Structure of [1.1]Ferrocenophanyllithium in the Solution and the Solid State. Absence of an Intramolecular [C−H−C]− Hydrogen Bond

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Abstract: [1.1]Ferrocenophanyllithium (**1**) is shown by dynamic NMR (DNMR) and isotopic perturbation to undergo a rapid intramolecular 1,12-proton transfer coupled with 1,12-lithium ion transfer. The first [C−H−C]− hydrogen bond previously reported to be present in **1** is shown by X-ray crystallography to be absent in the solid state. The ^{13}C NMR spectrum of the bridge-labeled compound [1,12-$^{13}C_2$][1.1]ferrocenophanyl[1-^{6}Li]lithium (**6**) in 2,5-dimethyltetrahydrofuran (DMTHF) displays a 1:1:1 triplet ($^1J(^{13}C,^6Li) = 4.0$ Hz) showing that ^{6}Li is bonded to C-1 and that **1** is monomeric. Transient nuclear Overhauser effects (tNOE's) measured in DEE-d_{10} in bridged monodeuterated **1** show that the bridges in **1** are *syn* and not *anti* to each other and that lithium is *exo*-coordinated to the anionic bridge carbon. The $^1J(^{13}C,^1H)$ coupling constants show that the hybridization of the carbanionic carbon is intermediate between sp^2 and sp^3. Thus the solution and solid state structures of **1** are similar. UV−vis spectroscopy shows that **1** exists mainly as contact ion pairs (CIPs) in the temperature range −100 to +25 °C in THF, DMTHF, and diethyl ether (DEE). In dimethoxyethane (DME), **1** is mainly CIPs above +25 °C but is mainly separated ion pairs (SIPs) below −30 °C.

Introduction

Despite the enormous usefulness of organolithium reagents in synthetic chemistry much remains to be known about structure and reactivity.[1] In this paper we present detailed structure studies of [1.1]ferrocenophanyllithium (**1**). Compound **1** has previously been prepared from [1.1]ferrocenophane (**2**) by lithiation of one of its bridge carbons using *n*-butyllithium (BuLi) in tetrahydrofuran (THF) (Scheme 1) by Mueller-Westerhoff and co-workers.[2a] Their NMR spectroscopic studies indicated that **1** contains a [C−H−C]− hydrogen bond which is either symmetric (**1a**) or asymmetric (**1b**) (Scheme 2). This was claimed to be the first verified [C−H−C]− hydrogen bond.[2]

Scheme 1

Scheme 2

Their conclusion was based upon the fact that one of the bridge protons in **1** appeared as a triplet and had a chemical shift of 1 ppm downfield relative to that of the precursor (**2**) bridge protons and that the ^{1}H NMR spectrum showed no significant temperature dependence. Thus, if the hydrogen bond is asymmetric, the proton is rapidly transferred between the carbons in **1b** on the NMR time scale. Compound **1** was proposed to be present as solvent-separated ion pairs.[2a]

Intrigued by these spectacular results by Mueller-Westerhoff and co-workers, we have investigated in detail the proposed [C−H−C]− hydrogen bond.[3] This follows our interest in hydrogen-bonded carbanions which are assumed to be reactive intermediates in essentially all proton transfers from carbon acids.[4]

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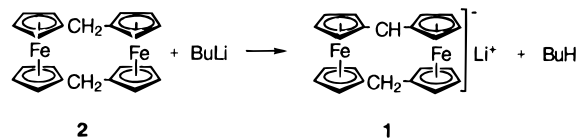† Göteborg University.
‡ Chalmers University of Technology.
⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1997.
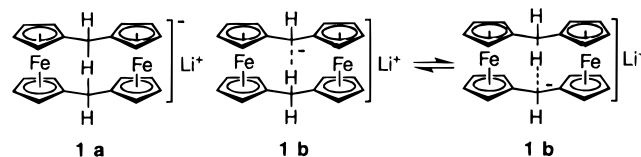(1) (a) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624. (b) *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley: New York, 1972; Vols. 1, 2. (c) Bauer, W.; Schleyer, P. v. R. *Adv. Carbanion Chem.* **1992**, *1*, 89. (d) Jackman, L. M.; Bortiatynski, J. *Adv. Carbanion Chem.* **1992**, *1*, 45. (e) Collum, D. B. *Acc. Chem. Res.* **1992**, *25*, 448. (f) Bernstein, M. P.; Collum, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 8008. (g) Kaufmann, E.; Gose, J.; Schleyer, P. v. R. *Organometallics* **1989**, *8*, 2577 and references cited therein. (h) Reich, H. J.; Green, D. P. *J. Am. Chem. Soc.* **1989**, *111*, 8729. (i) Barr D.; Doyle, M. J.; Mulvey, R. E.; Raithby, P. R.; Reed, D.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1989**, 318. (j) Reich, H. J.; Borst, J. P.; Dykstra, R. R.; Green, D. P. *J. Am. Chem. Soc.* **1993**, *115*, 8728 and references cited therein. (k) Fraenkel, G.; Cabral, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 1551. (l) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271. (m) Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 1. (n) Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47. (o) Mulvey, R. E. *Chem. Soc. Rev.* **1991**, *20*, 167. (p) Collum, D. B. *Acc. Chem. Res.* **1993**, *26*, 227 (q) Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1994**, *116*, 6009.
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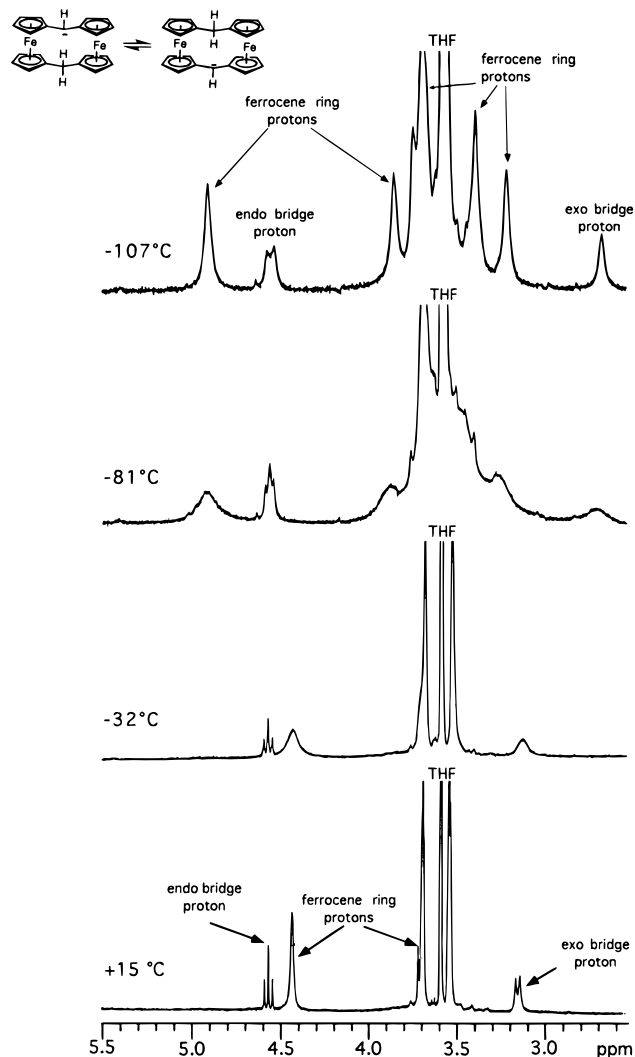
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Figure 1. ^{1}H NMR (obtained at 399.95 MHz) spectrum of **1** (the lithium cations are not shown in the structures) in THF-d_8 at different temperatures.

Figure 2. ^{1}H NMR spectrum (obtained at 399.95 MHz) in THF-d_8 at +20.5 °C: (a) of **4** and (b) of **1** (the lithium cations are not shown in the structures).

The results presented below are showing the absence of a hydrogen bond in **1**. Compound **1** undergoes a fast degenerate lithiation reaction. The structure of **1** in solution as well as in the solid state has been studied by NMR, UV–vis spectroscopy, and X-ray diffraction.

Results and Discussion

Solutions of compound **1** (0.002–0.01 M) in THF were prepared from **2** and BuLi directly in an NMR tube as described in the Experimental Section. ^{1}H NMR spectra were obtained in the temperature interval +45 to −108 °C. Contrary to a previous report,[2a] the spectra showed considerable temperature dependence (Figure 1). The spectrum at +17 °C was similar to that reported by Mueller-Westerhoff and co-workers.[2a] However, the ferrocene ring proton signal at δ 4.42 (4H) broadened upon the temperature being lowered. At −70 °C it had essentially disappeared, and at −78 °C two new signals at δ 3.88 (2H) and 4.92 (2H) were observed. Similarly the doublet at δ 3.12 ascribed to the two *exo*-hydrogens split into two new
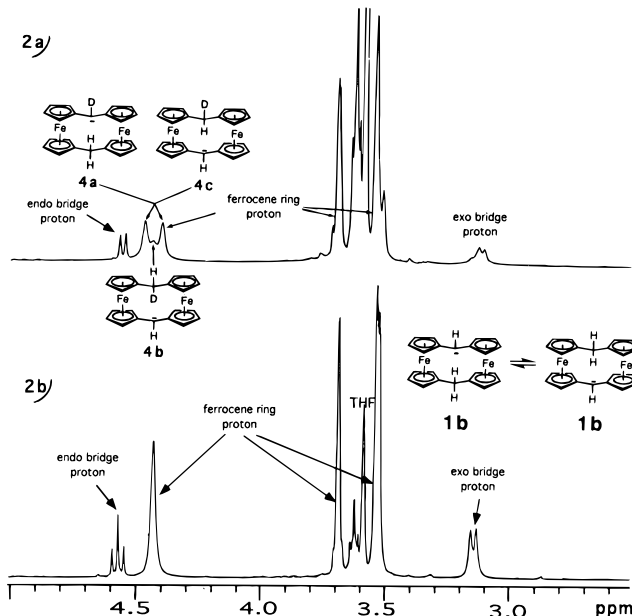
signals spaced ±0.42 ppm relative to the original signal. The one at lower field (δ 3.54) was hidden under the ferrocenophane ring proton signal at δ 3.53. Also the spectrum of the other ferrocenophane protons showed considerable temperature dependence. At about −100 °C the triplet at δ 4.56, assigned to the *endo*-proton, had changed into a 1:1 doublet with a splitting twice the triplet splitting measured in the fast exchange-averaged spectra. This is attributed to coupling to one of the *exo*-protons attached to the methylene carbon. The coupling with the other *exo*-proton appears to be negligible.

Our results exclude the possibility that the carbanion has a structure with a symmetrical hydrogen bond (**1a** in Scheme 2). It is concluded that the ferrocenophanyl anion is asymmetric and undergoes a fast degenerate 1,12-proton transfer (**1b**). The triplet pattern of the transferred proton shows that it is transferred intramolecularly. The rate constant for the degenerate rearrangement is 8×10^3 s^{-1} at −24 °C in THF which corresponds to a $\Delta G^{\ddagger}_{249K} = 42$ kJ mol^{-1}.[3a,b]

Isotopic Perturbation of the Degenerate Equilibrium of 1. Our investigation of **1** started with the idea that isotopic perturbation[5] of **1** might differentiate between structures **1a** and **1b** in Scheme 2. During this work we discovered the temperature dependence of the ^{1}H NMR spectrum. The bridge-monodeuterated ferrocenophane **3** was synthesized by quenching **1** with D$_2$O. The monodeuterium-substituted anion **4** was prepared in the usual way using BuLi. The ^{1}H NMR spectrum of **4** in THF-d_8 is shown in Figure 2a, and the spectrum of **1** is displayed for comparison in Figure 2b.

Obviously the deuterium substitution has caused major spectral changes. The triplet at δ 4.51 of **1** has changed into a doublet; the proposed hydrogen bond donor proton is now coupled to only one proton. The small J_{HD} coupling is not resolved. The ferrocenophane bridge proton signal of **4** at δ 4.42 (4 H) is split into three signals. The signal in the middle is assumed to be due to the isotopomer **4b** in which deuterium is transferred between the two bridge carbons. The other two peaks are caused by isotopic perturbation of the degenerate

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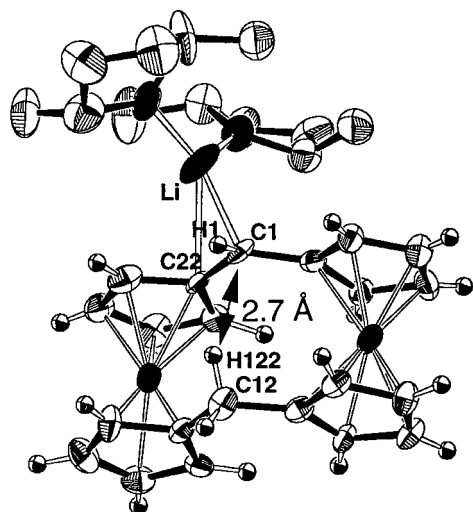
Structure of [1.1]Ferrocenophanyllithium

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Figure 3. A drawing of the solid state structure of **1**, crystallized from DMTHF.

equilibrium of **1**, i.e. *K* for the equilibrium between **4a** and **4c** favors isotopomer **4c**, because of zero-point energy differences. The equilibrium constant *K* is measured to 1.14 ± 0.01 at 302 K.

The results indicate that the hybridization of the carbanionic carbon is intermediate between sp^3 and sp^2 in solution.[3b]

Crystal Structure of 1. Compound **1** has been crystallized from a DMTHF/hexane solution. The crystals are dark red needles that decompose rapidly when isolated at ambient temperature, even under inert atmosphere. Special low-temperature handling techniques[6] have been employed for isolating, selecting, and mounting crystals of **1** for X-ray crystallographic studies. The solid state structure[3d] (cf. Figure 3) shows a long distance between the *endo*-bridge CH proton (H122) and the bridge C⁻ (C1), indicating the absence of an intramolecular hydrogen bond. **1** is monomeric, and the lithium atom is only coordinated to two carbons and two ether molecules. The structural aspects of organolithium complexes and reagents are currently receiving widespread attention, and the nature of the Li−C bond is subjected to experimental as well as theoretical studies.[7] The Li−C1 and Li−C22 bond distances are 2.18 and 2.37 Å, respectively. The C1−Li−C22 angle is 36.2°. Thus the Li atom can be considered tetrahedrally coordinated. The Li−O bond distances of 1.88 and 1.94 Å, respectively, are normal. The four cyclopentadienyl rings are almost coplanar, displaying strong resemblance to one of the polymorphs of the parent [1.1]ferrocenophane,[8] which has an approximate C_{2v} symmetry. The shortest intermolecular hydrogen contacts in **1** are in the range 2.3−2.7 Å, and packing effects cannot be disregarded when small conformational changes in flexible molecules like **1** are discussed. The Fe1−Fe2 intramolecular distance is 4.955 Å, and there is no indication of any metal−metal interactions.

The long C1−C12 distance (3.48 Å) indicates only a weak C1···H122−C12 interaction at the most. The nonlinear arrangement C···H122−C12 also indicates a weak interaction. The C1−H122 distance is 2.7 Å. This is a much longer distance than the sum of the covalent bond radii of −H and −C (1.07 Å), but close to the sum of the exposed radii (van der Waals

radii) of H (1.1 Å) and C (1.7 Å) atoms covalently bonded in molecules, i.e. 2.8 Å.[9a] This distance similarity indicates that any attraction between CH and ⁻C is not strong enough to cause bond shortening. Thus, no hydrogen bond is present in the solid state.

However, it could be argued that a carbanionic carbon should have a larger exposed radius than is normally used, since it is negatively charged. Therefore, it might be more reasonable to assume a 20% larger van der Waals radius for the carbanionic carbon (2.0 Å). Using this radius the sum of the exposed radii is 3.1 Å. This distance is 0.4 Å longer than the experimental C1−H122 distance and could be an indication of a weak CH···⁻C interaction. However, the shorter experimental distance could be due to the ferrocenophane anion structure forcing the groups to adopt the observed distance rather than being the consequence of a weak attraction. In comparison, the O−H distance in the H_2O-H_2O hydrogen bond is about 1.0 Å, but the intermolecular O···H distance is only 1.76 Å. This is much less than the 2.6 Å expected from summing the two van der Waals radii, but still larger than the covalent distance 1.0 Å.[9b]

It is interesting that the three covalent bonds to C1 are not in a single plane. The hybridization is close neither to sp^2 nor to sp^3. The angle between the C1−H1 bond and the plane defined by C1, C2, and C22 is 30°, i.e. the hybridization is approximately $sp^{2.5}$. Furthermore, the "anion" hybrid is pointing away from H122.

In conclusion, the results indicate the absence of a C⁻···H−C hydrogen bond in the ferrocenophanyllithium crystal.

Solution Structure of 1. Organolithium compounds in solution show a strong tendency to aggregate, and the degree of oligomerization affects the rate of reaction of such reagents.[10] Nuclear spin−spin couplings between ^6Li and ^{13}C have been used extensively to investigate the aggregation of organolithium compounds in solution.[11] The splitting pattern of the signal from the carbanionic carbon reveals the number of neighboring lithiums and, in turn, the state of aggregation.

To clarify the nature of **1** in solution, the $[1,12-^{13}C_2][1.1]$-ferrocenophane (**5**) with 99 atom % ^{13}C of the bridge carbons was synthesized[12] and the corresponding ^6Li salt (**6**) was prepared in DMTHF. The 1,12-proton transfer in **1** is much slower in DMTHF than THF, affording a "frozen" structure displaying couplings rather than a rapidly equilibrating species.

The ^1H decoupled ^{13}C NMR spectrum of **6** in DMTHF at 100 MHz was obtained at 20 °C. The signal from $H^{13}C^-$ appears as a broader singlet than that from $H_2{}^{13}C$. Upon the temperature being lowered to −45 °C, the $H^{13}C$ signal splits into a 1:1:1 triplet as shown in Figure 4. The coupling constant is 4.0 Hz.[3c] The $^{13}C,^6Li$ coupling constant 4.0 Hz is much smaller than that commonly observed for monomers of organolithium compounds. Recently Fraenkel and co-workers[7c] observed small $^{13}C,^6Li$ coupling constants in some substituted benzylic organolithium reagents.

These results suggest that each carbanionic carbon is bonded to only one ^6Li and that **6** is monomeric in DMTHF at −45 °C. To obtain further support for this conclusion, the proton-

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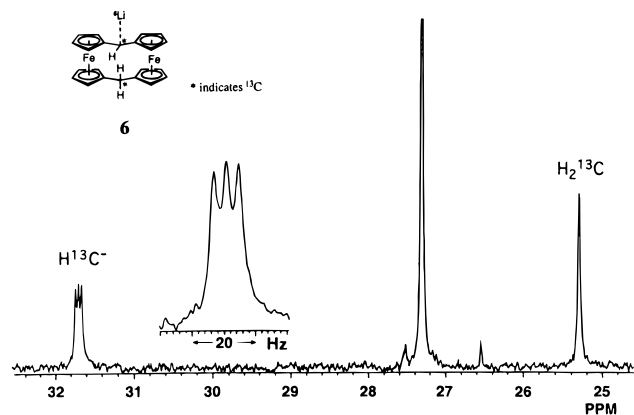(8) Håkansson, M.; Löwendahl, M.; Davidsson, Ö.; Ahlberg, P. *Organometallics* **1993**, *12*, 842.

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Figure 4. $^{13}C\{^1H\}$ NMR spectrum (obtained at 100 MHz) of **6** in DMTHF at −45 °C. The most high frequency signal from DMTHF, set to δ 75.6, was used as a reference.

Table 1. The ^{13}C NMR Chemical Shifts and $^{13}C,^1H$ Coupling Constants for **1** in Different Solvents

temp/°C	solvent	δ $^-$CH/ppm	δ CH$_2$/ ppm	$^1J(^-$CH)/ Hz	^1J(CH$_2$)/ Hz
20[a]	THF	29.5	29.5	63.9	63.9
−100	THF	35.2	24.5	141.3	124.4
−100	THF + 211[b]	35.9	22.4	163.3	124.8
20	DMTHF	31.7	25.3	139.4	125.3
20[a]	DME[c]	29.7	29.7	61.3	61.3
20	DEE	31.3	25.4	140.4	124.4

[a] Fast exchange on the NMR time scale. [b] Refers to Cryptofix 211. [c] Refers to dimethoxyethane.

decoupled ^{13}C NMR spectrum was obtained at 125 MHz using a triple resonance probe. At this higher magnetic field the $H^{13}C^-$ signal was not resolved at −45 °C as previously observed at 100 MHz, but appeared as a broad signal ($W_{1/2}$ = 10.8 Hz). Irradiation of a ^6Li signal at 73 MHz changed the carbon signal to a sharp singlet with the same width as that of the $H_2^{13}C$ signal. This reinforces the conclusion that lithium is bonded to the carbanionic carbon.[3c]

Compound **1** does not show any resolved scalar coupling in THF at any temperature (0 to −80 °C). The absence of resolved couplings may be due to fast intermolecular lithium exchange processes.
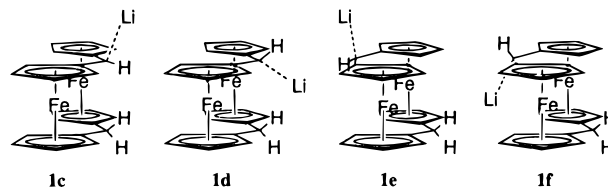
The above results unambiguously show that the carbanionic carbon of the benzylic like carbanion **1** is bonded to only one lithium in DMTHF and that **1** is mainly monomeric at the salt concentration and temperature used in the experiments.

The $^{13}C,^1H$ coupling constant for the CH$_2$ bridge in **1** was measured by ^{13}C NMR in different solvents (Table 1). The results show, as expected, that this carbon is sp^3 hybridized. Using the empirical correlation $^1J(C,H) = 500s$ Hz (s = fraction of s-character) and the data in Table 1 shows that the carbanionic carbon in THF, DMTHF, and DEE has a hybridization close to sp$^{2.5}$. In THF with addition of the Li$^+$-specific cryptand Cryptofix 211, the hybridization seems to be sp^2.
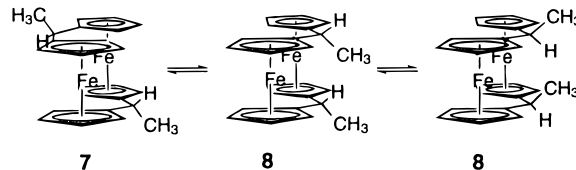
Thus, the structure of compound **1** in solution may be similar to its solid state structure with a *syn*-orientation and Li in an *exo*-position (**1c**) (Scheme 3). However, a number of other alternative structures have to be considered such as that in which Li is in an *endo*-position (**1d**).

Recently it was discovered that [1.1]ferrocenophanes such as **7** with *anti*-structures may exist.[13] Previously only *syn*-
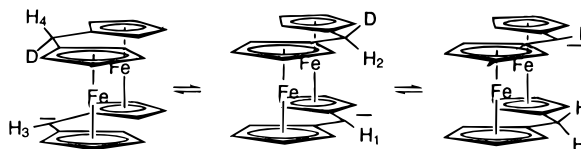
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Scheme 3

Scheme 4

Scheme 5

structures were assumed to be energetically possible.[2,14] The experimental results gathered so far do not distinguish *syn*-forms (**1c** and **1d**) from *anti*-forms (**1e** and **1f**) with the Li in *exo*- or *endo*-positions.

Since some [1.1]ferrocenophanes undergo very fast degenerate rearrangements (Scheme 4),[15] the structures in Scheme 4 may be in rapid equilibrium with each other. Experiments have been designed to differentiate between these possibilities using transient nuclear Overhauser effects (NOE's).[16]

Transient NOE Studies. For these experiments a solution of the bridged monodeuterated compound **4** was used in DEE-d_{10}. In this solvent the intramolecular 1,12 lithiation is slow on the NMR time scale. The ^1H NMR spectrum of the bridge protons showed the singlet from the proton bonded to the carbanionic carbon at δ 2.70, a doublet (H in CH$_2$) and a singlet (H in CHD) at δ 3.61−3.67, and a doublet (H in CH$_2$) and a singlet (H in CHD) at δ 4.50−4.56.

In Scheme 5 the three different isotopomers with *syn*-structures are shown together with their interconversions. For simplicity, the *exo*-coordinated Li$^+$ ions are not displayed. The signals from the protons at the carbanionic carbons (H$_1$ and H$_3$) in two of the isotopomers appear in one peak. These protons were simultaneously irradiated with a 180° pulse, and the initial buildup rates of the transient NOE's of the other bridge proton signals with time were studied. At short times (∼0.5 s) the signals from the protons at δ 4.50−4.56 showed positive NOE's, and those at δ 3.62−3.67 showed negative NOE's.

These results clearly demonstrate that in one of the isotopomers present in solution the HC$^-$ proton is close in space to the proton in the CHD group since a positive NOE is observed. This is not consistent with an *anti*-isomer, and therefore **1** has a *syn*-structure.

Furthermore, molecular models of **1** clearly show that for the HC$^-$ proton to be close in space to the CHD proton both protons have to be *endo*-positioned. Since there is not enough

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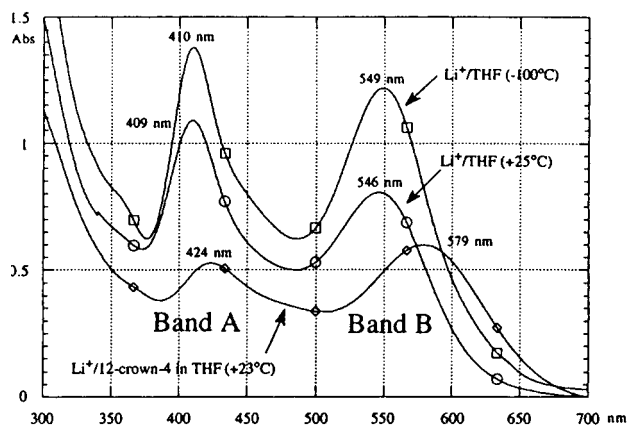*J. Am. Chem. Soc., Vol. 119, No. 7, 1997* 1749

Figure 5. The UV−vis spectrum of **1** in THF at two different temperatures and with 12-crown-4 added.
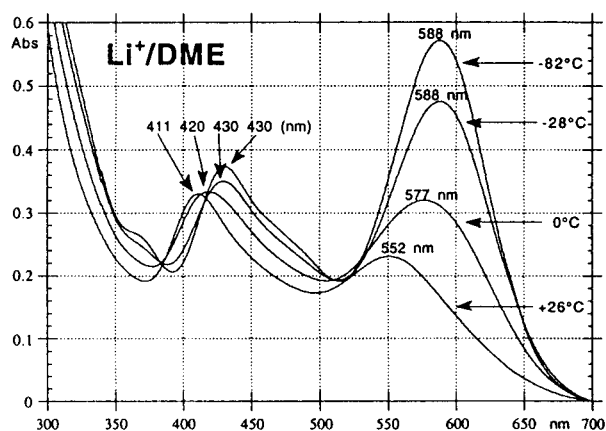

Figure 6. The temperature dependence of the UV-vis spectrum of **1** in DME.

space left to position the solvated lithium ion *endo*, it must be *exo*-ligated in **1**. Thus, the structure of **1** in solution appears to be similar to its structure in the solid state.

Ion Pairs and the Initial State of 1. UV−vis spectroscopy has been used to study ion pairing in solutions of **1**. Two broad bands, A and B, are observed (Figure 5). Band A is found in the 400−430 nm interval and band B in the 530−600 nm interval. These bands show solvent and temperature dependence.

Figure 5 shows spectra of **1** in THF. Absorption maxima of the two bands occur at 409 nm (band A) and 546 nm (band B) at +25 °C. The ratio of the absorbance of the two maxima, Abs_A/Abs_B, is 1.4. Upon the temperature being lowered to −100 °C , only small changes were observed. The maxima shifted slightly to lower frequencies. The absorbance ratio diminished slightly to 1.2. The color of the solution remained burgundy red all over the 125 °C interval.

Upon addition of a strong Li^+ complexing agent like 12-crown-4, the spectral changes were substantial (Figure 5). There were pronounced red shifts of bands A and B by 15 and 3 nm, respectively. The absorbance ratio was inverted: Abs_A/Abs_B = 0.9 (at +23 °C), and the solution turned dark blue-green. These results suggest that the addition of the crown ether separates the ions of a contact ion pair to yield a separated ion pair. The structure of these ion pairs remains to be clarified. The spectrum of **1** in DME (Figure 6) showed a dramatic temperature dependence. At 26 °C the spectrum was similar to that of **1** in THF: band A (411 nm), band B (552 nm), Abs_A/Abs_B = 1.5 (at +23 °C), burgundy red solution. Upon the temperature being lowered to −82 °C, there was a pronounced red shift similar to that observed upon addition of 12-crown-4

in THF. The shifts of the bands A and B were 19 and 36 nm, respectively. The absorbance ratio was inverted to 0.7, and the solution turned dark blue-green.

The effects of temperature and solvent are similar to those found by Hogen-Esch and Smid concerning the identification of solvent separated ion pairs (SSIP) and contact ion pairs (CIP).[17] Our results suggest that, upon the temperature being lowered, the ion pair equilibrium shifts from mainly CIP to more separated ion pairs that may be SSIPs in DME. An important note is that it is normally not possible to distinguish between SSIP and free ions with this method. Some further observations are also shown in Table 2.

The observed rate constant (k_{obs}) for the degenerate rearrangement of 1 has been measured at different temperatures. A plot of log k vs $1/T$ is not curved, which indicates that there is no dramatic change of the initial state with temperature in this solvent. In DME, on the other hand, the exchange is too fast to freeze out this process. It seems to be relatively faster at lower temperatures. This is consistent with formation of more reactive ionpairs. The increased reactivity of DME in comparison with THF may be due to the bidentate nature of DME.

UV−vis studies suggest that, although there is lengthening of the interionic distances in going from DEE to THF, there is an insignificant fraction of separated ion pairs in the initial state.

Experimental Section

General. All nondeuterated solvents were distilled in a nitrogen atmosphere from sodium/benzophenone prior to use. The deuterated solvents were stored over Deporex (Fluka AG), degassed, and distilled on a vacuum line prior to use. All handling of chemicals was in an inert atmosphere (nitrogen or argon), unless otherwise stated. The glovebox used was a Mecaplex GB-80 equipped with a gas-purification system which removes water and oxygen from the nitrogen atmosphere in the box. The water content in the glovebox atmosphere was shown with a Shaw hygrometer (model SHA-TR) to be <2 ppm. Only gas-tight syringes were used. Tetrahydrofuran-d_8 (THF-d_8) and diethyl ether-d_{10} (DEE-d_{10}) were purchased from Cambridge Isotope Laboratories, Inc.

Preparation. The ion precursors [1.1]ferrocenophane[18] (**2**), mono ^2H bridge-labeled [1-^2H][1.1]ferrocenophane[19] (**4**) and di ^{13}C bridge-labeled [1,12-$^{13}C_2$][1.1]ferrocenophane[12] (**5**) were prepared according to published procedures.

The lithium salts of the carbanions from the above precursors were made in the following way. About 1−5 mg of the anion precursor, weighed on a balance placed in the glovebox, was transferred to an NMR tube in the glovebox. The NMR tube (Wilmad/omnifit system, 507-OF) was sealed using a Wilmad/omnifit valve assembly (OFV). The glass equipment as well as the syringes were assembled in the glove box. The edges of the syringe needles were protected with a septum before the equipment was transferred from the glovebox. Approximately 50 μL of BuLi (1.6 M in hexane) was transferred to a

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Table 2.   Collection of UV−Vis Spectral Data for **1** in Some Solvents Together with Assignments of Dominating Type of Ion Pair

solvent/gegenion	temp/°C	Abs_A/nm	Abs_B/nm	ΔA^a/nm	ΔB^b/nm	Abs_A/Abs_B	dominating type of ion pair
DEE/Li$^+$	+25	401	533			1.7	CIP
DEE/Li$^+$	−116	403	537	+2	+4	1.5	CIP
DMTHF/Li$^+$	+25	401	536			1.7	CIP
DMTHF/Li$^+$	−114	405	538	+4	+2	1.4	CIP
THF/Li$^+$	+25	409	546			1.4	CIP
THF/Li$^+$	−100	410	549	+1	+3	1.2	CIP
DME/Li$^+$	+23	411	552			1.5	CIP
DME/Li$^+$	−82	430	588	+19	+36	0.7	SSIP
THF/12-crown-4/Li$^+$	+23	424	579			0.9	SSIP
THF/12-crown-4/Li$^+$	−100	429	585	+5	+6	0.7	SSIP

^{a} Δ nm A = (Abs$_{max}$ band A at low temperature) − (abs$_{max}$ of band A at high temperature) in the same solvent. ^{b} Δ nm B = (Abs$_{max}$ band B at low temperature) − (abs$_{max}$ of band B at high temperature) in the same solvent.

specially designed Schlenk apparatus. The solvent was removed on the vacuum line at a pressure of $<10^{-2}$ mbar. The remaining viscous oil of BuLi was cooled to about −70 °C and dissolved in 0.2 mL of freshly distilled THF-d_8.

The presursor was dissolved in 0.5 mL of THF-d_8 and precooled to −70 °C before about 75% of the equimolar amount of BuLi in THF-d_8 was added. The fraction of carbanion formed was monitored by ^{1}H NMR. Successive additions of BuLi in THF-d_8 gave solutions of wanted compositions. Between each addition the solution was warmed to approximately 0 °C to complete the carbanion formation. With some solvents like DME, BuLi in hexane was added directly to the precooled (−50 °C) precursor solution to avoid precipitation.

The additions of 12-crown-4 to the carbanion solutions were performed as follows. The crown ether (10 μL) was dissolved in a small volume (300 μL) of solvent. About 1.2 equiv of the complexing agent was added.

NMR Spectroscopy. The NMR experiments were carried out on a Varian XL-400 spectrometer or a Varian Unity 500 spectrometer operating at 399.95 and 499.92 MHz, respectively. The Varian Unity 500 was equipped with three channels. The low-temperature control system consists of "long hold VT-liquid nitrogen Dewar with a heat exchanger", attached to a mixer for mixing "cold" and "warm" nitrogen. Temperatures in the probe were measured with either the calibrated methanol thermometer supplied by Varian or a calibrated methanol/freon thermometer.[20]

Transient 1D NOE. The 1D transient NOE spectra were recorded using the Varian Unity 500 instrument. The spectra were obtained at 22 °C. The pulse sequence used was initiated by a selective 180° pulse of 200 ms followed by a hard 90° pulse of 8.5 μs. The following mixing times were used in the different experiments: 0, 0.2, 0.4, 0.8, 1.2, 1.6, and 3.0 s. In each experiment 32 transients were collected with a 20 s delay between the pulse cycles and a 3 s aquisition time. Spectra were aquired both with nonspinning and spinning tubes to exclude the possibility of phase errors.

UV−Vis Spectroscopy. All experiments were carried out with a Cary 04 spectrophotometer. The temperature was controlled with an Oxford variable temperature liquid nitrogen cryostat model DN1704 equipped with an ITC-4 temperature controller. The temperature was measured close to the sample using a S25421 thermolyzer (Systemteknik, Lidingö, Sweden) equipped with a Pt 100:1/10 DIN temperature sensor. The cuvettes were from Helma (No. 220-QS, 1 mm and 10 mm) onto which the top of a Wilmad/omnifit system, 507-OF NMR tube was welded. The Wilmad/omnifit valve assembly (OFV) was used to seal the cuvette. About 1 mg of **2** was dissolved in 1 mL of solvent in the cuvette, and usually 5 μL of 2.0 M BuLi was added.

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