(II) in the configurations t_{2g}^6 and $t_{2g}^4e_g^2$ of the same complex. Therefore, we propose that the present substance contains *spin-paired and spin-free iron(II) in a 2:1 ratio.* This inference is consistent with the empirical composition and the observed magnetic data. Thus, on the basis of the magnetism studied on bis(diimine)iron(II) complexes,[13] the moment values $\mu_{eff} \sim 1.0$ BM and $\mu_{eff} \sim 5.4$ BM may be estimated for the spin-paired and spin-free iron(II) in [$Fe(bipy)_2(NCSe)_2$], respectively. The average susceptibility for a 2:1 complex results then in a moment $\mu_{eff} = 3.36$ BM at 298°K, if due attention is paid to the assumed molecular weight. This value is in good agreement with the experimental moment of 3.42 BM. On the contrary, $\mu_{eff} = 4.05$ BM is predicted for a 1:1 complex and $\mu_{eff} = 2.96$ BM for a 3:1 complex.

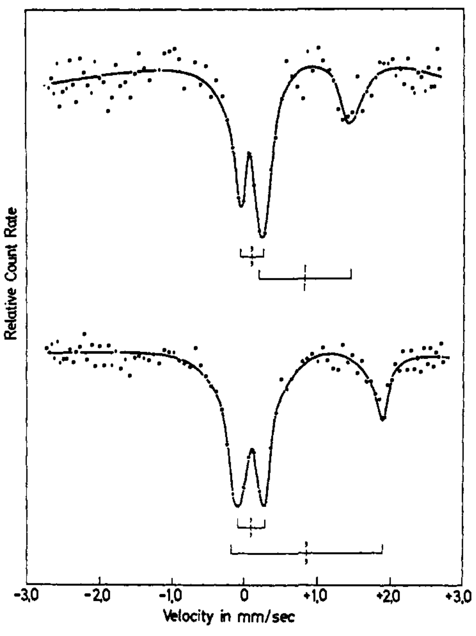

Figure 1. Mössbauer spectrum of $Fe(bipy)_{2.33}(NCSe)_2$ containing a 2:1 ratio of spin-paired and spin-free iron(II)[9] (upper spectrum at 293°K, lower spectrum at 77°K).

Employing single-crystal X-ray methods, the unit cell of the compound was shown to be orthorhombic: $a = 21.77 \pm 0.05$, $b = 25.33 \pm 0.05$, and $c = 13.68 \pm 0.04$ Å. From systematic absent reflections, the space group is Pmnb (D_{2h}^{16}, no. 62).[14] The density of the substance was determined by flotation to $D_m = 1.66 \pm 0.03$ g cm^{-3}. The only molecular weight consistent with these data is that of 1890.73 amu and the number of molecules per unit cell, $Z = 4$. The most obvious formulation of the molecular unit seems to be [$Fe(bipy)_2(NCSe)_2$]$_2$[$Fe(bipy)_3$]$(NCSe)_2$ (I) or [$Fe(bipy)(NCSe)_4$][$Fe(bipy)_3$]$_2(NCSe)_2$ (II). However, I would be expected to give a spin-paired, spin-free ratio of 1:2 which is in disagreement with Mössbauer spectrum and magnetism. Also, the [$Fe(bipy)_3$]$^{2+}$ ion of I and II is known for its crimson color due to a strongly polarized intense band at 18,800 cm^{-1} (ϵ 8600),[15,16] which is in sharp contrast to the light brown color and the optical spectrum of the present compound. Finally, the ionic $NCSe^-$ of I and II would be expected to give a CN stretch at 2070 cm^{-1}.[17] However, the infrared spectrum of the compound shows bands at 2053 and

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(9) All values are listed relative to the midpoint of the spectrum of an iron foil absorber at 293°K. ^{57}Co diffused into palladium was used as source. Following convention, δ is taken as positive when the source is moved toward the absorber.

(10) For the lower intensity spectrum, only approximate values of δ and ΔE_Q are listed, since one of the lines overlaps with the spectrum of the spin-paired ion. A detailed discussion of the temperature dependence will be published elsewhere.

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(14) The noncentrosymmetric space group $P2_1nb$ (C_{2v}^9, no. 33) is equally possible. However, this space group is extremely unlikely on the basis that three crystallographically independent molecular units (mass about 600 amu) would have to comprise the asymmetric unit.

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2081 cm^{-1} which are indicative of two kinds of coordinated NCSe$^-$ ions.

A less obvious formulation which *is* consistent with all experimental evidence may be written [Fe^{sp}(bipy)$_2$(NCSe)$_2$]$_2$[Fe^{sf}(bipy)$_2$(NCSe)$_2$]·(bipy), where Fe^{sp} and Fe^{sf} denote spin-paired and spin-free iron(II), respectively.[18] The space group Pmnb is centrosymmetric having one eightfold set of general equivalent positions and three sets of fourfold special equivalent positions. Of the latter, one set is characterized by m, the others by $\bar{1}$. It may be assumed that all the atoms of the [Fe^{sp}(bipy)$_2$(NCSe)$_2$]$_2$ unit occupy general positions. Furthermore, it is conceivable that Fe^{sf} atoms occupy $\bar{1}$ sites, thus requiring a *trans* arrangement of the [Fe^{sf}(bipy)$_2$(NCSe)$_2$] complex. This inference would account for both the small value of ΔE_Q as well as its large temperature dependence; *cf. trans*-[Fe(py)$_4$(NCS)$_2$].[19] Finally, bipy in *trans* arrangement may or may not occupy the remaining $\bar{1}$ sites of the other set.

Numerous other formulations were checked and found inadequate. Iron(III) impurities as possible cause of anomalous magnetic effects[20] were ruled out on the basis of analytic and spectroscopic results. Therefore, we suggest that the compound studied might represent the first example of a crystal containing two out of three iron(II) ions in a spin-paired configuration, while the remaining iron(II) is spin free. Presumably, all three iron(II) ions are in approximately octahedral coordination. This arrangement may be considered as analogous to that encountered in the yellow Lifschitz nickel(II) complexes.[21,22]

Acknowledgments. The authors appreciate cooperation with Dr. S. Hüfner and Dr. K. J. Watson in measurements of Mössbauer spectra and determination of the unit cell.

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[18] Coordination numbers higher than six are considered very unlikely.

[19] For *trans*-[Fe(py)$_4$(NCS)$_2$], we found ΔE_Q = 1.59 ± 0.04 mm/sec at 293°K and ΔE_Q = 2.02 ± 0.04 mm/sec at 77°K.

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[23] To whom correspondence should be addressed.

E. König[23]
Institut für Physikalische Chemie II
University of Erlangen-Nürnberg, 8520 Erlangen, Germany

K. Madeja, W. H. Böhmer
Institut für Anorganische Chemie
University of Greifswald, 22 Greifswald, Germany

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Anodic Substitution Reactions of Aromatic Hydrocarbon Cation Radicals. Unequivocal Evidence for ECE Mechanism

Sir:

The mechanism of anodic substitution and addition reactions of aromatic hydrocarbons (pyridination, cyanation, hydroxylation, etc.) has been of continuing interest to organic electrochemists.[1-12] It was shown that the primary pathway for such processes must normally involve electrooxidation of the hydrocarbon species.[4-6] Aromatic hydrocarbon radicals formed from one-electron anodic oxidations were shown to have long lifetimes in anhydrous solvents[13-14] and to be susceptible to nucleophilic attack.[15]

The stoichiometry of such reactions is clear. In the pyridination of anthracene, two electrons are removed per molecule of hydrocarbon and two molecules of nucleophile (pyridine) are consumed. Lund isolated the anthracene 9,10-dipyridinium diperchlorate long ago.[1] There has been much discussion regarding the correct sequence of electron transfer and chemical attack steps. Suggestions have included (a) initial two-electron loss from hydrocarbon followed by nucleophilic attack,[1-3] (b) two-electron loss from hydrocarbon *concerted with* ("assisted by") nucleophilic attack,[4,5,7] (c) a radical-chain mechanism terminated by pairing of hydrocarbon and nucleophile radicals.[11,12]

We have obtained from rotated disk electrode (RDE) measurements positive evidence that the reaction sequence is an ECE process consisting of: electron transfer oxidation of hydrocarbon to cation radical; chemical attack of cation radical by unoxidized nucleophile; and further electron transfer oxidation of cation radical–nucleophile adduct (easier to oxidize than the parent hydrocarbon by virtue of incorporation of the electron-rich nucleophile).

For the pyridination reactions considered herein such a scheme would be written as

$$\mathrm{Ar} \rightleftharpoons \mathrm{Ar}\cdot^{+} + e^{-} \qquad \text{(E)}$$

$$\mathrm{Ar}\cdot^{+} + \mathrm{Py} \longrightarrow \mathrm{ArPy}\cdot^{+} \qquad \text{(C)}$$

$$\mathrm{ArPy}\cdot^{+} \rightleftharpoons \mathrm{ArPy}^{2+} + e^{-} \rightsquigarrow \text{proton loss or second nucleophile attack} \qquad \text{(E)}$$

where Ar is the aromatic hydrocarbon and Py is pyridine or a 4-substituted pyridine.

The two-electron-transfer steps were separated by measuring limiting currents at a RDE where the rate of stirring is competitive with the rate of the intervening chemical reaction. This is, we believe, the first unequivocal evidence for an ECE mechanism describing the electrochemical incorporation of a nucleophilic moiety into an aromatic hydrocarbon.

The various electrochemical and RDE techniques were conventional and have been described amply in the literature[13-18] Platinum RDE's constructed after Marcoux[13] with geometric areas of 0.045 and 0.202

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