Alternative Routes for Reductive Alkylations in Liquid Ammonia and Their Selection via Spectroscopic Evidence[1]

Klaus Müllen,*[2a] Walter Huber,[2b] Gerd Neumann,[2a] Christoph Schnieders,[2a] and Heinz Unterberg[2a]

Contribution from the Institut für Organische Chemie der Johannes Gutenberg-Universität, D-6500 Mainz, Federal Republic of Germany, and the Institut für Physikalische Chemie der Universität, CH-4056 Basel, Switzerland. Received July 18, 1984

Abstract: A wide range of unsaturated hydrocarbons have been reduced with alkali metals in liquid ammonia and the carbanionic intermediates detected in situ by NMR and ESR spectroscopy. The substrates cluster into three different groups depending on whether they (i) persist as dianions, (ii) are protonated by ammonia to afford monohydro anions, or (iii) undergo further electron transfer/protonation steps to yield polyhydro derivatives. The alternative modes of behavior can be correctly predicted on the basis of the relevant atom localization energies. The spectroscopic findings are extremely helpful in rationalizing the results of reductive alkylation experiments and in controlling the regioselectivity of novel quenching reactions.
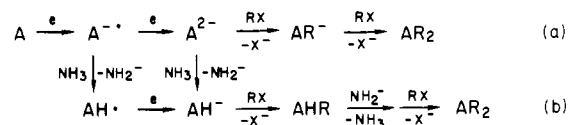
1. Introduction

Reductive alkylations of unsaturated hydrocarbons in liquid ammonia proceed via initial electron transfer and subsequent addition of electrophiles to the anionic intermediates. The astonishingly high regioselectivity of the kinetically controlled reactions can be rationalized by invoking the prevailing π-charge distributions. Toward this end, however, it must be firmly established which anionic derivative of the substrate is actually involved (see Scheme I): (i) the electron transfer may generate a radical anion $A^{-\cdot}$ or a dianion A^{2-}, and (ii) both species may be protonated by the ammonia. Thus, for example, the dianion A^{2-} gives rise to the monoanion $A\text{-}H^-$ plus the amide ion NH_2^-.[3-8]

One obvious consequence of the protonation is that upon subsequent alkylation with an electrophile RX, the monoanion $A\text{-}H^-$ gives rise to a monoalkyl derivative (AHR); the dianion A^{2-} forms a dialkyl (AR_2) derivative. The question as to whether A^{2-} is resistant to protonation by the ammonia may be considered to have only formal significance since in addition to the direct alkylation of A^{2-} (route a) there is another pathway (route b) to the dialkyl derivative, namely, deprotonation of AHR by the amide anion and subsequent alkylation of the resulting monoanion. One must be aware, however, that the alkylation reactions according to mechanism a or b are governed by the different π-charge distributions in A^{2-} or $A\text{-}H^-$ and may, therefore, produce different dialkyl adducts.

Having realized that the synthetic utility of metal–ammonia reductions depends critically on the control of the reaction mechanism, considerable experimental efforts have been made to identify and selectively prepare the relevant anionic intermediates.[3,5] The approach taken involves the analysis of the products which are obtained upon systematic variation of the experimental conditions: (i) the persistence of A^{2-} or $A^{-\cdot}$ with respect to protonation has been investigated by comparing different hydrocarbon substrates or by changing the ion pair structures;[5,6,8] (ii) the amount of AHR deprotonation has been reduced by the inverse quenching procedure (whereby the ammonia solution is

added to an excess of the alkylating agent RX) or increased by introducing additional amide as base;[5] (iii) the reductive alkylation reactions in liquid ammonia are contrasted with those conducted under strictly aprotic conditions in ethereal solvents.[9,10]

Complementing the above "indirect" evidence on the reaction mechanisms, the present paper is devoted to the in situ detection of reactive intermediates by ESR and NMR spectroscopy.[9] A broad range of structurally different substrates (1–14) is included in order to (i) solve apparent misinterpretations in the literature, (ii) arrive at a systematic description of the alternative reaction mechanisms, and (iii) conceive of novel modes of reductive alkylations.

Scheme I
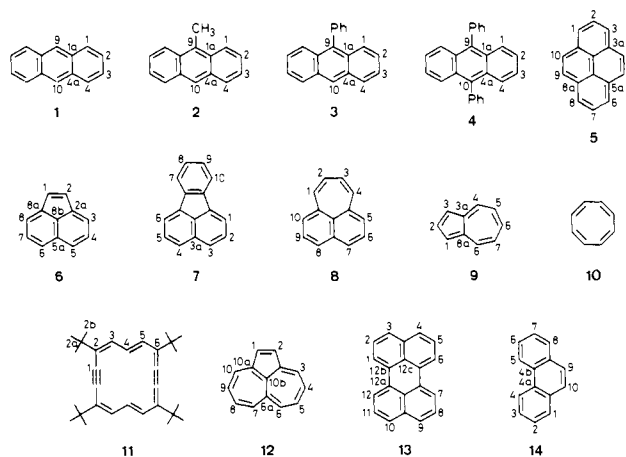
2. Results

Solutions of the hydrocarbon substrates in liquid ammonia/tetrahydrofuran (1:5) in sealed NMR tubes are placed in contact at low temperatures with freshly prepared alkali metal wire deposited in the upper part of the tube. The formation of the reduction products which gives rise to deeply colored solutions is monitored by ESR as well as ^{1}H and ^{13}C NMR spectroscopy.

(1) Reductive Transformations. 5. For part 4, see: Irmen, W.; Huber, W.; Lex, J.; Müllen, K. *Angew. Chem.* **1984**, *96*, 800; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 818.

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Table I. ^{1}H (δ_H) and ^{13}C (δ_C) Chemical Shifts of Mono- and Dianions in THF/NH$_3$[a]

	solvent	temp, °C	1–4, 5–8	1a, 4a, 5a, 8a	9	10	substituent
δ_C(1-H$^-$/Li$^+$)	THF/NH$_3$	−40	126.1, 126.1, 111.6, 107.6	145.6, 119.8	39.8	79.0	
δ_H(1-H$^-$/Li$^+$)	THF-d_8/NH$_3$-d_3	−40	6.30 (2 H), 5.94 (1 H), 5.68 (1 H)		3.50	4.35	
δ_C(2-H$^-$/Li$^+$)	THF/NH$_3$	−60	126.8, 126.0, 115.1, 108.9	143.1, 125.4	44.0	77.7	25.1 (CH$_3$)
δ_C(3-H$^-$/Li$^+$)	THF/NH$_3$	−40	126.4,[b] 125.7,[b] 112.0,[b] 110.7[b]	142.8, 121.1	91.9	40.9	147.7 (s), 133.5,[b] 129.0,[b] 121.4 (Ph)
δ_C(4-H$^-$/Li$^+$)	THF/NH$_3$	−40	128.5,[b] 128.1,[b] 113.5,[b] 110.8[b]	140.6, 123.7	54.8	90.9	150.8 (s), 147.4 (s), 125.3, 121.6, 133.7,[b] 128.9,[b] 127.9,[b] 125.8[b] (Ph)
δ_H(5-H$^-$/Li$^+$)	THF-d_8/NH$_3$-d_3	−30	5.87 (H-7), 5.69 (H-4), 5.48 (H-5), 5.48 (H-10), 5.44 (H-3), 5.29 (H-8), 5.13 (H-6), 4.88 (H-9), 4.31 (H-2), 4.17 (H-1)				
δ_C(5-H$^-$/Li$^+$)	THF/NH$_3$	−40	143.1 (s), 140.7 (s), 138.0 (s), 136.3 (s), 129.4, 126.8, 126.8, 126.5, 109.3, 108.3 (s), 107.9, 106.5 (s), 104.7, 104.7, 100.7, 34.0 (C-1)				
δ_H(6-H$^-$/Li$^+$)	THF-d_8/NH$_3$-d_3	−60	6.67 (H-6/H-8), 6.30 (H-3), 6.18 (H-7), 6.03 (H-1/H-2), 5.85 (H-6/H-8), 5.42 (H-1/H-2) 4.57 (H-4), 3.85 (H-5)				
δ_C(6-H$^-$/Li$^+$)	THF/NH$_3$	−60	132.4 (s), 129.1 (s), 128.1 (s), 128.4, 116.8, 115.1, 114.6, 109.1, 108.3 (C-4), 106.9 (s), 93.1 (C-1), 32.3 (C-5)				
δ_C(6^{2-}/2K$^+$)	THF/NH$_3$	−70	150.0 (C-5a), 139.4 (C-8b), 127.1 (C-4/C-7), 124.7 (C-2a/C-8a), 98.2 (C-3/C-8), 88.3 (C-1/C-2), 83.0 (C-5/C-6)				
δ_C(7-H$^-$/Li$^+$)	THF/NH$_3$	−40	138.0 (s), 132.8 (s), 127.3 (s), 125.9, 124.1 (s), 122.0 (s), 120.3, 120.2, 117.4, 116.6, 114.4, 114.2, 108.7, 104.2, 95.8 (s, C-3a), 32.7 (C-1)				
δ_H(8-H$^-$/Li$^+$)	THF-d_8/NH$_3$-d_3	−40	6.42 (H-10), 6.42 (H-8), 6.10 (H-6), 5.89 (H-3), 5.73 (H-5), 5.65 (H-9), 5.25 (H-7), 4.43 (H-4), 4.16 (H-2), 3.19 (H-1)				
δ_C(8-H$^-$/Li$^+$)	THF/NH$_3$	−40	147.4 (s), 142.1 (s), 140.0 (s), 132.7, 131.7 (s), 126.0, 126.0, 120.7, 115.9, 111.5, 102.1 (C-2), 98.0, 95.1 (C-4), 40.7 (C-1)				
δ_C(9-H$^-$/Li$^+$)	THF/NH$_3$	−40	131.5, 122.5 (C-3a/C-8a), 108.3 107.9, 104.7, 29.3 (C-6)				
δ_C(10^{2-}/2Li$^+$)	THF/NH$_3$		90.1				
δ_H(11^{2-}/2Li$^+$)	THF-d_8/NH$_3$-d_3	−70	0.03 (H-t-Bu), 2.02 (H-3), 23.4 (H-4)				
δ_C(12^{2-}/2Li$^+$)	THF/NH$_3$	−60	125.5 (C-2a/C-10a), 121.1, 120.1, 119.7 (C-6a), 113.3, 99.0, 92.9, 92.2 (C-10b)				
δ_C(13^{2-}/2Li$^+$)	THF/NH$_3$	−40	147.6 (s), 136.8 (s), 126.4, 121.8 (s), 99.1, 97.5				
δ_C(14-H$_3$$^-$/Li$^+$)	THF/NH$_3$	−80	138.0 (s), 137.3 (s), 125.8, 125.1, 125.0, 122.9 (s), 107.4, 103.8, 95.3, 89.5, 86.9 (s), 31.4 (t), 31.4 (t), 30.6 (t)				

[a] THF/NH$_3$, 5:1. [b] Assignment uncertain.

Careful control of the reduction seemed particularly critical owing to the possibility of successive electron transfers and of competing protonation steps. The examples of anthracene, pyrene, and phenanthrene are revealing and will be described in greater detail.

In the case of anthracene (2–2.5 equiv Li) the initial blue color rapidly turns to green within a few seconds. When the solution is allowed to stand at −78 °C for a few minutes, its color changes to orange, a process which can be accelerated by shaking the tube or by working in boiling ammonia. However, the NMR spectra from the very beginning indicate one main diamagnetic product (see below) which remains unaffected upon further standing at low temperatures. The latter behavior is irrespective of whether the alkali metal solution has been prepared from 2 equiv or from a large excess of the reducing agent (see Figure 1).

For pyrene the original deep red solution does not give rise to NMR signals. Further standing, however, while not changing the color produces a diamagnetic species which is readily detected by its NMR signals (see Table I). The dissolving metal reduction of phenanthrene will be shown below to generate a monoanionic trihydro derivative. This product is observed by NMR spectroscopy in early stages of the reduction even if one applies 2 equiv of the alkali metal.

Undoubtedly, the primary reduction products are the paramagnetic radical anions which can be detected by their well-known ESR spectra. It is important in view of the discussion below that the original radical anions of 1,[11] 5,[12] and 14[13] remain unaffected when kept without further metal contact at temperatures below ca. −50 °C. Further metal contact of the solutions of the radical anions 1⁻·, 5⁻·, and 14⁻· causes, firstly, an increase, and then a decrease of the ESR signals. Irradiation with UV light of the samples within the ESR cavity[9,14] fails to increase the signal intensity of the radical anions. According to the ESR spectroscopic
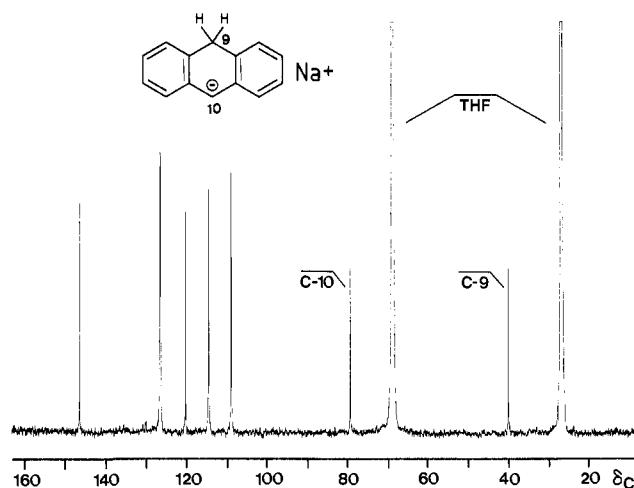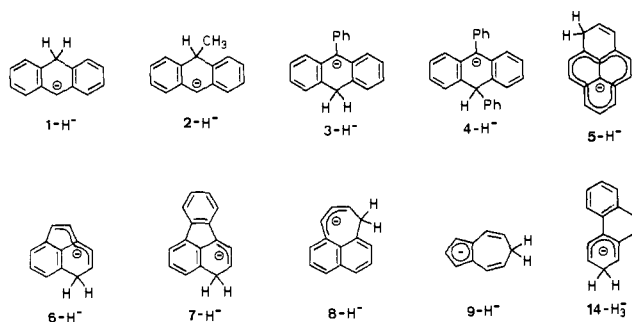

Figure 1. ^{13}C NMR spectrum (75 MHz, −40 °C) of 1-H$^-$/Na$^+$ in THF/NH$_3$.

analysis the final products of the anthracene and phenanthrene reduction are the radical anions of the dihydro derivatives 15 = 1-H$_2$[15] and 16 = 14-H$_2$,[16] respectively, which are identified from their well-known ESR spectra. A slightly different result is observed during the reduction of pyrene. If, after the disappearance of the radical anion signal, the solution is irradiated, one obtains the ESR spectrum of the neutral radical 17[17] which incorporates a phenalene moiety. The photoinduced formation of 17 is reversible; i.e., cutting off the light causes immediate disappearance of the ESR signal.

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Figure 2. ^{13}C NMR spectrum (75 MHz, −40 °C) of 9-H$^-$/Li$^+$ in THF/NH$_3$. The signals indicated by D are due to **9–9**$^{2-}$.

The information to be taken from the ESR spectroscopic experiments is that the reduction of **1, 5**, and **14** in liquid ammonia produces protonated species. The questions arise as to whether these are the main products and what are the structures of the diamagnetic systems. The ^{13}C (THF/NH$_3$) and ^1H (THF-d_8/ND$_3$) NMR spectra of the reduction products (lithium salts) (see Table I) reveal significant differences among the substrates. Only compounds **10, 12**, and **13** give rise to the NMR spectra of the dianions. The number of the ^{13}C signals firmly indicates the intact molecular frameworks of the π systems; moreover, the chemical shifts are very similar to those that we have measured for the dianions in solutions of pure THF (see Table I and Figure 4).

The ^{13}C NMR spectra obtained from the reductions of **1–9** in THF/NH$_3$ exhibit the following features: there is one high-field signal stemming from an aliphatic (methylene) carbon (see Figures 1, 2, and 3); the number of olefinic ^{13}C signals is larger than expected for the intact dianions; the charge-induced upfield shift of the center of gravity of the olefinic ^{13}C signals is much smaller than expected for a dianion.[10,18,19] One thus obtains strong evidence for the formation of monoprotonated monoanions rather than dianions as products of the reductions of **1–9**. This finding is still valid when the reduction of anthracene or pyrene is performed with sodium instead of lithium. Acenaphthylene (**6**) (see Figure 2) proves to be an outstanding example in that its behavior depends on the nature of the counterions. When reduced with lithium in NH$_3$/THF solution it transforms into the monohydro derivative **6-H$^-$** (see below); with potassium as reducing agent the dianion **6**$^{2-}$ is detected as sole product.

In an independent experiment 9-methyl-9,10-dihydroanthracene (**18**) has been deprotonated with sodium amide (THF/NH$_3$) or *n*-butyllithium (THF).[20,21] There is no doubt from the ^{13}C NMR spectra that the deprotonation process and the above reduction of 9-methylanthracene (**2**) yield one and the same monoanionic product **2-H$^-$**.

According to the above ESR spectroscopic evidence the reaction of **1** or **5** with an excess of lithium proceeds beyond the monohydro stage. Under the same experimental conditions it appears from the ^{13}C NMR spectra that, e.g., **1-H$^-$** and **2-H$^-$** (as main reduction products of **1** and **2**) are accompanied by small amounts of the dihydroanthracene species **1-H$_2$** and **2-H$_2$**. Upon standing at room temperature the amount of dihydro derivatives increases drastically. On the other hand, when the alkali metal reduction is performed in the presence of amide ions, the monoanions **1-H$^-$** and **2-H$^-$** are observed as sole products; i.e. there is neither a dihydro product nor a dianion. The failure to detect the anthracene dianion even in the presence of large amounts of alkali amide will be relevant for an interpretation of the alkylation experiments (see section 3.3).

Further protonation of the monohydro species at elevated temperatures is also observed for other examples, e.g., for **5** and **8**. The NMR signals of the secondary products are partly covered
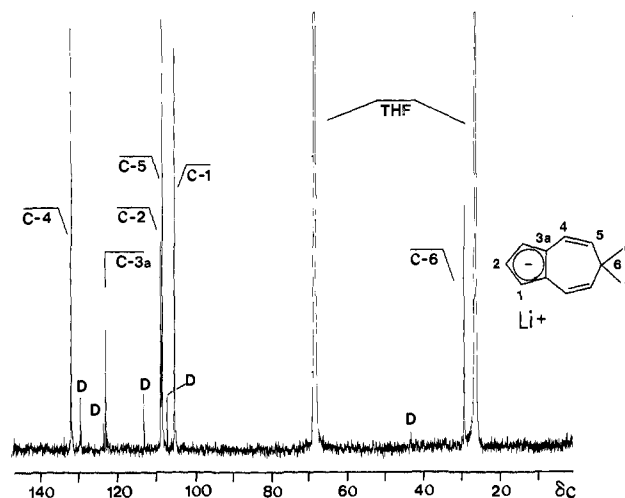
by those of the monohydro derivatives so that the structural elucidation of the former is not as straightforward as in the anthracene case.

Another side reaction occurs upon the reduction of azulene. It is known from the lithium reduction of **9** in THF[22,23] that the primary product is the dimeric dianion **9–9**$^{2-}$ which is formed via coupling of two radical anions **9**$^-$. Proof of the structure of **9–9**$^{2-}$ follows from NMR spectroscopic evidence (see Table I) and from protonation to yield product **20**. Upon further reduction the dimer **9–9**$^{2-}$ suffers from σ-bond cleavage and gives rise to the azulene dianion **9**$^{2-}$.

When azulene is reduced in THF/NH$_3$ the formation of **9-H$^-$** competes with the dimerization to **9–9**$^{2-}$. Species **9-H$^-$** appears to be the dominant product (see Figure 2); the relative amount of **9-H$^-$** and **9–9**$^{2-}$ cannot simply be inferred from the signal intensities since the dimer forms a white precipitate.[22,23]

The ^{13}C NMR spectrum taken upon the lithium reduction of phenanthrene (**14**) (2 equiv of Li) differs from the above examples in that from the very beginning it exhibits 11 olefinic (1 C each) and 2 aliphatic carbon signals (2 C, 1 C). While the spectrum indicates the presence of a single product in solution (see below), the sample tube contains a considerable amount of material as precipitate.

So far one has focussed on the identification of either intact dianions or their protonation products. Another question during the structural assignment of the hydro products is also concerns the site of attack of the proton and thus the position of the newly formed sp^3 carbon.

The number of signals observed in the ^{13}C NMR spectra of **1-H$^-$ – 3-H$^-$** is only compatible with protonation at C-9 or C-10. In the case of **2** and **3**, protonation at C-9 or C-10 will provide different monoanions. However, a ready decision can be made from the multiplicities in the off-resonance proton-decoupled ^{13}C NMR spectra.

The symmetry inherent in the ^{13}C spectrum of **9-H$^-$** points toward protonation at either C-2 or C-6. The ^1H spectrum taken in THF-d_8/ND$_3$ and in particular the vicinal coupling constant between H-4 and H-5 strongly suggest protonation in the seven-membered ring.

The structure of the monoanion **5-H$^-$** derived from pyrene has been carefully elucidated by us elsewhere.[9,24]

Reference to the ^1H NMR spectra is also necessary when describing the structures of **6-H$^-$ – 8-H$^-$** (see Table I and Figure 3). The structures finally identified are those indicated by the formulas.

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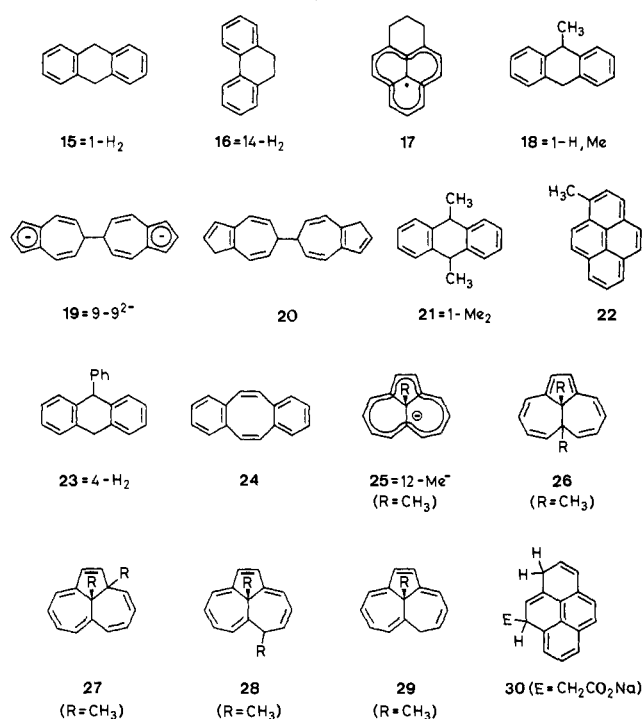(21) Daney, M.; Bonas-Laurent, H.; Calas, B.; Giral, L.; Platzer, N. *J. Organomet. Chem.* **1980**, *188*, 277.

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A basic aspect within the present work is the behavior of the intermediate reduction products upon reaction with alkylation reagents. Particularly critical is the formation of dialkyl adducts from those species which undergo protonation in liquid ammonia. We have therefore quenched the solution obtained from **1** and 2 equiv of lithium with methyl bromide and monitored the formation of the mono- and dimethyl adduct **18** = **1-H,Me** and **21** = **1-Me₂** by ¹H NMR. The relative yield of **18** and **21** as estimated from the signal intensities of the methyl protons and from GC/MS is 1:1,[4]
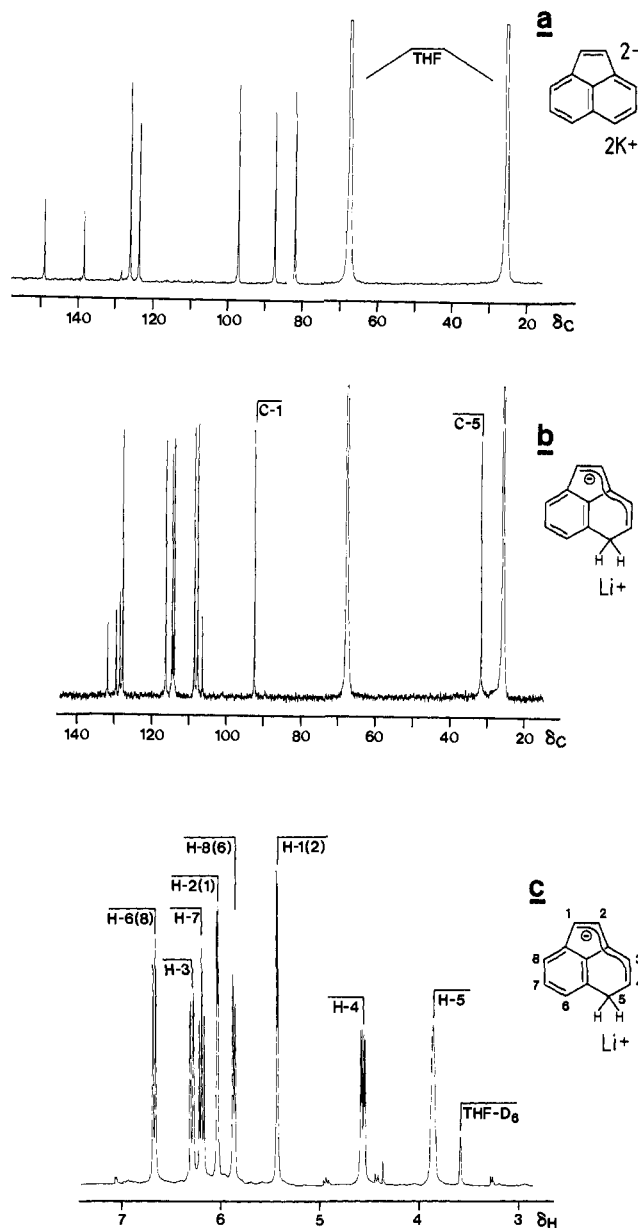
The literature provides a large number of publications devoted to reductive alkylations in liquid ammonia. Some of the arguments presented will have to be revised in the light of the above spectroscopic results. This is particularly striking for the pyrene case.[25,26] In the latter instance it was necessary to compare the alkylation in liquid ammonia with that in THF. The pyrene dianion (lithium salt) was therefore prepared in THF (sealed glass ampoule) and allowed to react at −78 °C with 1 equiv of methyl iodide. After aqueous workup the reaction mixture was dehydrogenated with dichlorodicyanobenzoquinone. The methyl derivative identified was 1-methylpyrene (**22**).

15 = 1-H₂   16 = 14-H₂   17   18 = 1-H,Me

19 = 9-9²⁻   20   21 = 1-Me₂   22

23 = 4-H₂   24   25 = 12-Me⁻ (R = CH₃)   26 (R = CH₃)

27 (R = CH₃)   28 (R = CH₃)   29 (R = CH₃)   30 (E = CH₂CO₂Na)

3. Discussion

3.1. Do Anions Resist Protonation in Liquid Ammonia?

The ¹³C NMR spectra of the hydrocarbon substrates **1 – 14** taken in a carefully dried (see Experimental Section) NH₃/THF (1:5)/Li solution suggest the following classification: compounds **1 – 9** exist as monoprotonated monoanions of general formula A-H⁻ (group 1), compound **10 – 13** as dianions A²⁻ (group 2), compound **14** as a trihydroanion A-H₃⁻.

The underlying spectroscopic arguments have been discussed in section 2. The most significant aspects are: (i) the overall number of ¹³C signals (protonation reduces the symmetry of the π system), (ii) the detection of aliphatic resonances (together with their multiplicity in the off-resonance proton-decoupled spectra), and (iii) the comparison with the spectra of authentic dianion samples recorded in ethereal solvents (**1**²⁻,[27,28] **5**²⁻,[24,29] **6**²⁻,[10,30]

Figure 3. (a) ¹³C NMR spectrum (75 MHz, −70 °C) of **6**²⁻/2K⁺ in THF/NH₃. (b) ¹³C NMR spectrum (75 MHz, −60 °C) of **6-H⁻/Li⁺** in THF/NH₃. (c) ¹H NMR spectrum (300 MHz, −60 °C) of **6-H⁻/Li⁺** in THF-*d₈*/ND₃.

7²⁻,[10,28,31] **8**²⁻,[10] **9**²⁻,[22,23] **10**²⁻,[32] **11**²⁻,[19] **12**²⁻,[22,30,33] **13**²⁻,[28,34] **14**²⁻[35]).

The anthracene systems **1 – 4** transform into monoanions which possess a diphenylmethyl anion moiety. The site of protonation in **2** and **3** can easily be identified as C-9 and C-10 (see formulas), respectively. Thus, the structures **2-H⁻** and **3-H⁻** conform to the prediction which one would have made for the first and second deprotonation step in 9-methyl-9,10-dihydroanthracene (**18**) and 9-phenyl-9,10-dihydroanthracene (**23**).[36,37] Supporting evidence for the above structural assignments is obtained from deprotonation experiments: it follows from the NMR spectra of the monoanions produced that the deprotonation of **1-Me,H** and the

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Table II. Atom Localization Energies A_μ for the Dianions 1^{2-}, 5^{2-}, 6^{2-}, 7^{2-}, 8^{2-}, 9^{2-}, 10^{2-}, 11^{2-}, 12^{2-}, 13^{2-}, 14^{2-}, 14-H_2^{2-} and the Monoanion 14-H^- Calculated by the HMO Procedure[40] Using $\alpha_\mu = \alpha$, $\beta_{\mu\nu} = \beta$.

1^{2-}	5^{2-}	6^{2-}	7^{2-}	8^{2-}	9^{2-}
$A_9 = 1.185\beta$	$A_1 = 1.300$	$A_5 = 1.400$ ($A_1 = 1.554$)^b	$A_3 = 1.336$	$A_1 = 1.099$ ($A_{4b} = 1.637$)^b	$A_6 = 1.187$ ($A_4 = 1.128$)^b

| 10^{2-}	11^{2-}	12^{2-}	13^{2-}	14^{2-}	14-H^-	14-H_2^{2-}
$A_1 = 1.602$	$A_4 = 1.335$ $A_4 = 2.711^a$	$A_{10b} = 1.660$ ($A_6 = 1.563$)^b	$A_3 = 1.445$ ($A_2 = 1.815$)^b ($A_{12a} = 2.083$)^b	$A_9 = 1.087$	$A_{10} = 0.767$	$A_2 = 1.038$

^{a} This value is obtained by taking into account the higher bond order of the C1–C14 and C7–C8 triple bonds by introducing $\beta_{1,14} = \beta_{7,8} = 1.5\beta$.
^{b} The A_μ^- values in parentheses represent atom localization energies for alternative centers with a high π-charge density.

ammonia reduction of **2** give rise to the same species. One notes that the charge-stabilizing effect of the phenyl groups is not sufficient to render the dianion 4^{2-} resistant to protonation by ammonia.

As has been mentioned in section 2, the structural assignment of the monoanions 5-H^- – 9-H^- requires both ^{13}C and ^{1}H NMR spectroscopic evidence. In any case the spectra indicate the presence of only one single monohydro structure. This finding suggests two important conclusions: (i) there is always *one* preferential site of protonation, and (ii) the dianions 1^{2-} – 9^{2-} which can be kept in ethereal solvents do not persist in liquid ammonia (as lithium salts).

Before proceeding to the preparative significance of these results, the mode of formation of A-H$^-$ must be considered in greater detail. In principle, both the dianion A^{2-} as well as the intermediate radical anion A$^-$· are prone to protonation by the solvent. Hydrocarbons **1, 5,** and **14** have been reduced in THF/NH$_3$ under ESR spectroscopic control. There is no doubt from the spectra taken below -50 °C that the initially formed radical anions resist protonation and are only modified upon further reduction.

One concludes that the monoanions A-H$^-$ are preferentially formed via protonation of the dianion according to the equation

$$A^{2-} + NH_3 \rightleftarrows NH_2^- + A\text{-H}^- \tag{1}$$
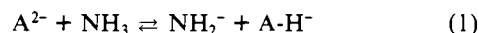
and that the equilibrium is on the right for group 1 compounds and on the left for group 2 compounds.

There is no evidence from the NMR spectra of group 1 systems for a significant equilibrium concentration of the dianion. A typical example is pyrene (**5**) where the absence of any ^{1}H resonances of 5^{2-} indicates the eventual dianion concentration to be lower than 10^{-3}% of that of the monoanion 5-H^-. Clearly, such a reasoning assumes that any nonprotonated reduction product exists as the dianion and that there is no line broadening (spectrum taken at -80 °C) due to rapid electron transfer with a radical anion. The absence of the dianion can also be deduced from photochemical evidence. Irradiation of dianion solutions with light of a UV lamp is known from broad experience to cause photooxidation to the radical anions[38] which can be detected by ESR spectroscopy. When monitoring the metal–ammonia reduction of **1, 5,** and **14** by ESR spectroscopy we submitted the samples to photolysis at different stages of the reduction. In no case did we observe an increase in the original ESR intensity or a reappearance of the ESR signals of A^-·.

There is convincing ESR and NMR spectroscopic evidence that the above classification must define a third group of substrates. When phenanthrene (**14**) is allowed to react with 2 equiv of lithium in liquid ammonia/THF one does not observe a hydrophenanthrenyl anion but a monoanion 14-H_3^- which has incorporated three protons. Obviously, the intermediate species 14-H^- suffers from rapid protonation. The resulting dihydro derivative, in turn (whose radical anion can be detected by ESR spectroscopy), transforms into 14-H_3^- by further reduction and protonation.

3.2. Energetic Considerations. Why do the title compounds classify into three distinct groups? A rather crude interpretation might consider the fact that the protonation of group 1 dianions produces monoanions with effective conjugative stabilization; thus, e.g., 1-H^-, 5-H^-, and 9-H^- possess anionic diphenylmethyl, phe-

nalenyl, and cyclopentadienyl subunits. Similarly, one can invoke the potential aromaticity or antiaromaticity of the dianions,[5] since the former should be expected to possess a higher persistance.

This argument has been applied when comparing the reductive alkylation of anthracene (**1**) and *sym*-dibenzocyclooctatetraene (**24**).[5] As is well known, the diatropic or paratropic behavior of cyclic π systems is often referred to in assessing their aromatic or antiaromatic character. It is, indeed, obvious, that the dianions 10^{2-} and 12^{2-} (group 2) are described by ^{1}H NMR spectroscopic evidence to be diatropic, while, for example, the dianions 1^{2-}, 5^{2-}, 9^{2-} (group 1), and 14^{2-} (measured in tetrahydrofuran solutions) are paratropic. The exception is the annulene dianion 11^{2-} which, although possessing a pronounced paratropic character, resists protonation by the ammonia.

A more promising approach will contrast the π-electron energy of the dianion with that of the corresponding monoanion.[39] From the difference of these energies, $E_\pi(A^{2-}) - E_\pi(A\text{-H}^-)$, one obtains, as has amply been described in the literature, the atom localization energies A_μ[40] which are a measure of the basicity of the corresponding dianions. Thereby, the tendency toward protonation should increase with a decreasing A_μ value. Moreover, for a particular substrate the A_μ values must be calculated for different protonation sites so that a prediction can be made as to the constitution of the monohydro product. This approach has been followed by us within a simple HMO model, and the resulting A_μ values are compiled in Table II.

It appears as a most significant result that the experimental detection of three groups of compounds is also borne out by the calculation: one obtains high, intermediate, and low A_μ values for compounds of group 2 (existing as dianions), group 1 (transforming into monoanions), and group 3 (undergoing further reduction/protonation steps). Moreover, for one and the same substrate the positions of protonation can correctly be predicted since they are characterized by the lowest A_μ values.

A few examples deserve special comment. The [14]annulene dianion resists protonation by ammonia although the A_μ value is relatively low. It is the particular property of a $[4n + 2]$ annulene with ideal D_{nh} symmetry that it possesses a pair of degenerate lowest lying unoccupied orbitals. Within the realm of a simple MO model this degeneracy is removed when accounting for the prevailing perturbations of the ideal perimeter situation. Among these are the existence of triple bonds or the alkyl substitution. It is characteristic that any perturbation increasing the splitting of the LUMO's of **11** also increases the A_μ value.

According to the A_μ values acenaphthylene (**6**) constitutes another borderline case since its A_μ is significantly larger than that of **1, 5,** and **7–9**. The fact that 5^{2-} persists in THF/NH$_3$ solution only as potassium salt indicates the role of ion-pairing effects which are neglected in the crude MO model used above. While ion-pair structures of monoanionic and dianionic hydrocarbons in ethereal solvents have been extensively studied, related information for ammonia solutions is not available. It has been deduced from preparative findings, however, that the lithium salts possess a stronger tendency toward solvent-separated ion pairs, the latter undergoing protonation more easily than contact ion

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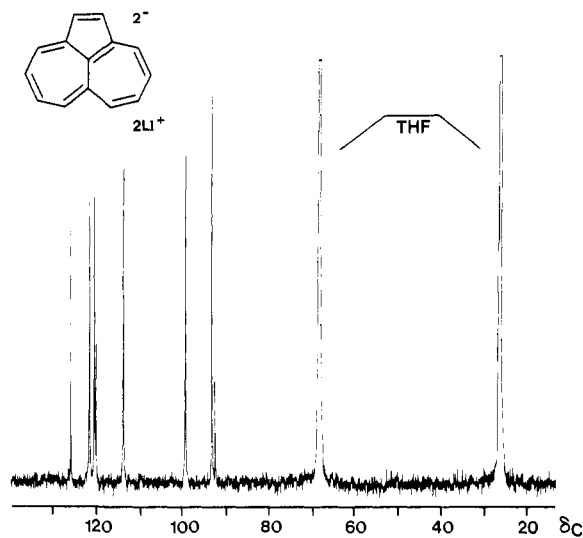
Figure 4. ^{13}C NMR spectrum (75 MHz, −60 °C) of $12^{2-}/2Li^+$ in THF/NH$_3$.

pairs.[4,5] In an alternative interpretation one might expect the (smaller) lithium counterion (with greater polarizing ability) to cause a localization of the π charge at certain positions[10] and, thus, increase the kinetic basicity of the dianion.

Considering the phenanthrene case it is clear that both the dianion 14^{2-} and the resulting monoanion 14-H$^-$ suffer from ready protonation by the ammonia (note that the A_μ value can also be determined for the transformation of 14-H$^-$ into the dihydrophenanthrene $16 = 14$-H$_2$). The dihydro derivative 14-H$_2$ incorporates a diphenyl moiety which again is susceptible to a reduction/protonation sequence. These findings provide sufficient explanation for both the spectroscopic and preparative (see below) results. 14-H$_3^-$ is observed as sole reduction product in solution even when applying only 2 equiv of lithium. Accordingly, under the prevailing ion-pair structures, the phenanthrene and dihydrophenanthrene must undergo reduction with similar ease.[8]

3.3. Addition of Electrophiles. Facing the chemical significance of the above spectroscopic findings, one will now consider the addition of electrophiles (alkylating agents) to the carbanionic intermediates. The two basic points at issue are: (i) which species actually accepts the electrophile and (ii) what is the site of attack of the electrophile. Is the reaction regioselective?

Considering, first, the regioselectivity of the quenching reaction, one is aware that the kinetically controlled addition of an electrophile should proceed at the position of the highest π-charge density.[33,41,42] It is well known from ^{13}C NMR studies of hydrocarbon monoanions and dianions that the individual carbon resonances depend critically upon the local π-charge densities and that one obtains a reliable picture of the π-charge distribution.[10,18,23] The dianions $1^{2-} - 9^{2-}$ have been prepared by us under strictly aprotic conditions in ethereal solvents and characterized spectroscopically. The important finding made for the lithium reduction of $1 - 9$ in liquid ammonia is that the protonation by the ammonia takes place at the carbon with the highest π-charge density in the dianion. The attack of the proton upon the dianion can thus be predicted from the ^{13}C chemical shifts of the dianionic intermediates. The next question is whether this argument will also hold for the use of an alkylating agent as an electrophile. A discussion of compounds from group 2 (dianions persistent in liquid ammonia) is straightforward. The alkylation of the cyclooctatetraene dianion 10^{2-} to yield dialkyl cyclooctatriene species has been performed in various solvents including liquid ammonia.[43,44] There are no significant solvent effects upon the prep-

arative results. The other substrates of group 2 differ from the cyclooctatetraene case by adopting a nonuniform π-charge distribution. The example of the tricyclic π system 12 which has been extensively studied by us is revealing. The central carbon C-10b is deduced from the ^{13}C NMR chemical shifts measured in both THF and THF/NH$_3$ solution to accept the highest π-charge density (see Figure 4). Indeed, the methylation proceeds at C-10b to yield the monoanion $25 = 12$-Me$^-$.[33] The addition of the second electrophile is, now, controlled by the π-charge distribution in the monoanion. Thus, the reaction of 12^{2-} ($2Li^+$, THF) with an excess of dimethyl sulfate affords a mixture of the dimethyl derivatives 26, 27, and 28. Moreover, the intermediate monoanion $25 = 12$-Me$^-$ is expected to react more slowly with the electrophile than the dianion. Consequently, the quenching of 12^{2-} may afford diadducts incorporating different electrophiles. The reaction of 12^{2-} ($2Li^+$, NH$_3$) with dimethylsulfate gives rise to compound 29 whereby the primary methylation product 12-Me$^-$ is protonated by the ammonium salt produced from ammonia and dimethyl sulfate. All compounds $26 - 29$ have in common the fact that the first electrophile has entered at the quaternary position C-10b in 12^{2-} which is the carbon center with the highest local π-charge density. It is important to note, however, that there is no difference of the regioselectivity if the reductive transformation is conducted in liquid ammonia or in ethereal solvents.

Having successfully correlated spectroscopic and preparative results for substrates from groups 1 and 2, we now consider the nature of the carbanionic intermediate involved in the alkylation of group 1 compounds.

One readily realizes that the dialkyl adducts obtained from anthracene do not necessarily imply the intermediacy of the dianion, but can be formed via alkylation of the monoanion 1-H$^-$, and subsequent reaction with the amide ion (produced upon protonation of 1^{2-} by ammonia) to yield another monoanion which is again alkylated. In dealing with these mechanistic alternatives, the quenching procedure turns out to be a most important factor.[5] A reverse quenching experiment (where the electrophile is added to the ammonia solution of the carbanionic intermediate) produces mostly monoalkyl derivatives. This finding indicates the dominant role of 1-H$^-$ as intermediate. Upon inverse quenching over varying periods of time, there is little variation in the amount of dialkylation, an outcome which does not support the intermediacy of the dianion. It should be noted within the present context that we have performed a reverse quenching experiment (1-H$^-$, −78 °C, CH$_3$Br) within the NMR tube. The relative amount of the mono- and diadducts (18, 21) is ca 1:1 which is the same as that obtained in preparative experiments.[4] The initially observed ratio of 18 and 21 is not affected upon standing which means that the deprotonation and subsequent methylation of 18 have proceeded rapidly.

The failure to spectroscopically detect the dianions $1^{2-} - 9^{2-}$ in liquid ammonia does not rigorously exclude their role as the main intermediates during the reductive alkylation. It is reasonable to assume that A^{2-} reacts with the electrophile much faster than A-H$^-$. Thus, although equilibrium 1 lies very much in favor of A-H$^-$ for group 1 substrates, the equilibrium may act to provide a stationary concentration of the much more reactive dianion A^{2-}. As a consequence the alkylation could well proceed via the dianion.

When deciding on the intermediacy of the dianion or monoanion one could invoke the observed regioselectivity of the reductive alkylation. Both species A^{2-} and A-H$^-$ may differ in their π-charge distribution and may, therefore, force the kinetically controlled attack of the electrophile into different positions. Thereby, anthracene is not a favorable case since both the dianion 1^{2-} and the monoanion 1-H$^-$ are predicted to accept the incoming alkyl group in the central position C-9 (C-10). In the case of pyrene, however, the regioselectivity of the alkylation is expected to be different depending on whether the electrophile attacks 5^{2-} or 5-H$^-$.[9,24]

The reductive alkylation of pyrene in liquid ammonia has been reported to yield the adduct 30.[25,26] The introduction of the

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electrophile E at position 5 must be taken as evidence for the intermediacy of the monoanion 5-H⁻ since the dianion would have been attacked at carbon C-1. This argument is supported by the protonation of 5^{2-} to yield 5-H⁻ and by the quenching of $5^{2-}/2Li^+$ (THF) with 1 equiv of methyl iodide (see section 2). As expected, the product obtained after workup and dehydrogenation is 1-methylpyrene (**22**).

The pyrene reduction, thus, leads to several important conclusions typical for group 1 compounds: the participation of the monoanionic intermediates can be deduced from the observed regioselectivity of the quenching reaction; working in ethereal solvents or liquid ammonia may afford different results since the former experiment involves the dianion A^{2-} and the latter the monoanion A-H⁻ as intermediates; the pyrene dianion is attacked by methyl iodide in the same position as by the proton—the soft and hard electrophiles thus provide the same product; the regioselectivity of the quenching reaction can be predicted from the π-charge distribution in the anion, information that can be determined from ¹³C chemical shift data. The latter approach, clearly, requires a reliable identification of the carbanionic intermediate. The formation of **30** upon reductive alkylation of pyrene in liquid ammonia has been explained by invoking a distorted dianion structure with the highest π-charge density at C-5.[25] Our results indicate that the species involved is the monoanion 5-H⁻ rather than a distorted dianion.

Considering the ammonia reduction of phenanthrene, we recall that the only species detected by NMR spectroscopy in solution is $14\text{-}H_3^-$. This is true even if only 2 equiv of lithium is applied. One must be aware that the sample contains some solid material. Thus, it cannot be excluded that for solubility reasons and/or due to some rapid intermolecular electron exchange other species such as **14** (14⁻·) or 14-H₂ ($14\text{-}H_2^-$·) (see section 2) escape NMR spectroscopic detection. Nevertheless, phenanthrene is well known from preparative reduction experiments in liquid ammonia to undergo overreduction. This tendency can only partly be overcompensated by the careful adjustment of the lithium/substrate ratio. Toward the synthesis of 9,10-dihydro derivatives, colloidal iron has been applied since it consumes surplus lithium.

4. Outlook

The emphasis within the above discussion of the reductive alkylation in liquid ammonia has been put on the correlation of spectroscopic and preparative results. A typical conclusion is that if one wants to alkylate pyrene in the 4 or 5 positions (e.g., with a bifunctional reagent), one has to work in liquid ammonia while the reductive preparation of a 1-alkyl derivative should only be feasible in ethereal solvents. Along with these arguments one should be able from spectroscopic evidence to conceive of novel alkylation reactions with carefully controlled regioselectivity. Toward this end we have spectroscopically followed the reduction

of acenaphthylene under various conditions (alkali metal, temperature, solvent) and, in a complementary approach, were able to conduct alkylation (including cycloannelation with bifunctional alkylation reagents) in either the five- or six-membered rings. The results of this work will be reported separately.[45]

5. Experimental Section

Compounds **1–7, 9, 10, 13**, and **14** are commercially available. They were recrystallized twice prior to use. Compounds **8**,[46] **11**,[47] and **12**[48] were prepared according to literature procedures. The reduction techniques have been described by us elsewhere.[10,19] Lithium, sodium, and potassium were prepared as wire within thin-walled glass ampoules with a specially constructed press in vacuo. The ampoules were weighted after sealing and were broken in vacuo within the sample tube containing the adequate amounts of the compound in carefully dried, degassed THF/ NH₃ solutions. Ammonia was distilled from alkali metal. THF was distilled into the sample tube from a side arm containing the THF solution of the respective dianions.

¹H and ¹³C NMR measurements were recorded (300 MHz, 75 MHz) on a Bruker WM 300-spectrometer within tubes of 8-mm diameter. If THF-d_8 was present in the sample, the corresponding deuterium resonance was taken as lock signal. Chemical shifts were taken from the solvent signals as internal reference and converted to the Me₄Si standard by using the appropriate increments. ESR spectra were recorded on a Varian E9 spectrometer.

Quenching of $5^{2-}/2Li^+$ with Methyl Iodide. A solution of **5** (510 mg, 2.5 mmol) in 40 mL of dry absolute THF in a sealed glass ampoule was contacted at −78 °C with freshly pressed lithium wire. To the deep blue solution of the dianion (formed after ca. 12 h) was added with a syringe 150 μL (2.5 mmol) of methyl iodide in 2 mL of THF. The solution whose color changes to red was allowed to warm to room temperature, and 1 mL methanol was added. To the yellow solid obtained after workup was added 420 mg (2 mmol) of DDQ in toluene (30 mL), and the mixture was refluxed for 1.5 h. After filtration of the reaction mixture and evaporation of the solvent, the residue was extracted with *n*-hexane and the product chromatographed on silica gel (*n*-hexane). A mixture of two compounds was obtained (208 mg of **5**, 41%; 52 mg of **22**, 9.5%). The separation of pyrene and 1-methylpyrene was only achieved by gas chromatography (20% Carbowax/Chromosorb.). Compound **22** was identified by comparison with the data given in the literature.[49]

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