nique which has the capability to selectively and quantitatively image a component within the interface will become extremely useful.

Acknowledgment. This work was supported in part by the Office of Naval Research. The sabbatical hospitality of the Naval Research Laboratory is gratefully acknowledged by one of us (L.G.B.). David G. Cory acknowledges a National Research Council/Naval Research Laboratory postdoctoral associateship.

Registry No. 4-Bromobenzoic acid, 586-76-5; ammonia, 7664-41-7; toluic acid, 25567-10-6.

Spectroscopic Evidence for the Formation of a Bridged Lithium Dicyclopentadienyl Lithiate Complex

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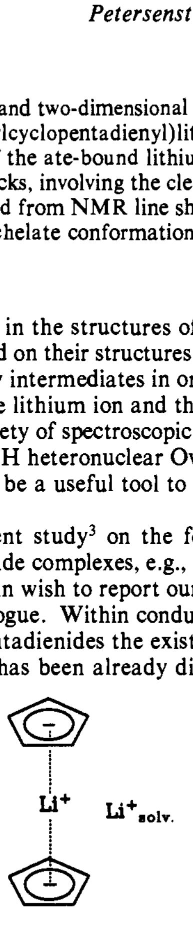
Abstract: One- and two-dimensional NMR and DNMR studies including ^{6}Li NMR prove the formation of a ferrocene-bridged lithium bis(vinylcyclopentadienyl)lithiate complex **8** in THF solution. Two different dynamic processes could be detected: the exchange of the ate-bound lithium ion with the solvent-separated lithium species and the intramolecular rotation of the hydrocarbon decks, involving the cleavage of the ate complex in the transition state. From the activation parameters of both processes derived from NMR line shape simulation it is shown that the lithium ion exchange process should proceed without the loss of the chelate conformation.

Exceptional interest in the structures of organolithium compounds has been focused on their structures in solution, since they have importance as key intermediates in organic synthesis. The interaction between the lithium ion and the carbanion has been investigated with a variety of spectroscopic methods.[1] From the NMR techniques, ^{6}Li,^{1}H heteronuclear Overhauser effect spectroscopy was shown to be a useful tool to detect short lithium–hydrogen distances.[2]

Prompted by a recent study[3] on the formation of ate-type lithium cyclopentadienide complexes, e.g., **1**, and its structure in THF solution, we herein wish to report our results concerning a ferrocene-bridged analogue. Within conductivity measurements of alkalimetal cyclopentadienides the existence of a Li(C$_5$H$_5$)$_2^-$ species as a triple ion has been already discussed earlier.[4]



1

In the course of our studies on kinetically stabilized vinylogous 6-cyclopentadienylpentafulvenes[5] as potential precursors for the synthesis of dinuclear transition-metal complexes, 6-cyclopentadienyl-6-methylpentafulvene **4** was prepared from sodium *tert*-butylcyclopentadienide (**2**) and *N*,*N*-dimethylmethoxyacetiminium methanosulfate (**3**) as a mixture of four structural isomers with *tert*-butyl substituents in β-position with respect to the bridge. Whereas treatment of **4** with 2 equiv of lithium 2,2,6,6-tetramethylpiperidide (LiTMP) furnishes dilithium ethylene-1,1-bis-(3-*tert*-butylcyclopentadienide) (**5**), the reaction with potassium *tert*-butanolate yields potassium 3-*tert*-butyl-1-(2-*tert*-butyl-6-methyl-6-pentafulvenyl)cyclopentadienide (**6**) exclusively. Both compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, establishing symmetrical structures and detecting rapid rotation of the five-membered rings vs the bridge carbon atom at room temperature in the NMR time scale.

Addition of anhydrous ferrous chloride to a solution of **6** in THF leads to the formation of a mixture of various isomeric ferrocenes **7**. Simple column chromatography on basic alumina allows the isolation of one isomer, 3,3′-di-*tert*-butyl-1,1′-bis-(*Z*-2-*tert*-butyl-6-methyl-6-pentafulvenyl)ferrocene (**7a**). The structure of this compound was established using additionally ^{1}H NOE difference experiments and the 2D ^{1}H,^{13}C shift correlation spectrum. A NOE effect is observed from the methyl groups to H-2 as well as to H-5 in each ferrocene ring; this is probably caused by a rapid rotation of the pentafulvalene moieties vs the ferrocene system. However, no conclusions can be drawn on whether the configuration of **7a** is meso or dl (accidental spectroscopic isochronicities of a mixture of both excluded) since all attempts to separate these by chromatography using a chiral column phase (polytriacetylcellulose/ethanol) failed.

The 2-fold deprotonation of **7a** with ^{6}Li-enriched LiTMP in THF-d_8 yields a brown 0.1 M solution of the salt **8** which was studied by NMR spectroscopy. At room temperature, various signals in the ^{1}H and ^{13}C NMR spectra belonging to the ferrocene moiety and the vinyl groups show line-broadening effects which disappear when the sample is heated to 313 K. ^{1}H NOE difference spectra of **8** taken at this temperature prove that rapid rotation occurs around the bonds connecting the five-membered rings to the ethylene groups. Below the 273 K signal splitting is observed in the ^{1}H (Figure 1) and in the ^{13}C NMR spectra, pointing on

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(1) (a) Becker, B.; Enkelmann, V.; Müllen, K. *Angew. Chem.* **1989**, *101*, 501–503; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 458. (b) Gronert, S.; Streitwieser, A. *J. Am. Chem. Soc.* **1988**, *110*, 2836–2842. (c) O'Brien, D. H.; Russell, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 633–639. (d) Grutzner, J. B.; Lawlor, J. M.; Jackman, L. M. *J. Am. Chem. Soc.* **1972**, *94*, 2306–2315. (e) Johnels, D.; Edlund, U. *J. Am. Chem. Soc.* **1990**, *112*, 1647–1649. (f) Fraenkel, G.; Hallden-Abberton, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5657–5664. (g) Cox, R. H.; Terry, H. W. *J. Magn. Reson.* **1974**, *14*, 317–322.

(2) (a) Hoffmann, D.; Bauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1990**, 208–211. (b) Bauer, W.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 970–977.

(3) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776–8789.

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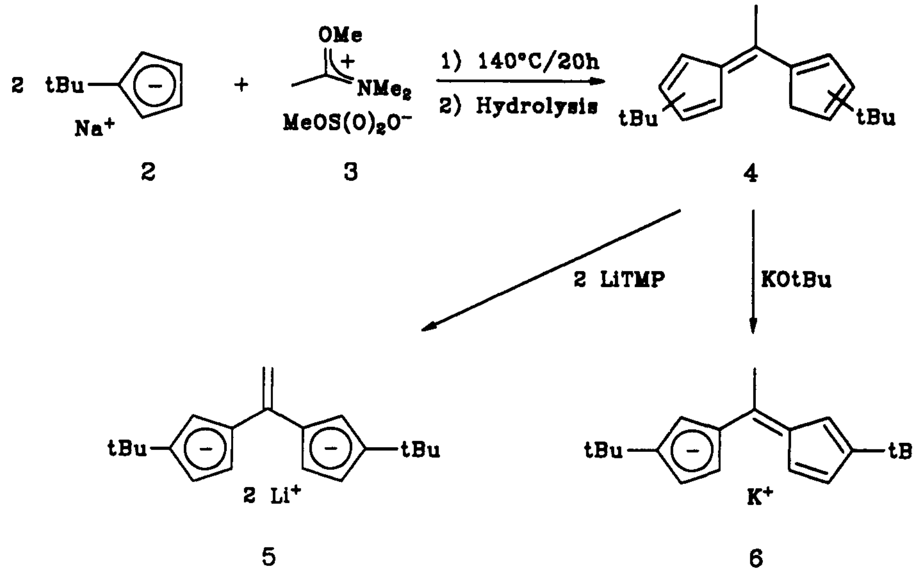
(5) Eiermann, M.; Stowasser, K.; Hafner, K.; Bierwirth, K.; Frank, A.; Lerch, A.; Reusswig, J. *Chem. Ber.* **1990**, *123*, 1421–1431.

Scheme I



Scheme II

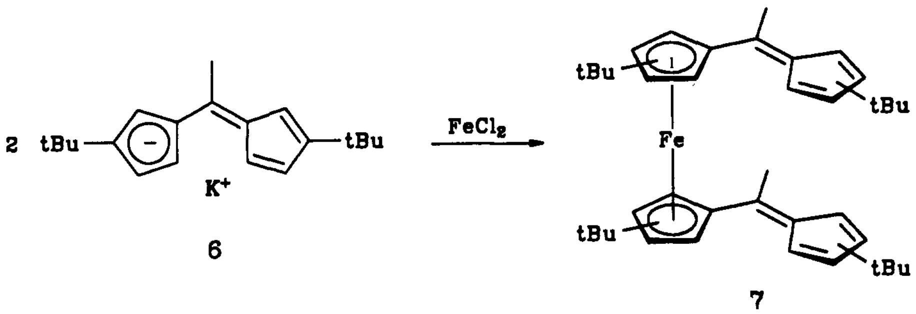
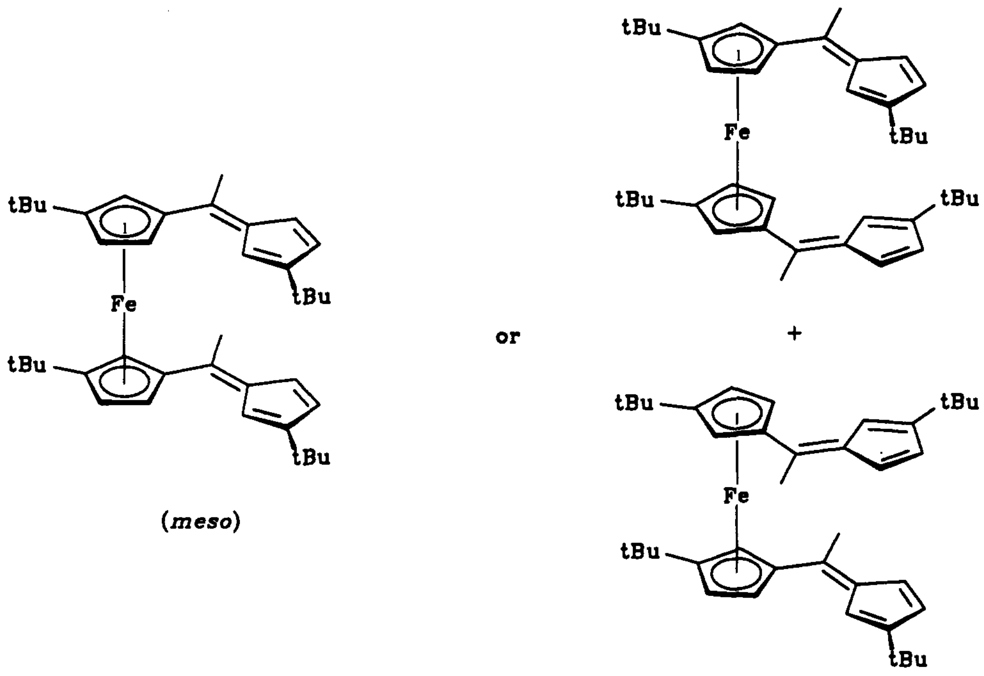


Chart I



(*meso*)

7a

(*dl*)

a restricted dynamic process (see below for the discussion of the possible structures).

Additional information about this interesting behavior was expected from the ^{6}Li NMR spectra of **8**. The spectrum taken at room temperature exhibits only one broad peak centered at $\delta_{Li} = -5.6$. When the temperature of the sample is decreased, this signal splits into two peaks at $\delta_{Li} = -1.6$ and $\delta_{Li} = -11.7$ (Figures 2 and 3) at 213 K (at lower temperatures (193 K), no further

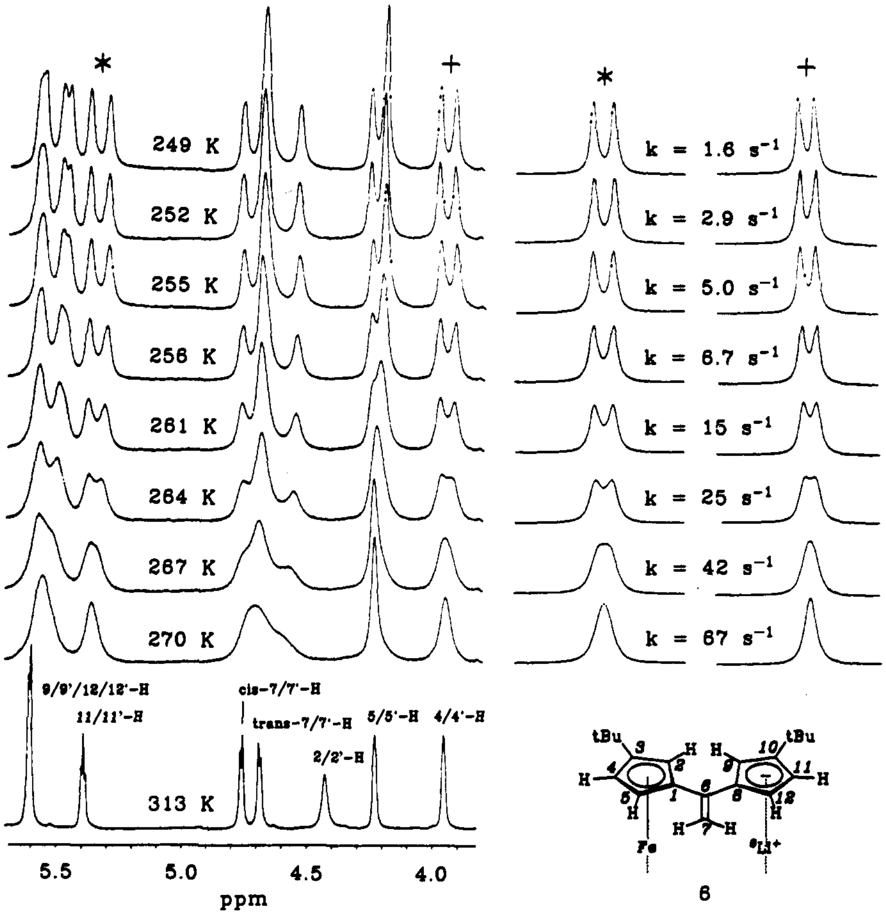
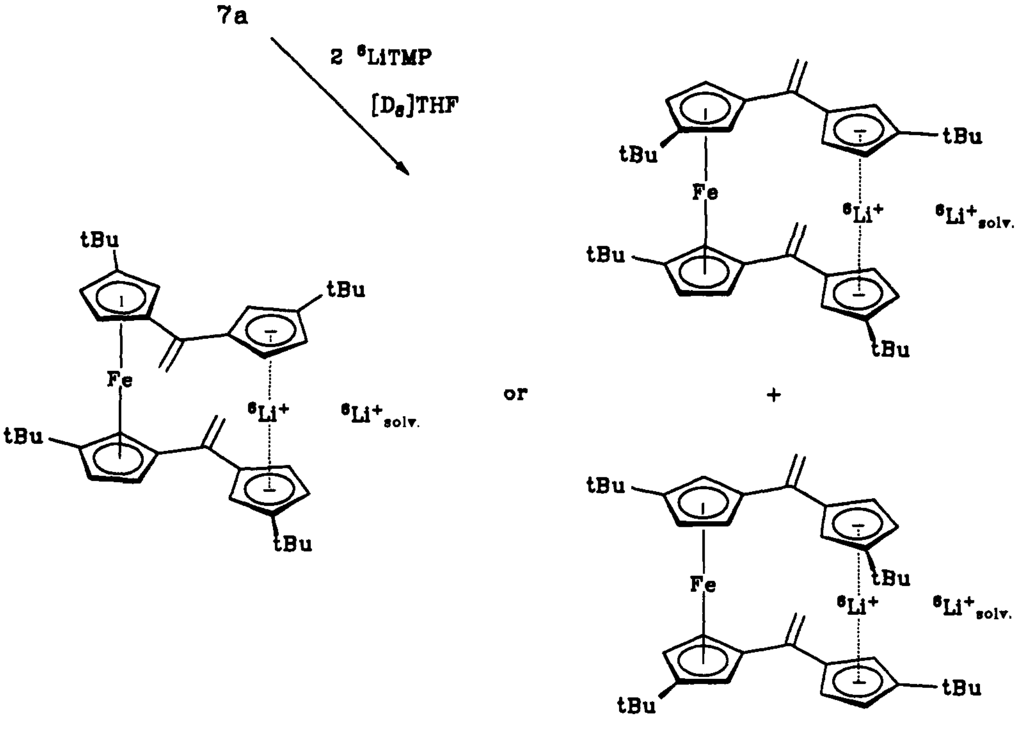


Figure 1. Left side: The olefin region of the ^1H NMR of **8** at various temperatures. The individual intensity scales at different temperatures are roughly comparable. Right side: Numerical simulations for the peaks at $\delta_H = 5.34$ (*) and $\delta_H = 3.96$ (+) in the ^1H NMR spectra of **8**. The numbering of **8** used in the text is shown below. It was chosen for clearness within the discussion and does not correspond to nomenclature. The numbering of the second deck is similar, but with an apostrophe (1′, 2′, etc.).

Scheme III



8

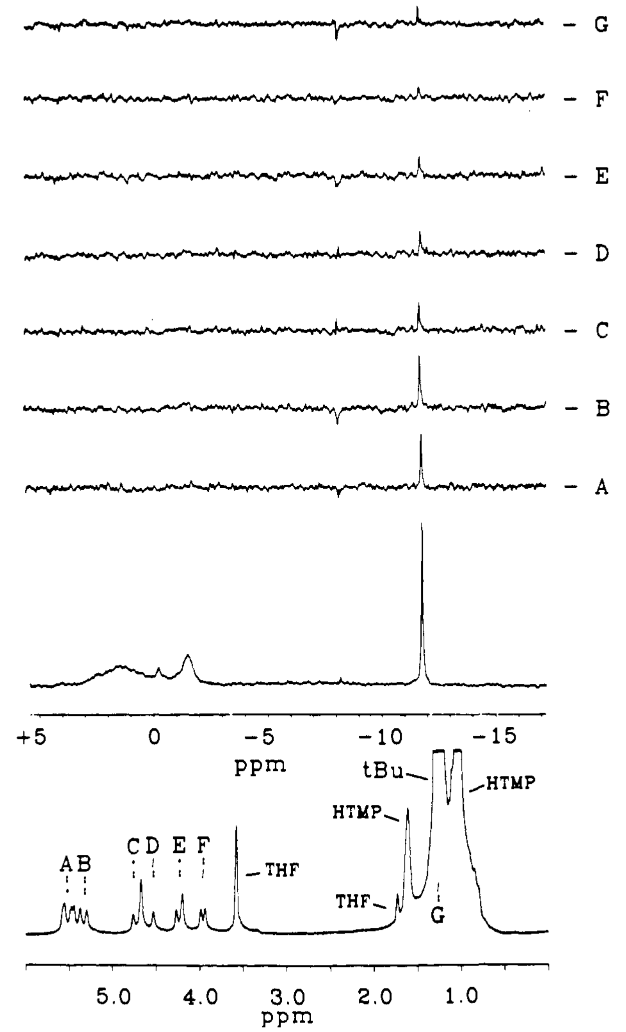


Figure 2. $^6Li\{^1H\}$ NOE difference spectra (A–G) and the related ^6Li and ^1H NMR spectra of **8** at 213 K. The letters A–G in the latter indicate the ^1H irradiation frequencies of the NOE experiments (see text). The signals at $\delta_{Li} = 1.5$ and $\delta_{Li} = -0.2$ belong to excess of base. The spike at $\delta_{Li} \approx -8.1$ is a disturbance.

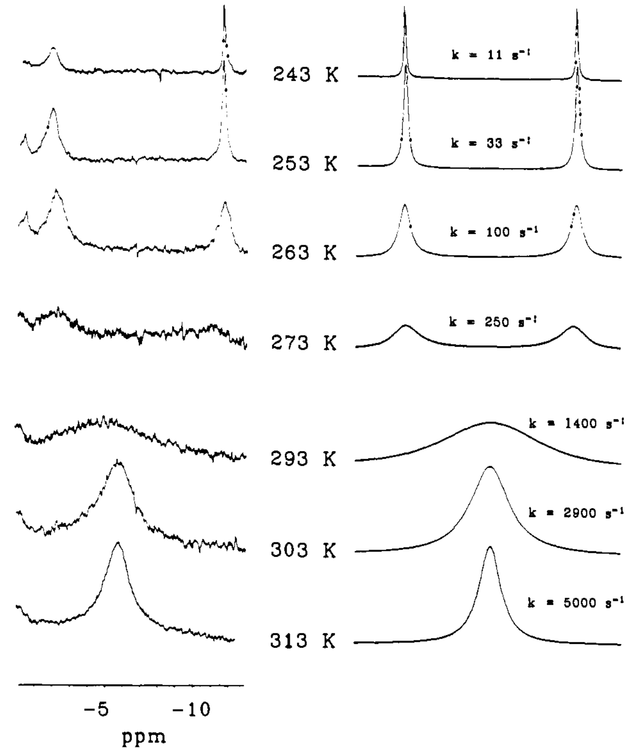
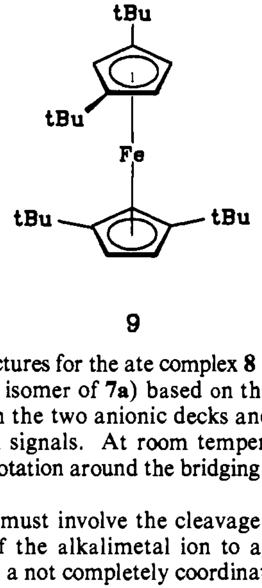


Figure 3. The high field region of the ^6Li NMR spectra of **8** at various temperatures (left side) and simulated spectra (right side). The simulations are based only on the line shape of the high field peak at $\delta_{Li} = -11.7$. The individual intensity scales at different temperatures are not comparable and were chosen for clearness.

changes can be observed). These results can be explained in terms of an ate-complex-type structure of **8** wherein one lithium ion is presumably coordinated to four solvent molecules (low field signal), whereas the other is located in between the two anionic five-membered rings which causes a significant high field shift in the ^6Li NMR spectrum. The spectroscopic data can be compared directly with those of **1**.[3]

Additionally, the $^6Li\{^1H\}$ NOE difference NMR spectra taken at 213 K confirm the presence of a chelate complex, exhibiting strong signal enhancements for the protons of the cyclopentadienide moieties (Figure 2A,B). The effect is less pronounced for the signals of the ferrocene hydrogen atoms as well as of the vinyl protons (C, D). Only weak enhancements are observed in case of resonances belonging exclusively to the ferrocene ring (E, F) or to the *tert*-butyl substituents (G).

This raises the question as to how the dynamic effects observed in the NMR spectra can be interpreted. It is very unlikely that the signal splitting is due to the formation of two different ate-complex species, since the integral ratio of the split signals is 1:1, independent of temperature between 213 and 250 K, and since the splitting is symmetrical with respect to the chemical shifts of the signals observed at rapid exchange. It is rather caused by a "frozen" internal motion with a loss of symmetry in the NMR time scale. This means that the two hydrocarbon decks are becoming different, possibly due to the influence of the *tert*-butyl groups. With regard to that observation, one has to take into account that the substituents in 1,1′,3,3′-tetra-*tert*-butylferrocene (**9**) due to transannular steric interactions prefer a staggered conformation rather than an eclipsed one.[6]



9

All possible structures for the ate complex **8** (derived from either the meso or the dl isomer of **7a**) based on these data possess no symmetry between the two anionic decks and should thus show two sets of proton signals. At room temperature, rapid interconversion due to rotation around the bridging bonds causes signal coalescence.

Such a process must involve the cleavage of at least one coordinative bond of the alkalimetal ion to a cyclopentadienide ligand, resulting in a not completely coordinated contact ion pair species in the transition state. The formation of such a species should possess a large activation enthalpy $\Delta H^{\ddagger}$ and also a positive value for the activation entropy $\Delta S^{\ddagger}$, due to the increase in the number of degrees of freedom. In fact, the comparison of the ^1H NMR signal line shapes of two different protons (one belonging to the ferrocene moiety (H-4), the other belonging to the cyclopentadienide rings (H-11)) with those obtained from numerical simulation[7] allowed the determination of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Figure 1)[8] for the decoordination process:

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(6) Kaluski, Z. L.; Gusev, A. I.; Kalinin, A. E.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1972**, *13*, 950–953; *Chem. Abstr.* **1973**, *78*, 34920a.

(7) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228–1234.

$$\Delta H^{\ddagger} = 97 \pm 8 \text{ kJ/mol} \qquad \Delta S^{\ddagger} = 151 \pm 29 \text{ J/mol·K}$$

These values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are in agreement with the model for the observed exchange process as described above. The positive $\Delta S^{\ddagger}$ value demonstrates the increase of the number of degrees of freedom in the transition state due to intramolecular rotation. Together with the large activation enthalpy it also supports the idea of the formation of a not completely coordinated lithium species; otherwise, one would expect a negative value on the same order of magnitude. In this case, free solvent molecules must be attached to the metal atom, reducing the number of particles and therefore decreasing the entropy of the system. This effect can be compared with the well-known formation of a solvent-separated ion pair from a contact ion pair and a solvent molecule. The entropy of this equilibrium process has been determined in a number of cases;[1b–d,5] the values are of a comparable order of magnitude but with a negative sign.

The dynamic effects observable in the ^{6}Li NMR spectra were subject to numerical line shape simulation, too. Surprisingly, the values obtained for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ differ considerably from those derived from the ^{1}H NMR data:[8]

$$\Delta H^{\ddagger} = 55 \pm 6 \text{ kJ/mol} \qquad \Delta S^{\ddagger} = 5 \pm 10 \text{ J/mol K}$$

This result can only be explained by the occurrence of two separated dynamic processes. Obviously, the lithium ion exchange is more facile than the conformational changes of the ligands. As the latter should incorporate a cleavage of at least one coordinative bond between the alkalimetal ion and a cyclopentadienide system, the former is supposed to proceed without a complete ring opening of the metallocenophane system in the transition state. A possible mechanism which also accounts for the negligable value of $\Delta S^{\ddagger}$ obtained from the ^{6}Li NMR spectra deals with a replacement of the chelated lithium ion by a solvent-coordinated one which takes place between the two cyclopentadienide decks and which is accompanied by successive changes of the solvation sphere of both the entering and the leaving alkalimetal ion.

The results presented in this work prove the formation of a ferrocene-bridged dicyclopentadienyl lithiate complex **8** and allowed the study of intramolecular exchange processes. Further investigations on this interesting chelate complex and related structures are in progress.

Experimental Section

All experiments involving organolithium compounds were carried out in flame-dried glassware under an atmosphere of dry nitrogen. The solvents used were purified according to standard procedures. For column chromatography, basic alumina (activity II-III (Brockmann) ICN Woelm) and silica gel (70–230 mesh (ASTM) Merck) were used.

The physical data of the compounds were obtained using the following equipment: NMR Bruker WM 300, AC 300 (^{1}H, 300 MHz; ^{13}C, 75.47 MHz; ^{6}Li, 44.13 MHz). The chemical shifts are given relative to TMS (^{1}H, ^{13}C) and 1 M LiBr in THF-d_8 (^{6}Li). In case of the organolithium compounds **5**, **6**, and **8**, the remaining hydrogen signals of THF-d_8 (MSD Isotopes) served as standard; MS Finnigan MAT 311-A/100 MS; IR Beckman IR-5A, Perkin-Elmer 125; UV Beckman DK-2A, UV-5240; elemental analysis, Perkin-Elmer CHN 240A and 240B. The melting points were determined with a Kofler apparatus (Reichert, Vienna, Austria).

DNMR Measurements of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The $\Delta G^{\ddagger}$ values were obtained from comparison of calculated[7] and measured line shapes as shown (Figures 1 and 3). $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ could be derived from a plot of $\Delta G^{\ddagger}$ as a function of T. The following parameters were used for the line shape calculation:

	^{6}Li NMR	^{1}H NMR	
	(δ −5.6)	(δ 5.34)	(δ 3.96)
natural line width	3 Hz	8 Hz	7 Hz
population ratio	1:1	1:1	1:1
frequency site A	−517.4 Hz	1589.4 Hz	1176.2 Hz
frequency site B	−65.5 Hz	1612.3 Hz	1194.1 Hz

The results of the simulations are as follows:

^{6}Li	T (K)	243	253	263	273	293	303	313	
	$\Delta G^{\dagger}$(kJ/mol)	54.2	54.2	54.0	54.1	54.0	54.2	54.6	
^{1}H	T (K)	249	252	255	258	261	264	267	270
	$\Delta G^{\dagger}$(kJ/mol)	59.6	59.2	58.7	58.2	57.8	57.3	56.9	56.4

NMR line shape simulation allows the measurement of $\Delta G^{\ddagger}$ with a typical absolute error $\Delta_{abs}(\Delta G^{\ddagger}) \approx 0.84$ kJ/mol.[8] The relative error in a series of $\Delta G^{\ddagger}$ values should be much smaller and can be derived from various simulations at the same temperature with slightly differing $\Delta G^{\ddagger}$ values: $\Delta_{rel}(\Delta G^{\ddagger}) \approx 0.3$ kJ/mol in case of the ^{1}H NMR data and $\Delta_{rel}(\Delta G^{\ddagger}) \approx 0.5$ kJ/mol for the ^{6}Li NMR spectra. Whereas the Δ_{rel} value has effect on both $\Delta(\Delta H^{\ddagger})$ and $\Delta(\Delta S^{\ddagger})$, the other affects only $\Delta(\Delta H^{\ddagger})$. Thus in a diagram $\Delta G^{\ddagger}$ as a function of T one can estimate a maximum and a minimum slope for the regression line connecting the $\Delta G^{\ddagger}(T)$ values, considering only $\Delta_{rel}(\Delta G^{\ddagger})$, obtaining maximum and minimum values for $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$. The error of the latter must then be increased by the $\Delta_{abs}(\Delta H^{\ddagger})$ value.

(*E*/*Z*)-3-*tert*-Butyl-6-((3/4)-*tert*-butylcyclopentadienyl)-6-methylpentafulvene (4). *N*,*N*-Dimethylacetamide (1.74 g, 20.0 mmol) and 2.52 g (20.0 mmol) of dimethyl sulfate were heated to 60 °C for 2 h under stirring. After cooling down to room temperature, the colorless oil **3** was extracted twice with dry ether and added to 40 mL (44 mmol) of a refluxing 1.1 M solution of sodium *tert*-butylcyclopentadienide (**2**) in DME/diethylene glycol dimethyl ether (1:1). After heating for 24 h, the mixture was cooled down to room temperature and hydrolyzed by addition of 100 mL of a deoxygenated saturated aqueous solution of ammonium chloride. One hundred milliliters of ether was added, and the organic phase was separated and extracted five times with water. After drying with magnesium sulfate and removal of the solvent in vacuo, the brown oil was chromatographed on a silica gel column (6-cm diameter, 60-cm length) with *n*-pentane. From the second fraction 2.2 g (8.2 mmol, 41%) of **4** were obtained as brown oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19/1.20/1.21/1.21 (4 s, 36 H, *t*-Bu) 1.22/1.22 (2 s, 36 H, *t*-Bu), 2.34 (s, 3 H, Me), 2.36 (s, 6 H, Me), 2.37 (s, 3 H, Me), 3.28/3.33 (2 s, 4 H, $-CH_2-$), 3.37 (s, 4 H, $-CH_2-$), 6.10–6.35 (m, 8 H, $=CH-$), 6.50–6.98 (m, 12 H, $=CH-$); MS (70 eV), *m*/*e* (rel intensity) 268 (M^+, 100), 253 (M^+ − Me, 92), 211 (M^+ − *t*-Bu, 82), 197 ($M^+ - C_4H_8$ − Me, 83), 155 ($M^+ - C_4H_8$ − *t*-Bu, 33), 57 (*t*-Bu, 68); UV (*n*-hexane), λ_{max} (ϵ) (nm) 245 (7280), 367 (20 600); IR (KBr), ν (cm^{-1}) 2860 (s, C–H), 1560 (s, C=C), 1460 (s, C–H), 1350 (s, C–H). Anal. Calcd for $C_{20}H_{28}$: C, 89.48; H, 10.52. Found: C, 89.05; H, 10.51.

Dilithium Ethylene-1,1-bis(3-*tert*-butylcyclopentadienide) (5) (0.5 M Solution in THF-d_8). In a 5-mm NMR tube connected by melting to a small flask equipped with a septum and a tap leading to a vacuum pump was treated 1.2 mL (0.72 mmol) of a 0.6 M solution of 99% ^{6}Li-enriched *n*-propyllithium in *n*-hexane at 0 °C under stirring with 130 mg (0.90 mmol) of 2,2,6,6-tetramethylpiperidine. After 10 min the mixture was warmed to room temperature, and stirring was continued for 20 min. The solvent was removed in vacuo, and the colorless residue was dissolved in 0.4 mL of THF-d_8 and treated with 80 mg (0.30 mmol) of **4** in 0.2 mL of THF-d_8. The orange solution was cooled to −196 °C, and the NMR tube was evaporated (10^{-4} Torr) and separated from the flask by melting: ^{1}H NMR (300 MHz, 313 K, THF-d_8) δ 1.24 (s, 18 H, *t*-Bu), 4.61 (s, 2 H, 2-H), 5.55 (m, 2 H, 4′-H, 4″-H), 5.81/5.87 (2 br s, 4 H, 2′-H, 2″-H, 5′-H, 5″-H); ^{13}C NMR (75.5 MHz, 313 K, THF-d_8) δ 34.1 [$-C(CH_3)_3$], 99.6 (br, C-2, invisible in DEPT experiment), 99.9/101.7/103.8 (C-2′, -2″, -4′, -4″, -5′, -5″), 123.8 (C-1′, -1″), 131.0 (C-3′, -3″), 150.1 (C-1).

Potassium 3-*tert*-Butyl-1-(2-*tert*-butyl-6-methyl-6-pentafulvenyl)cyclopentadienide (6) (0.75 M Solution in THF-d_8). In a 5-mm NMR tube connected by melting to a small flask equipped with a septum and a tap leading to a vacuum pump were dissolved 80 mg (0.30 mmol) of **4** and 56 mg (0.50 mmol) of potassium *tert*-butylate in 0.4 mL of THF-d_8. The deep orange-brown solution was cooled to −196 °C, and the NMR tube was evaporated (10^{-4} Torr) and separated from the flask by melting: ^{1}H NMR (300 MHz, 313 K, THF-d_8) δ 1.22 (s, 18 H, *t*-Bu), 2.41 (s, 3 H, Me), 6.03 (m, 2 H, 3′-H, 4-H), 6.24/6.40 (2 br s, 4 H, 1′-H, 2-H, 4′-H, 5-H); ^{13}C NMR (75.5 MHz, 313 K, THF-d_8) δ 21.2 (6′-CH_3), 33.3 [$-C(CH_3)_3$], 33.9 [$-C(CH_3)_3$], 111.0/116.8/117.6 (C-1′, -2, -3′, -4, -4′, -5), 126.9 (C-1, -5′), 144.6/148.2 (C-2′, -3, -6′).

3,3′-Di-*tert*-butyl-1,1′-bis((*E*/*Z*)-2-*tert*-butyl-6-methyl-6-pentafulvenyl)ferrocene (7). **4** (0.80 g, 3.0 mmol) was dissolved in 25 mL of THF and treated with 390 mg (3.5 mmol) of potassium *tert*-butylate. After 20 min 250 mg (2.0 mmol) of anhydrous ferrous chloride was added in small portions over a 1-h period. Stirring was continued for 1 h, and the mixture was then hydrolyzed with 20 mL of a saturated aqueous solution of ammonium chloride. After addition of 20 mL of ether and separation of the phases, the organic phase was passed with ether through a short column of basic alumina. After removal of the

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solvent in vacuo, chromatography of the red oil on a column (basic alumina, 6-cm diameter, 50-cm length) with *n*-pentane yielded in the first fraction small amounts of **4**. The following red fraction contained after removal of the solvent 350 mg (0.59 mmol, 40%) of **7** as red glass: mp 73–78 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19/1.19/1.20/1.20/1.23/1.24/1.28/1.28/1.29 (9 s, 36 H, *t*-Bu), 2.11/2.13/2.16/2.16 (4 s, 3 H, $-CH_3$), 2.48 (s, 3 H, $-CH_3$), 4.20–4.63 (m, 6 H, 2-H, 2′-H, 4-H, 4′-H, 5-H, 5′-H), 6.04–6.22 (m, 2 H, 3″-H, 3‴-H), 6.41–6.55 (m, 4 H, 1″-H, 1‴-H, 4″-H, 4‴-H); MS (70 eV), *m/e* (rel intensity) 540 (M^+, 100), 57 (*t*-Bu, 29); UV (*n*-hexane), λ_{max} (ϵ) (nm) 287 sh (16 000), 324 (31 800), 343 sh (28 500), 423 (4410), 488 (3270); IR (KBr), ν (cm^{-1}) 2900 (s, C–H), 1590 (s, C=C), 1350 (s, C–H). Anal. Calcd for $C_{40}H_{54}Fe$: C, 81.33; H, 9.21; Found: C, 81.88; H, 9.40.

3,3′-Di-*tert*-butyl-1,1′-bis(*Z*-2-*tert*-butyl-6-methyl-6-pentafulvenyl)ferrocene (7a). Chromatography of **7** on basic alumina (6-cm diameter, 80-cm length) with *n*-pentane allowed the separation of a small red zone behind the main fraction. After removal of the solvent 50 mg (0.08 mmol, 6%) were obtained as red crystals (mp 129–134 °C (2-propanol)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (s, 18 H, 2″-*t*-Bu, 2‴-*t*-Bu), 1.21 (s, 18 H, 3-*t*-Bu, 3′-*t*-Bu), 2.46 (s, 6 H, $-CH_3$), 4.32 (dd, J_1 = 1.5 Hz, J_2 = 2.6 Hz, 2 H, 5-H, 5′-H), 4.37 (dd, J_1 = 1.5 Hz, J_2 = 2.6 Hz, 2 H, 4-H, 4′-H), 4.44 (t, J = 1.5 Hz, 2 H, 2-H, 2′-H), 6.20 (m, 2 H, 3″-H, 3‴-H), 6.54 (m, 2 H, 1″-H, 1‴-H), 6.55 (m, 2 H, 4″-H, 4‴-H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.1 (6″-CH_3, 6‴-CH_3), 29.7 [2″-$C(CH_3)_3$, 2‴-$C(CH_3)_3$], 30.8 [$-C(CH_3)_3$], 31.5 [3-$C(CH_3)_3$, 3′-$C(CH_3)_3$], 32.2 [$-C(CH_3)_3$], 67.7 (C-2, -2′), 68.8 (C-4, -4′), 71.8 (C-5, -5′), 85.8/105.4 (C-1, -1′, -3, -3′), 112.7 (C-3″, -3‴), 122.1/129.6 (C-1″, -1‴, -4″, -4‴), 142.2/145.3/156.8 (C-2″, -2‴, -5″, -5‴, -6″, -6‴).

Lithium 3,3′-Di-*tert*-butylferrocenylene-1,1′-bis[1-(3-*tert*-butylcyclopentadienido)vinylidene]lithiate (8) (0.1 M Solution in THF-d_8). Similar to the preparation of **5**, **8** was prepared from 0.60 mL (0.36 mmol) of a 0.6 M solution of ^{6}Li-enriched *n*-propyllithium in *n*-hexane, 60 mg (0.43 mmol) of 2,2,6,6-tetramethylpiperidine, 60 mg (0.10 mmol) of **7a**, and 1.0 mL of THF-d_8: ^{1}H NMR (300 MHz, 313K, THF-d_8) (The numbering is according to Figure 1 and does not correspond to nomenclature.) δ 1.25 (s, 18 H, 10-*t*-Bu, 10′-*t*-Bu), 1.29 (s, 18 H, 3-*t*-Bu, 3′-*t*-Bu), 3.96 (br s, 2 H, 4-H, 4′-H), 4.23 (br s, 2 H, 5-H, 5′-H), 4.43 (br s, 2 H, 2-H, 2′-H), 4.69 (d, J = 2.9 Hz, 2 H, trans-7-H, -7′-H), 4.76 (d, J = 2.9 Hz, 2 H, cis-7-H, -7′-H), 5.39 (m, 2 H, 11-H, 11′-H), 5.61 (m, 4 H, 9-H, 9′-H, 12-H, 12′-H); ^{13}C NMR (75.5 MHz, 313 K, THF-d_8) δ 31.7/32.5 [$-C(CH_3)_3$], 32.8 [3-$C(CH_3)_3$, 3′-$C(CH_3)_3$], 33.7 [10-$C(CH_3)_3$, 10′-$C(CH_3)_3$], 66.6 (C-4, -4′), 86.3 (C-1, -1′ or C-3, -3′), 100.8 (br, C-7, -7′, invisible in DEPT experiment), 101.7 (C-11, -11′), 102.4/102.5 (C-9, -9′, -12, -12′), 119.8 (C-8, -8′), 131.6 (C-10, -10′), 146.6 (C-6, -6′). One signal belonging to either C-1, -1′ or C-3, -3′ could not be identified and was supposed to be hidden at δ ≈ 102 (from comparison with **7a**).

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Supplementary Material Available: Additional spectroscopic data of **7a** and **8** (NOE and COSY) (2 pages). Ordering information is given on any current masthead page.

Influence of Micellar Size on the Decay of Triplet-Derived Radical Pairs in Micelles[†]

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Abstract: The photoreduction of butyrophenone by α-tocopherol in anionic micelles has been examined by laser flash photolysis. The reaction leads to a triplet-derived radical pair that decays by a competition of escape processes and geminate reactions. The dependence of both processes on the surfactant's chain length, the addition of electrolytes, and the temperature were examined in detail. The rate constants for radical exit from the micelles (k_-) follow Arrhenius-type behavior; for example, the exit from sodium dodecyl sulfate micelles occurs with an activation energy of 6.5 kcal/mol and log (A/s^{-1}) = 10.7. The results suggest that entropy plays an important role in determining the dynamics of escape processes. The rate constants for geminate reaction (k_{gem}) are largely determined by the size of the micelles. Both spin evolution and the frequency of reencounters are important in controlling geminate processes. For the radical pair examined, spin evolution is believed to be controlled by hyperfine couplings, while the frequency of reencounters depends upon micellar size and intramicellar diffusion dynamics.

Introduction

The impact of organized media on the kinetics of chemical reactions is now widely recognized.[1] In particular, triplet-derived geminate radical pairs or radical ion pairs sequestered in a micellar environment can often retain their geminate character for sufficiently long times that the radical pair can access the singlet surface, ultimately leading to closed shell products.[2-6] This is due to compartmentalization of the radical pair by the micelle and is in contrast to homogeneous solution where radical separation is so rapid that geminate reaction is generally a very minor process for triplet-derived neutral radical pairs[7-9] as well as some radical cation–radical anion pairs.[10]

Time-resolved studies of micellized, neutral triplet-derived radical pairs have concentrated mainly on carbon-centered species,[6]

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