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New Modes of Reactivity in the Threshold of the Reduction Potential in Solution. Alkylation of Lithium PAH (Polycyclic Aromatic Hydrocarbon) Dianions by Primary Fluoroalkanes: A Reaction Pathway Complementing the Classical Birch Reductive Alkylation

Cristóbal Melero, Raquel P. Herrera, Albert Guijarro,* and Miguel Yus*[a]

Dedicated to Professor Jan-Erling Bäckvall on occasion of his 60th birthday

Abstract: Some of the most highly reduced organic species in solution, such as the dianions of PAHs (polycyclic aromatic hydrocarbons) display unexpected reactivity patterns when they react with an appropriate counterpart. As seen before in their reaction with propene and other alkenes, $PAHs^{-2}$ apparently react with fluoroalkanes in a nucleophilic fashion in spite of being generally regarded as powerful electron-transfer reagents in their reactions with haloalkanes. This methodology complements the current methodologies on reductive alkylation of polycyclic arenes by allowing access to a new set of regioisomers, the regiochemistry of which can be easily predicted by simple MO calculations.

Keywords: alkylation · fluoroalkanes · lithium · polyaromatic hydrocarbons (PAHs) · semi-empirical calculations

Introduction

The investigation of new patterns of reactivity in species that have very high-energy occupied orbitals affords exciting results, both from the fundamental point of view of reactivity,[1,2] as well as from a more practical point of view regarding synthesis.[3,4] Highly reduced polycyclic aromatic hydrocarbons (PAHs) occupy an advantageous position in this scenario, because of their rich structural diversity and the easy availability of many of them. In these anionic species, the π-extended vacant orbitals of the hydrocarbon (π-LUMOs) have been occupied by a number of extra electrons, which often come from the direct reaction with an alkaline metal. The resulting polyanionic species thus have both very high-lying and highly delocalized electrons. This eventually dictates much of their reactivity, which in many cases is reminiscent of the alkaline metal that they originated from.[5] For instance, the lithium salts of anionic naphthalene or biphenyls are mostly regarded as ET (electron-transfer) reagents and have seen much success in preparative organic chemistry as lithiating reagents.[5] In general, arene radical anions and dianions react with conventional electron acceptors such as alkyl halides (X = Cl, Br, or I) or carbonyl compounds through an ET process to give rise to radicals, which evolve towards more or less complex mixtures of products. These reaction crudes can consist of: 1) mainly the carbanionic reagent, that is, the organolithium reagent for M = Li (e.g., with primary chloroalkanes and haloarenes); 2) mixtures of radical-coupling products and organolithium reagent (e.g., with secondary and tertiary alkyl chlorides and alkyl bromides and iodides); or 3) mainly coupling products (e.g., from the pinacol synthesis and the Wurtz coupling, particularly with allylic and benzylic halides, alkyl iodides as well as other organic halides). A mechanistic study on competitive kinetics[6] reported recently, suggests that the naphthalene dianion ($Li_2C_{10}H_8$) reacts through a nucleophilic substitution reaction pathway with primary alkyl fluorides.[1] Indeed, highly reduced anionic-PAHs offer a valuable opportunity to explore the dichotomy between nucleophilic substitution (S_N2) and electron transfer (ET)

[a] C. Melero, Dr. R. P. Herrera, Dr. A. Guijarro, Prof. Dr. M. Yus
Instituto de Síntesis Orgánica and
Departamento de Química Orgánica
Facultad de Ciencias, Universidad de Alicante
Apdo. 99, 03080-Alicante (Spain)
Fax: (+34) 965-90-35-49
E-mail: aguijarro@ua.es
yus@ua.es

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reactivity. The naphthalene dianion result was extended and applied to a variety of PAHs, which after reduction to the dianion by using $Li_{(s)}$ in tetrahydropyran (THP) afforded octyldihydroarenes by reaction with *n*-octyl fluoride.[3] Interestingly, we found that this type of reactivity appeared to be distinctive of PAH dianions (at least for those of the small-to-medium size that were tested), the corresponding radical anions remained unreactive under identical conditions, except for a few PAHs of very high reduction potential, and therefore enhanced ET ability. This distinctive behavior of the radical anions and dianions of PAHs has also been manifested before in other reagents, including low-strained alicyclic ethers,[2] and especially in terminal alkenes,[4] which display a distinctly different reactivity with respect to these two kind of highly reduced reagents. From our preliminary studies, the electrophilic role of primary alkyl fluorides is also remarkable. In general, conventional nucleophiles display low reactivity in their reactions with fluororalkanes.[7] This is in part due to the high LUMO energies of fluororalkanes that prevent easy access to these orbitals by making certain transition states such as the S_N2 difficult. This seems to be, however, an advantage for the fluororalkanes when they react with PAHs dianions. The reactivity pattern that is displayed suggests a reaction pathway that is increasingly dominated by the overlap of orbitals (i.e., a nucleophilic substitution); this corresponds to a decrease in the ET character of the interaction. In the present article, we expanded the number of PAH dianions that are suitable for alkylation with primary fluororalkanes. Both alternant and non-alternant PAHs are considered: naphthalene, biphenyl, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, tetraphene, *o*-terphenyl, *p*-terphenyl, acenaphthylene, and 1,1′-binaphthyl. In addition, we provide further data that supports the hypothesis of a S_N mechanism for the alkylation process. Finally, the factors that control the regioselectivity of the process are discussed in light of simple MO calculations.

Abstract in Spanish: *Algunas de las especies orgánicas más reducidas en disolución, como los dianiones de HAP (hidrocarburo aromático policíclico), muestran patrones de reactividad imprevistos cuando reaccionan con el sustrato apropiado. Tal y como se vio anteriormente frente a propeno y otros alquenos, los HAP^{-2} reaccionan aparentemente como nucleófilos con fluoruros de alquilo, a pesar de ser considerados generalmente como poderosos agentes de transferencia electrónica frente a halogenuros de alquilo. Esta metodología complementa las actuales metodologías de alquilación reductora de arenos policíclicos, permitiendo el acceso a un nuevo grupo de regioisómeros, cuya regioquímica puede ser fácilmente predicha por medio de simples cálculos de orbitales moleculares.*

Results and Discussion

Naphthalene (**1**) has the most negative second reduction potential among all the PAHs except for benzene itself (see below).[8] We have observed previously that in the presence of an excess of $Li_{(s)}$, naphthalene is doubly reduced in THF or THP to its dianion, Li_2-**1**.[9,2] Based on the reduction potential criteria,[8] the remaining PAHs (**1**–**12**) are also expected to be reduced to the corresponding dianions (Li_2-**1**–Li_2-**12**) under the same conditions, according to Equation (1). This is certainly so for those PAHs for which spectroscopic evidence of the corresponding dianions is available. However, the actual extent to which these reductions take place has not been studied. It might vary for different PAHs and should be understood in the context of different heterogeneous equilibria depending on a number of variables [Eq. (1)]. These include the second reduction potential of the PAH (E_2^o), the ion-pairing equilibria of the dissolved species, the complexation ability of the medium towards the different species in solution, the concentration, and the temperature, all of which can be further complicated by the appearance of new crystalline phases. Disproportionation equilibra are profoundly affected by the medium (e.g., by small changes in the solvent),[10] and the complex kinetics inherent to heterogeneous ET process on metal surfaces and the intrinsic high reactivity of the involved species makes the determination of the actual composition of the reaction media difficult. In addition to spectroscopic claims, we have included electrochemical data from the literature on the generation of PAH dianions so that the arguments that concern the generation and stability of some of these highly reduced species do not rest exclusively on spectroscopic grounds. When available, references for the crystal structure are given. Further, the experimental regioselectivity can be reproduced by means of facile semiempirical calculations on the dianion (Figure 1; see the Supporting Information for details). In all cases but one (i.e., the biphenyl dianion) the alkylation takes place at the carbon atom of the PAH^{-2} that supports the highest coefficient in the HOMO of the dianion. Apparently, reactions at other positions that support lower HOMO coefficients are not competitive. The corresponding calculated Mulliken charges, which were obtained from the Mulliken population analysis, are also given. For the purpose of pinpointing the reactive sites, we have not seen any qualitative difference in the results that were obtained when performing the density functional theory (DFT) calculations on the same dianionic substrates, therefore the simplest method is reported (see biphenyl dianion for an example; see also the Supporting Information). Different types of geometries (planar and nonplanar) have been tested for each molecule, but only those results that correspond to the lowest true minima that were found in the potential-energy hypersurface, and were confirmed by the corresponding vibrational analysis have been reported. Besides 1,1′-binaphtyl and *o*-terphenyl dianions (C_2), all PAHs adopt a flat conformation in the ground state as dianions, including the nonplanar conformationally dependent polyary-

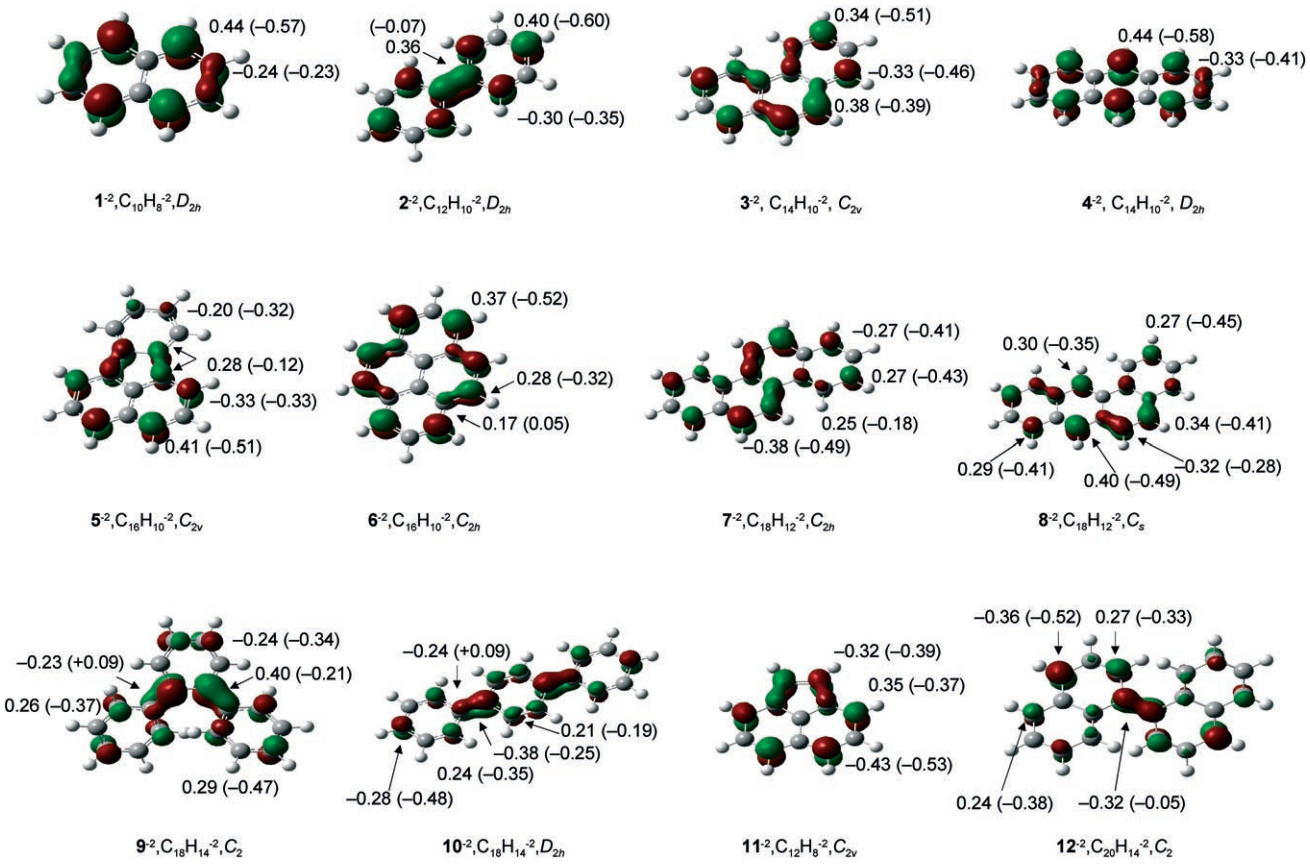


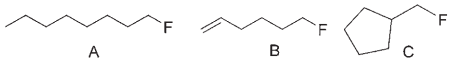
Figure 1. PM3 HOMO coefficients and Mulliken charges (in parenthesis) as well as the observed molecular point group of symmetry for the PAH dianions $\mathbf{1}^{-2}$–$\mathbf{12}^{-2}$.

lenes such as biphenyl and *p*-terphenyl (see also phenanthrene dianion for more specifications).

$$\underset{\textbf{1 to 12}}{PAH_{(THP)}} \overset{Li_{(s)}}{\rightleftharpoons} \underset{\text{Li-1 to Li-12}}{[Li^{+}\,PAH^{-\bullet}]_{(THP)}} \overset{Li_{(s)}}{\rightleftharpoons} \underset{\text{Li}_2\text{-1 to Li}_2\text{-12}}{[2Li^{+\bullet}\,PAH^{-2}]_{(THP)}}$$

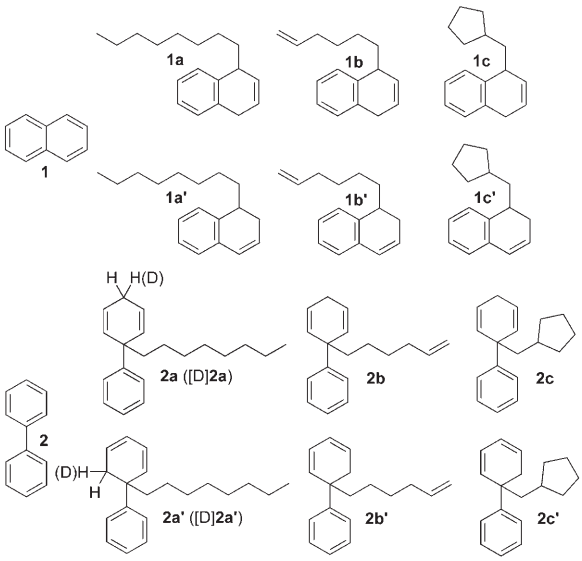
Naphthalene dianion: The naphthalene dianion ($\mathbf{1}^{-2}$, $C_{10}H_8^{-2}$) is an extremely reduced organic species. In fact, at present it is over the limit of the reduction potential that is workable in solution by electrochemical means. By cyclic voltammetry, naphthalene displayed a first reduction wave ($E_1^{o} = -2.53$ V vs. Ag/AgCl) in DMA/TBAB (DMA = dimethylamine, TBAB = tetrabutylammonium bromide) that corresponds to the reduction to the radical anion ($\mathbf{1}^{\bullet -1}$, $C_{10}H_8^{-}$). In contrast to the rest of arenes that were studied, no second reduction wave could be measured for naphthalene before solvent discharge, in spite of the careful choice of the electrolytic media to shift the cathodic limits to very negative electrochemical potentials.[8] However, as a lithium salt, the naphthalene dianion (Li_2-**1**, $Li_2C_{10}H_8$) is relatively stable in THP at room temperature and in THF at low temperatures, and can be prepared by direct exposure of the hydrocarbon to $Li_{(s)}$ in these solvents.[2,9] Compound **1**-Li_2 was first prepared by double deprotonation of 1,4-dihydronaphthalene with BuLi, crystallized (coordinated with *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethanediamine (TMEDA)) and its structure was determined by X-ray diffraction.[11] The ^{1}H and ^{13}C NMR spectra of Li_2-**1** have also been reported.[12] Its reactivity is mainly unexplored, probably due to its prevailing ET reactivity, although unique reactivity profiles that are different from ET are beginning to be identified. We found recently that Li_2-**1** reacts nucleophilically with terminal alkenes to afford carbolithiation products.[4] In its reaction with primary fluoroalkanes, it gives high yields of alkylation products in a regioselective way (Table 1, entries 1–3; Scheme 1). The reaction of Li_2-**1** with 1-fluorooctane afforded a mixture of 1-octyl-1,4- and 1-octyl-1,2-dihydronaphthalene in 84% overall yield (**1a** and **1a′**, respectively; **1a**/**1a′** = 1.4:1). This reaction is notorious for several reasons. It cleanly affords alkylation products in high yields (**1a**+**1a′**: 84%), in the absence of any detectable amount of Wurtz coupling products (0% of *n*-hexadecane by GLC), while the analogous reaction with *n*-chlorooctane, which proceeds through a well-established ET mechanism,[1,2,13] gives high yields of *n*-octane after hydrolysis (89% of *n*-octane). Although the alkylation reaction of Li_2-**1** with primary fluoroalkanes is believed to proceed through an S_N2 transition state, the potential role of radicals in the reaction could not be fully discarded. As a first approach to study the radical reaction pathway, the behavior of 5-hexenyl radical probes

Table 1. Reactions of compounds **1**–**12** with 1-fluorooctane (A), 6-fluorohex-1-ene (B), and fluoromethylcyclopentane (C). For the structures of the starting materials and the products see the schemes in the text.



	PHA	RCH_2F	Products (yields [%])[a]			
1	**1**	A	**1a** (49)	**1a′** (35)		
			1a (77)[b]	**1a′** (0)[b]		
2	**1**	B	**1b** (42)	**1b′** (34)	**1c** (0)	**1c′** (0)
3	**1**	C	**1b** (0)	**1b′** (0)	**1c** (35)	**1c′** (30)
4	**2**	A	**2a** (48)	**2a′** (33)		
			([D]**2a**, 47)[c]	([D]**2a′**, 31)[c]		
			2a (87)[b]	**2a′** (1.6)[b]		
5	**2**	B	**2b** (48)	**2b′** (32)	**2c** (0)	**2c′** (0)[b]
			2b (70)[b]	**2b′** (0)[b]	**2c** (0)	**2c′** (0)[b]
6	**2**	C	**2b** (0)[b]	**2b′** (0)[b]	**2c** (72)[b]	**2c′** (0)[b]
7	**3**	A	**3a** (22)[d]	**3b** (45)[d]		
			3a (78)[e]	**3b** (0)[e]		
8	**4**	A	**4a** (36)[f]	**4b** (57)[f]		
			4a (75)[g]	**4b** (0)[g]		
9	**5**	A	**5a** (53)			
10	**6**	A	H_2-**6a**[h]	**6a** (72)		
11	**6**	B	H_2-**6b**[h]	**6b** (63)	H_2-**6c** (0)	**6c** (0)
12	**6**	C	H_2-**6b** (0)	**6b** (0)	H_2-**6c**[h]	**6c** (46)
13	**7**	A	**7a** (73)			
14	**7**	B	**7b** (73)	**7c** (0)		
15	**7**	C	**7b** (0)	**7c** (54)		
16	**8**	A	**8a** (54)	**8b** (22)[i]		
17	**9**	A	**9a** (76)			
18	**10**	A	*cis*-**10a**	*trans*-**10a** (84)[j]	**10b**	
19	**11**	A	**11a** (63)			
20	**12**	A	**12a** (58)			

[a] Yields were determined by quantitative GLC and by using decane/dodecane as an internal standard. [b] CH_3CN was used instead of H_2O for hydrolysis. [c] 4-Deuterio-1-octyl-1,4-dihydrobiphenyl ([D]**2a**, 47%, 53:47 dr, >98.5% deuterium incorporation) and 2-deuterio-1-octyl-1,2-dihydrobiphenyl ([D]**2a′**, 31%, 62:38 dr, >99.8% deuterium incorporation) were obtained by using D_2O for deuterolysis (diastereomeric ratio by ^1H and ^{13}C NMR spectroscopy, deuterium incorporation by MS and ^1H NMR spectroscopy, the natural isotopic distribution was corrected). [d] Phenanthrene/*n*-fluorooctane = 1:1.2. Yields were determined by quantitative GLC by using a calibration curve and Ph_2CH_2 as internal standard. [e] Ratio phenathrene/*n*-fluorooctane = 5:1, in THP. Yields by quantitative GLC as in footnote [d]. [f] Anthracene/*n*-fluorooctane = 1:1.5. Yields were determined by quantitative GLC by using a calibration curve and diphenylformamide as internal standard. [g] Anthracene/*n*-fluorooctane = 5:1. Yields were determined by quantitative GLC as in footnote [f]. [h] Identified by ^1H NMR spectroscopy in the reaction crude, along with a second regioisomer, presumably the 1-alkyl-1,5-dihydropyrene (H_2-**6a′–c′**), but isolated as the corresponding 1-alkylpyrene. [i] Obtained after the DDQ rearomatization of an inseparable mixture of 7-octyldihydrobenzo[*a*]anthracenes. [j] *cis*-**10a**/*trans*-**10a**/**10b** 1:0.44:0.48.



Scheme 1.

was studied. 6-Fluorohex-1-ene was treated with an excess of Li_2-**1** in THP at 0°C ($C_6H_{11}F/Li_2$-**1** = 1:10, formal [Li_2-**1**] = 0.2 M). After the reaction was complete, hydrolysis afforded the non-rearranged products **1b** and **1b′** in 76% overall yield, but the rearranged (cyclized) products **1c** and **1c′** could not be detected by GLC (Table 1, entry 2, Scheme 1). To confirm this finding beyond doubt, **1c** and **1c′** were synthesized directly from fluoromethylcyclopentane by reaction with Li_2-**1** in 65% overall yield (Table 1, entry 3; Scheme 1), and were used as control substances in GLC analyses. The reaction of Li_2-**1** with 6-fluorohex-1-ene was also carried out under different dilution conditions (formal [Li_2-**1**] = 0.1, 0.05, and 0.01 M). In all cases, rearranged products (**1c** and **1c′**), if any, were below the detection limits.

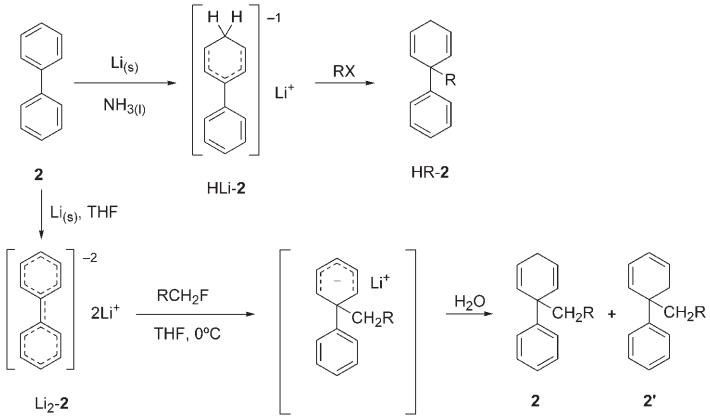
As a precedent, the reaction of 6-fluorohex-1-ene with the radical anion sodium naphthalene ($NaC_{10}H_8$) in 1,2-dimethoxyethane (DME) at 25°C is documented in the literature.[14] In those studies, only low-boiling products were fully identified, with emphasis given to the 1-hexene/methylcyclopentane ratios, even though the combined yield was only 48% (±10%).[14a] Those studies were consistent with ET as the key step in the formation of the light hydrocarbons (C_6H_{12}), although major products of the type **1b**, **1b′**, **1c**, and **1c′** were overlooked.

For secondary and tertiary fluoroalkanes (i.e., 2-fluorooctane and 2-methyl-2-fluoroheptane), the reaction with Li_2-**1** is interpreted in terms of an ET process that is followed by a competition between radical coupling with the radical anion, and further reduction with either the radical anion or the dianion. The result is a mixture of coupling and reduction products that consist of isomeric octyldihydronaphthalenes, plus the corresponding octanes (*n*-octane or isooctane).[1]

Biphenyl dianion: Biphenyl (**2**, $C_{12}H_{10}$) has the highest first reduction potential ($E_1^o = -2.68$ V in DMA/TBAB vs. Ag/AgCl) among the PAHs that are considered here, and in general among all the PAHs, except for benzene. Reduction of biphenyl affords the corresponding radical anion (**2**$^{\bullet -1}$, $C_{12}H_{10}^{-}$), which can be further reduced electrochemically to biphenyl dianion (**2**$^{-2}$, $C_{12}H_{10}^{-2}$). The second reduction potential lies at very negative cathodic potential ($E_2^o = -3.18$ V vs. Ag/AgCl), although, in contrast to naphthalene, it is still within the measurable range.[8] The reason for this apparent misplacement of the second reduction potential values (E_2^o) could be interpreted in terms of π-aromaticity. Indeed, at-

tainment of Hückel aromaticity in $\mathbf{2}^{-2}$ (14 π e^-) could favor the second electron uptake, the opposite being true for naphthalene dianion $\mathbf{1}^{-2}$, which attains to a certain degree an antiaromatic character with the second reduction. Descriptive work of the biphenyl dianion includes the ^{1}H and ^{13}C NMR spectra of Li_2-**2** ($Li_2C_{12}H_{10}$) at −80 °C in [D_8]THF,[15] and the UV and IR spectra of different alkali metal salts of biphenyl in sublimed layers.[16] In addition to that, Li_2-**2** has been suggested to be a component of the Li–biphenyl solutions of 2:1 stoichiometry in THF used for reductive cleavage applications akin to $Li_{(s)}$.[17]

The reaction of a solution of Li_2-**2** in THF at 0 °C (see Experimental Section for details) with *n*-fluorooctane affords a mixture of two regioisomers **2a** and **2a′** after hydrolysis with water, in 81 % overall yield (Scheme 2, Table 1, entry 4; Scheme 1). We have developed a different hydrolysis protocol that avoids mixtures of products in the hydrolysis step (e.g., **2a**+**2a′**) and simplifies the isolation of products. The best results were obtained by using acetonitrile (CH_3CN, $pK_a \approx 25$),[18] which is a weaker proton source. Selective protonation of the delocalized anionic intermediate with acetonitrile affords the 1,4-dihydro derivatives as major products. We can also take advantage of CH_3CN in the protonation step of different alkylated PAHs (Table 1, footnote [b]). Deuterolysis with D_2O affords [D]**2a** and [D]**2a′** in 78 % overall yield, with excellent deuterium incorporation (see Table 1, footnote [c]); this supports the presence of a living dianionic species in the reaction medium that is alkylated by *n*-fluorooctane, and is in agreement with Scheme 2.



Scheme 2. Reductive alkylation of biphenyl under Birch conditions and alkylation of dilithium biphenyl (Li_2-**2**, $Li_2C_{12}H_{10}$) with *n*-fluorooctane.

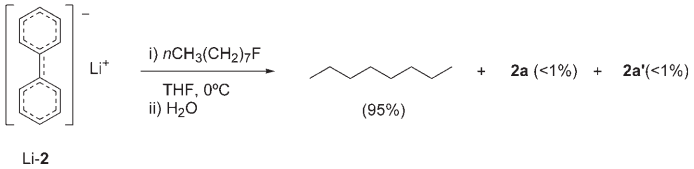
As in the case of the naphthalene dianion, a potential radicalary reaction pathway was also examined by using 5-hexenyl radical probes. The results are summarized in Table 1, entries 5 and 6 (Scheme 1). When 6-fluorohex-1-ene was treated with an equivalent of Li_2-**2** in THF at 0 °C (formal [Li_2-**2**] = 0.2 M), the reaction crude afforded the non-rearranged products **2b** and **2b′** in 80 % overall yield. Again, the rearranged (cyclized) products **2c** and **2c′** could not be detected by GLC. This was confirmed by direct synthesis of **2c** and **2c′** from fluoromethylcyclopentane by reaction with Li_2-**2** (72 % overall yield), and by using the pure product as a control in GLC analyses.

Apparently, the regioselectivity that is displayed by the biphenyl dianion (i.e., alkylation at the C_1 position as shown in Table 1) is not well predicted by means of MO calculations (Figure 1). PM3 HOMO coefficients predicts that for $\mathbf{2}^{-2}$ the C_4 (or *para* position) should be the reacting site in the isolated dianion instead of the C_1 (*ipso* position), which supports a somewhat lower HOMO coefficient: C_1 0.36 (−0.07); C_4 0.40 (−0.60) (Mulliken charges in parenthesis). We have also carried out DFT calculations,[19] by using the B3LYP exchange–correlation functional,[20] on $\mathbf{2}^{-2}$ with similar results. The geometry of the isolated dianion was optimized in the gas phase by using the 6–311G(d,p) basis set.[21] A stationary point of C_{2h} symmetry was found (and confirmed by vibrational analysis), which has the following atomic gross populations for the HOMO and Mulliken charges (in parenthesis): C_1 0.12 (−0.05); C_4 0.17 (−0.24). As in the previous calculations, this indicates that the attack is expected to take place at the C_4 position of $\mathbf{2}^{-2}$, which is the carbon atom that supports the highest contribution to the HOMO of the dianion. The reason for this misbehavior is not clear yet. We have observed attack at the C_4 position in other types of reactions that involve $\mathbf{2}^{-2}$, which is in agreement with the MO calculations.[4] On the other hand, biphenyl is the only PAH for which this apparent misconduct is observed, the remaining eleven PAHs that were used in this study are all well behaved in regard to the calculated and the observed reacting site.

Reductive alkylation of biphenyl with $Li_{(s)}/NH_{3(l)}$ followed by treatment with bromomethane affords 1-methyl-1,4-dihydrobiphenyl (**2**-HR, R = Me, Scheme 2).[22] Protonation of $\mathbf{2}^{-2}$ by ammonia is proposed as an intermediate step that leads to HLi-**2** in this synthesis.

The analogous reaction that was carried out by using the radical anion of biphenyl (Li-**2˙**, $LiC_{12}H_{10}$) has a very different outcome. By using a substoichiometric amount of $Li_{(s)}$ with respect to biphenyl in THF at 0 °C, *n*-fluorooctane is mainly reduced to *n*-octane (95 %); only trace amounts of **2a** and **2a′** are observed in this reaction by quantitative GLC (Scheme 3). This is a recurrent behavior that is observed for many of the PAH dianions investigated here, and it illustrates the clear differences in reactivity between radical anions and dianions of PAHs.

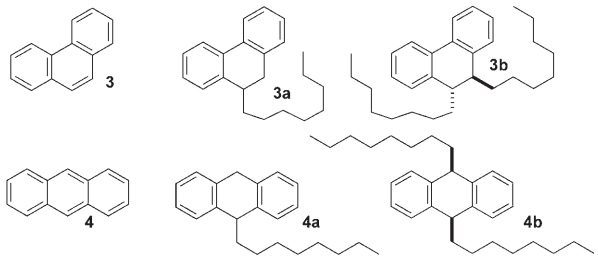
Phenanthrene dianion: Phenanthrene (**3**, $C_{14}H_{10}$) has the first and second reduction potential at a substantially negative cathodic potential ($E^o_1 = -2.49$ V, $E^o_2 = -3.13$ V in DMA/



Scheme 3. Reaction of lithium biphenyl ($LiC_{12}H_{10}$) with *n*-fluorooctane.

TBAB vs. Ag/AgCl);[8] it ranks third among the non-substituted PAHs. As a lithium salt, the phenanthrene dianion ($Li_2C_{14}H_{10}$, Li_2-**3**) can be prepared by direct exposure of phenanthrene to $Li_{(s)}$.Compound Li_2-**3**,[23] has been studied at −70 °C in THF by NMR spectroscopy.[24] At room temperature, the NMR spectra were not resolved, which is most likely due to a thermally accessible triplet state of the species. The results were interpreted to mean that $\mathbf{3}^{-2}$ has a certain degree of intrinsic structural twisting, which prevents its 16 π-electron cloud from developing an excessive antiaromatic character.[25] Although PM3 and other semiempirical calculations (MINDO/3, MNDO, AM1) afford a planar geometry for $\mathbf{3}^{-2}$ ($C_{14}H_{10}{}^{-2}$, C_{2v}), the implementation of an extended basis set (3–21G to 6–311G**) to ab initio methods affords a different non-planar geometry for $\mathbf{3}^{-2}$ (C_2), which might originate from the system's driving force to reduce antiaromaticity.[26]

The PM3 HOMO coefficients of $\mathbf{3}^{-2}$ predict that C_9 should be the reacting site in the isolated dianion (Figure 1). It is worth noting that the alkylation takes place at the carbon that bears the largest HOMO coefficient rather than at the site of the largest calculated density of charge (C_3). This indicates that the transition state of the alkylation step is mainly driven by the overlap of orbitals rather than by Coulombic interactions, in spite of the charged nature of the dianions and the polarization of the C–F bond. The reaction of Li_2-**3** with *n*-fluorooctane in THP at 0 °C affords **3a** and **3b** in 67 % overall yield when the reagents are present in stoichiometric amounts (Table 1, entry 7, footnote [d]; Scheme 4). The double alkylation that affords **3b** is a com-



Scheme 4.

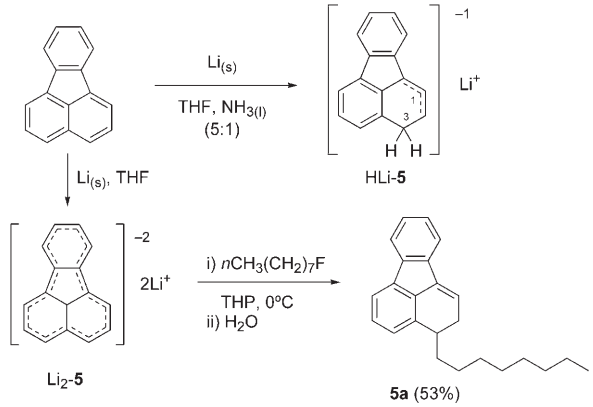
plication that can be minimized by employing an excess of Li_2-**3** with respect to the *n*-fluorooctane. By using a 5:1 excess (Table 1, entry 7, footnote [e]), **3a** is obtained in 78 % yield in the absence of the dialkylated product. Assignment of the *trans* stereochemistry of the dialkylated product **3b** was done on the basis that the *trans* geometry is obtained by alkylation of the 9-alkyl-9,10-dihydrophenanthen-10-yl lithium, and it was confirmed by comparison of the NMR chemical shifts with the *cis* and *trans*-9,10-diethyl-9,10-dihydrophenanthrene.[27] The reaction of the radical anion of phenanthrene (Li-**3**$^{\bullet}$, $LiC_{14}H_{10}$) has a very different outcome. Reaction of Li-**3**$^{\bullet}$ with *n*-fluorooctane in THP at 0 °C affords only minor amounts of alkylation products (**3a** <1 %, **3b** 8 %); *n*-octane is the major reaction product.

Anthracene dianion: Anthracene (**4**, $C_{14}H_{10}$, $E_1^o = -2.04$ V, $E_2^o = -2.64$ V in DMA/TBAB vs. Ag/AgCl)[8] is reduced much more easily than its isomer phenanthrene. The lithium salt of the anthracene dianion ($Li_2C_{14}H_{10}$, Li_2-**4**) can be prepared either by double deprotonation of the 9,10-dihydroanthracene,[28] or by direct reaction of anthracene with $Li_{(s)}$ in THF;[29] a reaction in which the radical anion ($LiC_{14}H_{10}$, Li-**4**$^{\bullet}$) is formed in an initial step as expected.[29] In contrast to Li_2-**3**, the ^{1}H NMR spectrum of Li_2-**4** is well resolved at room temperature.[25,29] The ^{7}Li NMR spectrum of Li_2-**4** has also been studied.[30]

As in the case for Li_2-**3**, the reaction of Li_2-**4** with *n*-fluorooctane in THP at 0 °C affords a separable mixture of both the mono- and the dialkylated species **4a** and **4b** in 93 % overall yield (Table 1, entry 8, footnote [f]). The **4a**/**4b** ratio was improved by performing the reaction with an excess of Li_2-**4** (Table 1, entry 8, footnote [g], Scheme 4). Assignment of the *cis* stereochemistry of the dialkylated product **4b** was done on the basis that a *cis* geometry is obtained by alkylation of the 9-alkyl-9,10-dihydroanthracen-10-yl lithium,[31] and it was confirmed by comparison of the NMR chemical shifts with the *cis* and *trans*-9,10-diethyl-9,10-dihydroanthracene.[32]

Fluoranthene dianion: Fluoranthene ($C_{16}H_{10}$, $E_1^o = -1.78$ V, $E_2^o = -2.37$ V in methylamine/tributylmethylammonium iodide (MA/TBMAI please define) vs. Ag/AgCl)[8] is reduced with $Li_{(s)}$ to the intermediate radical anion (Li-**5**$^{\bullet}$),[29] and then to the dianion (Li_2-**5**); the structure of the ion pair was determined by ^{1}H NMR spectroscopy for the sodium,[29] and lithium salts,[33] and was studied by ^{7}Li NMR spectroscopy[30] in [D_8]THF.

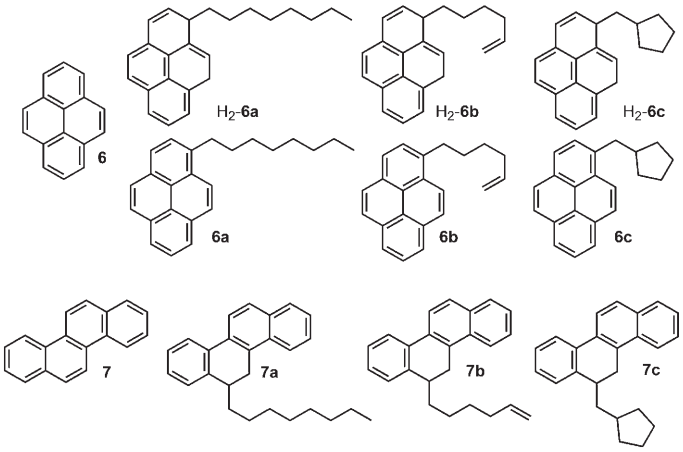
The reaction of Li_2-**5** with *n*-fluorooctane in THP at 0 °C affords 3-octyl-2,3-dihydrofluoranthene (**5a**) in 53 % yield (Scheme 5, Table 1, entry 9). Interestingly, a classical Birch approach for the reductive alkylation with $Li_{(s)}$ in THF/$NH_{3(l)}$ affords the protonated intermediate HLi-**5**, which subsequently gives a different set of alkylation products (Scheme 5). This is consistent with the quenching of the di-



Scheme 5. Reduction of fluoranthene under Birch conditions to afford HLi-**5** ($LiC_{16}H_{11}$), and alkylation of dilithium fluoranthene (Li_2-**5**, $Li_2C_{16}H_{10}$) with *n*-fluorooctane.

anion Li_2-**5** by the ammonia in the reaction media to give HLi-**5**, as determined by ^1H and ^{13}C NMR spectroscopy.[34]

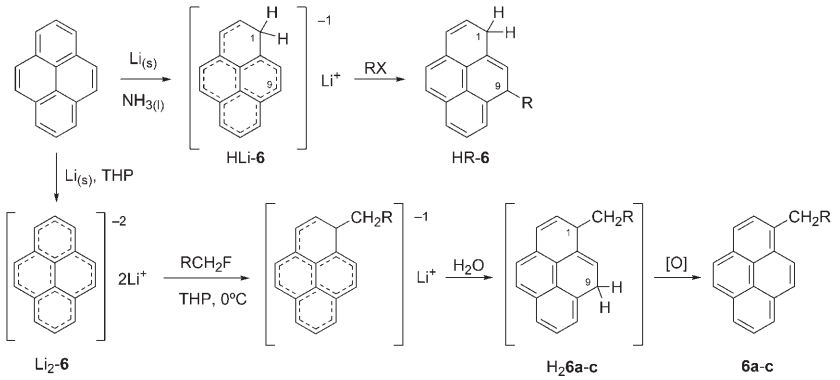
Pyrene dianion: Pyrene (**6**, $C_{16}H_{10}$, $E_1^o = -2.13$ V, $E_2^o = -2.86$ V in DMA/TBAB vs. Ag/AgCl)[8] is reduced with $Li_{(s)}$ in THF to the intermediate radical anion (Li-**6**$^{\bullet}$),[35] and with an excess of $Li_{(s)}$ to the dianion Li_2-**6** as determined by ^1H,[36] ^{13}C,[37] and ^7Li NMR spectroscopy.[30] The reaction of a solution of Li_2-**6** in THP at 0 °C with *n*-fluorooctane affords two major components after hydrolysis with water, which were tentatively assigned as 1-octyl-1,9-dihydropyrene (H_2-**6a**) and a second component, presumably the isomeric 1,5-dihydropyrene derivative (1-octyl-1,5-dihydropyrene, H_2-**6a′**-H_2) in similar amounts. 1-Alkyldihydropyrenes can appear as eight possible regioisomers, out of which the 1,2, 1,5 and 1,9-dihydropyrene isomers display only three vinylic signals. After ruling out the 1,2-dihydro isomer, which has an easily recognizable C*H*$_2$C*H* aliphatic pattern by ^1H NMR spectroscopy, the remaining structures are H_2-**6a** and H_2-**6a′**. The actual structure assignment of regioisomeric dihydropyrenes, in particular those of 1,5 and 1,9-dihydropyrene has been proposed several times,[38,39] and contested.[40] In our hands, these two isomers are unstable towards oxidative rearomatization, and no further efforts to secure their proposed structure have been undertaken. After workup and chromatographic isolation, the only product that was obtained was 1-octylpyrene (**6a**), which is derived from H_2-**6a** and H_2-**6a′** by oxidation during handling (Scheme 6 and Table 1, entry 10). As in previous cases, 5-hexenyl radical probes were tested with similar results (Table 1, entries 11 and 12). When 6-fluorohex-1-ene was treated with an equivalent of Li_2-**6** in THP at 0 °C (formal [Li_2-**6**] = 0.2 M, see Experimental Section), the reaction afforded the non-rearranged product H_2-**6b**, which was isolated as **6b** in 63% yield. The rearranged (cyclized) products H_2-**6c** and **6c**, if any, were below the detection limits by GLC. Further confirmation of that came by the direct synthesis of H_2-**6c** and **6c** from fluoromethylcyclopentane by reaction with Li_2-**6** (46% yield, Table 1, entry 12, Scheme 7).



Scheme 7.

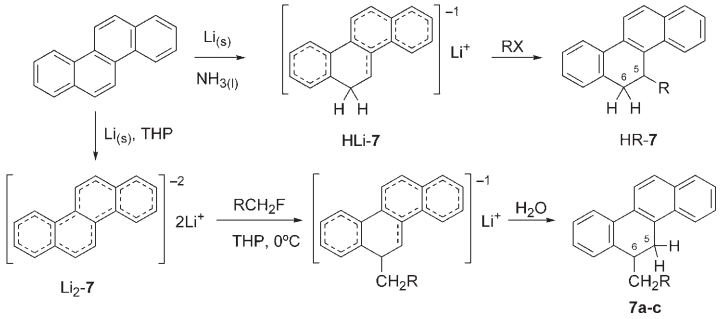
The regiochemical outcome of this alkylation is again complementary to the classical Birch reductive alkylation of pyrene,[34] which allows access to a different set of regioisomers. Pyrene reacts with Li/$NH_{3(l)}$, followed by alkylation to afford 9-alkyl-1,9-dihydropyrenes (HR-**6**) (Scheme 6).[38,41] The structure of the monoanionic intermediate HLi-**6**, which is present in solutions that contain $NH_{3(l)}$ has been established by ^1H and ^{13}C NMR spectroscopy,[41a,34] and is consistent with a monoprotonation of the pyrene dianion by $NH_{3(l)}$. Interestingly, previous attempts to directly alkylate the dianion of pyrene, which was prepared in ethereal solvents with conventional electrophiles, was met with only very limited success. Thus, the dianion of pyrene (Li_2-**6**) reacts with one equivalent of iodomethane in THF at −78 °C to afford only a 9.5% of 1-methylpyrene, along with a 41% of pyrene after hydrolysis and rearomatization with 2,3-dichloro-5,6-dicyano-*p*-quinone (DDQ).[34] This exposes the strong ET character of Li_2-**6** with respect to conventional "electrophiles", which rather than undergoing S_N reactions, behave as ET acceptors when they react with the pyrene dianion.

Chrysene dianion: Chrysene (**7**, $C_{18}H_{12}$) can be doubly reduced in a reversible way by cyclic voltammetry at −10 °C; it displays $E_{1/2(1)} = -0.61$ V, $E_{1/2(2)} = -1.12$ V as first and second half-wave reduction potentials in DMF/TMAB vs. perylene/perylene.[42] For the sake of comparison with other PAHs in this paper, a semiquantitative value can be obtained by adding the redox potential of perylene vs. Ag/AgCl to the $E_{1/2}$ values: E_1^o (perylene) = −1.70 V in DMA/TBAB vs. Ag/AgCl.[8] This is only an approximate value because of the different experimental conditions and expression of the potentials from different sources, but it is still a



Scheme 6. Reductive alkylation of pyrene under Birch conditions and alkylation of dilithium pyrene ($Li_2C_{16}H_{10}$) with primary fluoroalkanes.

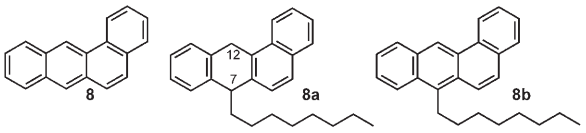
good approach for our purposes. Chemical reduction of chrysene with $Li_{(s)}$ was performed in THF (among other solvents) to yield the dianion ($C_{18}H_{12}Li_2$, Li_2-**7**), which has been identified by ^1H,[43] ^{13}C,[44] and ^7Li NMR spectroscopy.[30] The reaction of a solution of Li_2-**7** in THP at 0 °C with *n*-fluorooctane affords 6-octyl-5,6-dihydrochrysene (**7a**) after hydrolysis with water and chromatographic isolation (Schemes 7 and 8, Table 1, entry 13). When 6-fluorohex-1-ene was treated with one equivalent of Li_2-**7** in THP at 0 °C (formal [Li_2-**7**] = 0.2 M, see Experimental Section), the reaction afforded only the non-rearranged product **7b** in 73 % yield, without any detectable amount of **7c**. The rearranged product, **7c** was prepared by direct synthesis from fluoromethylcyclopentane by reaction with Li_2-**7** in 54 % yield (Table 1, entry 15).



Scheme 8. Reductive alkylation of chrysene under Birch conditions and alkylation of dilithium chrysene ($Li_2C_{18}H_{12}$) with primary fluoroalkanes.

The regiochemical outcome of the reductive alkylation of chrysene under Birch conditions is shown in Scheme 8. By analogy with the reductive alkylation of pyrene, a parallel sequence of steps can be anticipated. In the presence of $NH_{3(l)}$ the crysene dianion (Li_2-**7**), is protonated to afford HLi-**7**, which subsequently undergoes alkylation at the C_5 position to yield 5-alkyl-5,6-dihydrochrysenes (HR-**7**).[45]

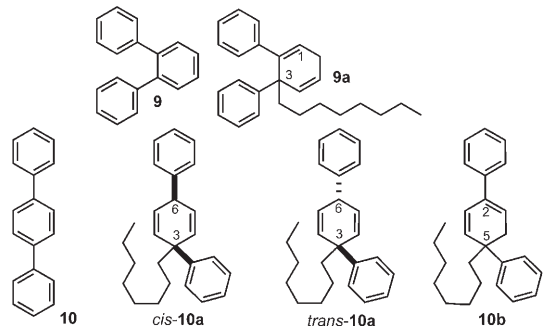
Benzo[*a*]anthracene dianion: Benzo[*a*]anthracene (or tetraphene, **8**, $C_{18}H_{12}$) can be doubly reduced in two reversible steps by cyclic voltammetry at −10 °C in DMF/TMAB; it displays $E_{1/2(1)} = -0.34$ V, $E_{1/2(2)} = -1.00$ V as first and second half-wave reduction potentials vs. perylene–perylene.[42] Again, for the sake of comparison, a semiquantitative value can be obtained by adding the redox potential of perylene vs. Ag/AgCl: E°_1 (perylene) = −1.70 V in DMA/TBAB *vs.* Ag/AgCl to the $E_{1/2}$ values.[8] Benzo[*a*]anthracene is also chemically reduced with $Li_{(s)}$ in THF to afford the corresponding dianion, Li_2-**8**, which has been characterized by ^1H,[46] and ^7Li NMR spectroscopy.[30] Dianion Li_2-**8** reacts with 1-fluorooctane in THF at 0 °C to afford 7-octyl-7,12-dihydrobenzo[*a*]anthracene (**8a**) as the major reaction product in 54 % yield (Table 1, entry 16). An inseparable mixture of minor isomeric byproducts was also observed in the crude mixture and chromatographic fractions by ^1H and ^{13}C NMR spectroscopy; it gave a unique peak by GLC or GC–MS (*m/z*: 342, $C_{26}H_{30}$, in about 22 % GLC yield, assuming that the response factor is identical to **8a**). Treatment of the mixture with DDQ ($CHCl_3$, RT, 12 h) afforded an unique rearomatized product, which was identified as 7-octylbenzo[*a*]anthracene (**8b**, Table 1, entry 16; Scheme 9).The Birch reduction



Scheme 9.

($Li_{(s)}/NH_{3(l)}$,THF) of benzo[*a*]anthracene followed by EtOH protonation yields 7,12-dihydrobenzo[*a*]anthracene.[47] The same type of 7,12-dihydro derivatives are observed in the reduction of substituted benzo[*a*]anthracenes, such as 7-methylbenzo[*a*]anthracene which affords 7-methyl-7,12-dihydrobenzo[*a*]anthracene.[48] We have found no data on attempts to obtain alkylated dihidrobenzo[*a*]anthracenes by reductive alkylation of benzo[*a*]anthracene under Birch condition, as seen above for other PAHs. However, given the information that was collected on reduction potentials, an estimate for the second reduction potential of benzo[a]anthracene can be made: $E^{\circ}_2 \approx -1.70$ V+(−1.00); $V = -2.70$ V in DMA/TBAB vs. Ag/AgCl. This value is more negative than those of fluoranthene ($E^{\circ}_2 = -2.37$ V), anthracene ($E^{\circ}_2 = -2.64$ V), and 9-phenylanthracene ($E^{\circ}_2 = -2.55$ V),[8] among others; all of these vales are reported vs. Ag/AgCl. For last named compounds it is known that the corresponding dianions are strong bases, which are protonated in $NH_{3(l)}$ to afford stable monoprotonated monoanionic intermediates (e.g., HLi-**5**, Scheme 5); these intermediates can be alkylated in an additional step. This is the expected behavior for benzo[*a*]anthracene under Birch reductive alkylation conditions. As in the cases that were considered before, direct alkylation of the dianion with fluoroalkanes represents a complementary synthetic route for the reductive alkylation of benzo[*a*]anthracene.

o-Terphenyl and p-terphenyl dianions: *o*-Terphenyl and *p*-terphenyl (**9** and **10**, respectively, $C_{18}H_{14}$) are electrochemically reduced in two reversible steps (*o*-terphenyl: $E^{\circ}_1 = -2.62$ V, $E^{\circ}_2 = -2.72$ V; *p*-terphenyl: $E^{\circ}_1 = -2.40$ V, $E^{\circ}_2 = -2.70$ V in DMA/TBAB vs. Ag/AgCl).[49,8] *o*-Terphenyl reacts with $Li_{(s)}$ in [D_8]THF to afford a dianion (Li_2-**9**), which has been studied by ^1H and ^{13}C NMR spectroscopy.[15] NMR spectroscopy studies of the lithium salts of the *o*-terphenyl (Li-**10** and Li_2-**10**) are also available.[50] In our hands, Li_2-**9** and Li_2-**10**, which were prepared in THP at 0 °C, react with 1-fluorooctane to give alkylation at the inner ring, as predicted by calculations (Figure 1). Hydrolysis affords 3-octyl-2,3-diphenyl-1,4-cyclohexadiene (**9a**) in 76 % yield (Table 1, entry 17; Scheme 10), and 3-octyl-3,6-diphenyl-1,4-cyclohexadiene (*cis* and *trans*-**10a**) and 2,5-diphenyl-5-octyl-1,3-cyclohexadiene (**10b**) in 84 % overall yield, as a



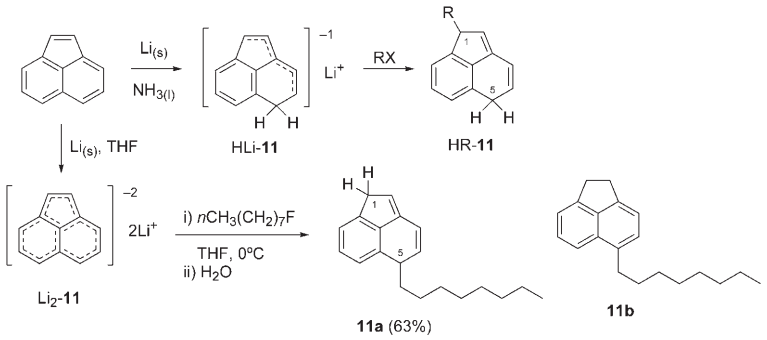
Scheme 10.

1:0.44:0.48 mixture of the *cis* and *trans*-1,4-dihydro and 1,2-dihydro isomers, respectively (Table 1, entry 18; Scheme 10).

Reductive methylation of *p*-terphenyl with $Li_{(s)}/NH_{3(l)}$/THF and bromomethane or chloromethane at −33 °C under a variety of reaction conditions gives complex mixtures that contain both the dimethylated compounds in the inner ring (3,6-dimethyl-3,6-diphenyl-cyclohexa-1,4-dienes) along with large amounts of recovered *p*-terphenyl (**10**) as their major components, and other products.[51] A number of arguments are given to explain these facts, which include the slow kinetics of protonation of the dianion in ammonia, or the involvement of NH_2^- as a base for multiple alkylations. In any case, it is clear that ET pathways are competitively involved. A complex mixture is obtained for *o*-terphenyl under analogous conditions; monomethylated compounds prevail at the inner ring (up to four isomers), as well as dimethylated compounds at the inner ring, along with some recovered *o*-terphenyl (**9**) for CH_3Cl at −78 °C.[51] Calculations on $\mathbf{9}^{-2}$ and $\mathbf{10}^{-2}$ predict the alkylation at the inner ring well (see Figure 1), but as in the earlier case, it must be remarked upon that the alkylation does not take place at the carbon atom that bears the largest density of charge in *o*- or *p*-terphenyl dianions.

Acenaphthylene dianion: Although no electrochemical data has been found on the second reduction potential of acenaphthylene (**11**, $C_{12}H_8$), there is enough evidence of the occurrence of its dianion. Compound **11** is reduced with $Li_{(s)}$ in THF to give the radical anion (Li-**11**$^{\bullet}$),[29,52,33] and the dianion,[29] which has been studied as the lithium salt (Li_2-**11**) by ^1H,[53,33] ^{13}C,[53] and ^7Li NMR spectroscopy.[30,53] It has been also obtained by double deprotonation of acenaphthene with BuLi·TMEDA,[54] and characterized by single-crystal X-ray crystallography.[55,56] We have carried out the reaction of a solution of Li_2-**11** in THF with 1-fluorooctane at 0 °C, which affords 5-octyl-1,5-dihydroacenapthylene (**11a**) in 63% yield after hydrolysis with water. Compound **11a** undergoes a [1,5]-H rearrangement to the more stable isomeric acenaphthene **11b** slowly (within hours), although both **11a** and **11b** could be isolated as pure substances (Scheme 11).

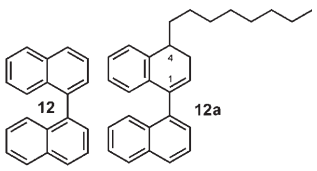
In contrast, the reduction of acenaphthylene with $Li_{(s)}$ in $THF/NH_{3(l)}$ mixtures affords the stable intermediate HLi-**11** (likely by protonation of Li_2-**11**), which has been identified by ^1H and ^{13}C NMR spectroscopy in the reaction media.[34] Compound HLi-**11** can be further alkylated to afford the regioisomeric 1-alkyl-1,5-dihydroacenaphthylenes HR-**11**



Scheme 11. Reduction of acenaphthylene under Birch conditions to afford HLi-**11** ($LiC_{16}H_{11}$), which can be alkylated in a subsequent step, and the alkylation of dilithium acenaphthylene (Li_2- **11**, $Li_2C_{12}H_8$) with *n*-fluorooctane.

(Scheme 11). An equivalent strategy has been described by quenching Na_2-**11** in THF with one equivalent of MeOH followed by conventional alkylation, which affords 1-alkyl-1,5-dihydroacenaphthylenes (HR-**11**) along with its regioisomeric 2*a*-alkyl-2*a*,5-dihydroacenaphthylenes.[57]

1,1′-Binaphthyl dianion: Little information is found in the literature on the reduced forms of 1,1′-binaphthyl (**12**, $C_{20}H_{14}$), which was attained either electrolytically or by means of alkali metals. The reduction of **12** with potassium in DME is reported to initially afford EPR-active solutions that are further reduced to a diamagnetic species (presumably a dianion or higher polyanions), along with some conversion to perylene.[58] Under our conditions, binaphthyl is reduced with an excess of $Li_{(s)}$ in THP at 0 °C, the resulting mixture could be alkylated with 1-fluorooctane as in the previous instances. After hydrolysis, 4-octyl-3,4-dihydro-1,1′-binaphthyl (**12a**) was isolated from the crude (Table 1, entry 20; Scheme 12). Compound **12a** displays hindered ro-



Scheme 12.

tation in the 300 MHz ^{1}H NMR spectrum at 25 °C in $CDCl_3$, but also displays a single set of resonances at 80 °C. Alkylation took place principally at the 4 position, as expected from calculations. We have chosen in Figure 1 the *transoid*-**12**$^{-2}$ instead of the *cisoid*-**12**$^{-2}$ (both of C_2 symmetry) as the more stable conformation of **12**$^{-2}$ ($\Delta E_{(trans-cis)} = 1.37$ kcal mol^{-1}). This is not a critical point here, because the same conclusions are drawn for both symmetries regarding regioselectivity.[3]

Conclusion

In conclusion, we describe new synthetic applications that are derived from PAH dianions, which apparently react as nucleophiles with fluoroalkanes in spite of being generally regarded as powerful and rather intractable electron-transfer reagents. So far, all of the PAHs that were tested, except for biphenyl, afforded the expected alkylation products. The reaction products are regiochemically controlled, alkylated dihydroarenes. These are interesting molecules, in which one ring is dearomatized; this allows further functionalization in the polycyclic framework. In most cases it is possible to evaluate the reacting site within the polycyclic structure by simple MO calculations. This methodology therefore complements the current methodologies on the reductive alkylation of polycyclic arenes, and allows access to a new set of regioisomers, the regiochemistry of which is dictated by the HOMO coefficients on the dianion. Classical metal/-ammonia reductive alkylations afford, in general, a different set of alkylated regioisomers, which correspond to the alkylation of the monoprotonated monoanionic PAH intermediate. The transition state for the alkylation seems to be driven by the overlap of orbitals rather than by polar interactions, despite the charged nature of the dianion and the highly polarized character of the C–F bond. This can be seen in the phenanthrene and *o*- and *p*-terphenyl examples, for which the alkylation does not take place at the carbon atom that bears the highest charge, but at the carbon atom with the highest HOMO coefficient. In the remaining cases, the carbon atom that bears the highest coefficient also concentrates the charge. This is currently the subject of deeper studies regarding structural features and their correlations with reactivity. It is also significant that, in most cases, the arene radical anion was unable to afford substantial amounts of alkylated products. In these cases ET is the prevailing reactivity, and octane was the main reaction product. Finally, an improved hydrolytic protocol (by using acetonitrile as a source of protons) that affords an improved ratio of regioisomers in the last protonation step is also reported.

Experimental Section

Caution: It should be noted that the International Agency for Research on Cancer (IARC) classifies the following PAHs as Group 1 (carcinogenic to humans), Group 2 A (probably carcinogenic to humans), or Group 2B (possibly carcinogenic to humans).[59] A potency equivalency factor (PEF) with respect to the reference benzo[*a*]pyrene is also given (Table 2).[60]Appropriate safety measures must be enforced when manipulating these PAHs, and in general, all PAH derivatives are of unknown toxicity.

Table 2. Carcinogenicity of some PAHs.

PAH	IARC Group	PEF
benzo[*a*]pyrene	1	1
benzo[*a*]anthracene	2A	0.1
chrysene	2B	0.01
naphthalene	2B	0.001

General: All reactions were carried out under an atmosphere of dry argon in oven-dried glassware. THF was distilled from sodium benzophenone ketyl. THP was distilled from Na/K alloy. IR spectra were measured (neat) with a Nicolet Impact 400 D-FT Spectrometer. NMR spectra were recorded on Bruker AC-300 or a Bruker Avance-500 spectrometers with $CDCl_3$ as a solvent at 25 °C, unless otherwise stated. Chemical shifts (δ) are in ppm relative to internal TMS and coupling constants (J) are in Hz. LRMS and HRMS were measured with a Shimadzu GC/HS QP-5000 and Finingan MAT95 S spectrometers, respectively. Gas chromatographic analyses (GLC) were determined with a Hewlett–Packard HP-5890 instrument equipped with a flame ionization detector (FID) and a 12 m capillary column (0.2 mm diameter, 0.33 μm film thickness), by using nitrogen (2 mL min^{-1}) as a carrier gas, $T_{injector} = 275$ °C, $T_{detector} = 300$ °C, $T_{column} = 60$ °C (3 min) and 60–270 °C (15 °C min^{-1}), $P = 40$ kPa as routine working conditions. Dianionic PAHs (Li_2-**1** to Li_2-**12**) were prepared by using standard methods of manipulation under an argon atmosphere from the corresponding PAHs and an excess of mechanically activated lithium powder at 0 °C. The best grade PAHs that were commercially available (Acros, Aldrich), as well as 1-fluorooctane were used. When given, the concentrations of Li_2-**1** to Li_2-**12** are formal, the actual concentration of the dianionic species was not determined. The lithium granules (Aldrich) were mechanically activated by milling under mineral oil by using a rotary mill, the resulting lithium powder was washed repeatedly with dry hexane.

General procedure for the reductive alkylation of PAHs 1–12 with fluoroalkanes—preparation of compounds 1a–c to 12a: A suspension of lithium (70 mg, ca. 10 mmol) and the corresponding PAH (**1**–**12**, 2 mmol) was prepared by stirring in dry THP (10 mL) at 0 °C for 1 h under an argon atmosphere. A solution of the corresponding fluoroalkane (1-fluorooctane, 6-fluorohex-1-ene, or fluoromethylcyclopentane, 2 mmol) in THP (1 mL) was added dropwise to this suspension. After 30 min, the mixture was hydrolyzed with water (5 mL) and neutralized with 3 M HCl; hydroquinone (10 mg) was added, and the organic phase was analyzed by quantitative GLC, after the addition of a carefully weighed amount of decane, dodecane, or diphenylmethane (ca. 1 mmol) as an internal standard. The reaction products were isolated from the reaction crudes without internal standard by extracting with Et_2O (3×20 mL), drying over Na_2SO_4, removing the solvents in vacuo, and by purifying the resulting residue by column chromatography (silica gel doped with 5% hydroquinone, hexane). Pure isolated products were used in the calibration curves. For the non-isolable minor isomers, an identical response factor to the major isomer was assumed. If necessary, a 1% solution of hydroquinone was added to the purified products to prevent decay during storage. Alternatively, the yield was also determined by the addition of a carefully weighed amount of an internal standard (diphenymethane or diphenylformamide) to the extracted reaction crudes and by submission to NMR spectroscopy analysis. As representative examples, a full description of the isolated dihydrochrysenes **7a–c** is given in this section:

6-Octyl-5,6-dihydrochrysene (7a): $R_f = 0.50$ (hexane); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.84$ (apparent t, $J = 6.6$ Hz, 3H; CH_3), 1.07–1.50 (m, 14H; 7×CH_2), 2.92–3.06 (m, 1H; CH_2CHCH_2), 3.20 (dd, $J = 15.8$, 5.8 Hz, 1H; $C_{arom}CHHCHCH_2$), 3.50 (dd, $J = 15.8$, 3.6 Hz, 1H; $C_{arom}CHHCHCH_2$), 7.22–7.29 (m, 2H; 2×CH_{arom}), 7.29–7.40 (m, 1H; CH_{arom}), 7.40–7.58 (m, 2H; 2×CH_{arom}), 7.75–7.88 (m, 3H; 3×CH_{arom}),

7.93 (apparent d, $J=8.6$ Hz, 1H; CH_{arom}), 8.16 ppm (apparent d, $J=8.5$ Hz, 1H; CH_{arom}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=14.07$ (CH_3), 22.61 (CH_3CH_2), 25.57, 28.62, 29.24, 29.51, 29.61 ($5\times CH_2$), 31.82 ($C_{arom}CH_2$), 33.56 (CH_2CH_2CH), 38.21 (*C*H), 122.15, 123.68, 124.49, 125.35, 126.12, 126.82, 126.89, 127.22, 127.90, 128.59 ($10\times CH_{arom}$), 130.98, 131.05, 132.33, 133.23, 134.02, 141.03 ppm ($6\times C_{arom}$); IR (film): $\nu=3059$, 2924, 2853, 1462, 1377, 816, 757 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 344 (1.16) $[M+2H]^+$, 343 (6.40) $[M+1H]^+$, 342 (22.85) $[M]^+$, 230 (19), 229 (100), 228 (36), 43 (12), 41 (11); HR-MS: *m*/*z* calcd for $C_{26}H_{30}$: 342.2348; found 342.2362.

6-(5-Hexenyl)-5,6-dihydrochrysene (7b): $R_f=0.28$ (hexane); ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.14$–1.56 (m, 6H; $3\times CH_2$), 1.86–2.04 (m, 2H; $CHCH_2CH_2$), 2.92–3.05 (m, 1H; CH_2CHCH_2), 3.20 (dd, $J=15.8$, 5.6 Hz, 1H; $C_{arom}CHHCH$), 3.50 (dd, $J=15.8$, 3.6 Hz, $C_{arom}CHHCH$), 4.80–4.97 (m, 2H; CH_2=CH), 5.72 (ddt, $J=17.0$, 10.1, 6.7 Hz, 1H; CH=CH_2), 7.21–7.29 (m, 2H; $2\times CH_{arom}$), 7.30–7.39 (m, 1H; CH_{arom}), 7.42- 7.56 (m, 2H; CH_{arom}) 7.75–7.89 (m, 3H; CH_{arom}), 7.92 (apparent d, $J=8.6$ Hz, 1H; CH_{arom}), 8.15 ppm (apparent d, $J=8.3$ Hz, 1H; CH_{arom}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=27.01$ (CH_2), 28.60 ($C_{arom}CH_2CH$), 28.83, 33.37 ($2\times CH_2$), 33.63 ($CHCH_2CH_2$), 38.18 (CH_2CHCH_2), 114.23 (CH_2=CH), 122.16, 123.67, 124.51, 125.37, 126.15, 126.86, 126.95, 127.24, 127.90, 128.61 ($10\times CH_{arom}$), 130.95, 130.98, 132.33, 133,23, 134.01 ($5\times C_{arom}$), 138.88 (CH=CH_2), 140.91 ppm (C_{arom}); IR (film): $\nu=3062$, 2974, 2927, 2853, 1639, 1597, 1486, 1461, 1449, 1430, 1378, 1257, 1030, 993, 909, 860, 815, 762, 736 cm^{-1}; MS: *m*/*z* (%): 316 (0.01) $[M+4H]^+$, 315 (0.13) $[M+3H]^+$, 314 (1.55) $[M+2H]^+$, 313 (12.36) $[M+1H]^+$, 312 (48.01) $[M]^+$, 230 (19), 229 (100), 228 (44), 226 (12); HR-MS: *m*/*z* calcd for $C_{24}H_{24}$: 312.1878; found 312.1883.

6-(5-Cyclopentylmethyl)-5,6-dihydrochrysene (7c): $R_f=0.30$ (hexane); ^1H NMR (400 MHz, $CDCl_3$): $\delta=0.94$–1.13 (m, 2H; $2\times CHH$ of cyclopentyl), 1.32–1.61 (m, 6H; $4\times CHH$ of cyclopentyl, $CHCH_2CH(CH_2)_2$), 1.62–1.73 (m, 1H; *CH*H of cyclopentyl), 1.75–1.86 (m, 2H; CH*H* of cyclopentyl, $CH_2CH(CH_2)_2$), 3.02–3.11 (m, 1H; $CH_2CH(C_{arom})CH_2$), 3.21 (dd, $J=15.8$, 5.7 Hz, 1H; $C_{arom}CHHCH$), 3.52 (dd, $J=15.9$, 3.0 Hz, 1H; $C_{arom}CHHCH$), 7.23–7.31 (m, 2H; CH_{arom}), 7.30–7.38 (m, 1H; CH_{arom}), 7.42–7.49 (m, 1H; CH_{arom}), 7.49–7.58 (m, 1H; CH_{arom}), 7.77–7.88 (m, 3H; CH_{arom}), 7.93 (apparent d, $J=8.6$ Hz, 1H; CH_{arom}), 8.15 ppm (app. d, $J=8.6$ Hz, 1H; CH_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 25.16, 25.18 ($2\times CH_2$ of cyclopentyl), 28.83 ($C_{arom}CH_2CH$), 32.69, 32.86 ($2\times CH_2$ of cyclopentyl), 37.09 ($CH_2CH(C_{arom})CH_2$), 37.40 ($CH_2CH(CH_2)_2$), 40.21 (CH_2 of cyclopentyl), 122.14, 123.70, 124.55, 125,36, 126.12, 126.82, 126.90, 127.23, 127.85, 128.61 ($10\times CH_{arom}$), 130.95, 131.05, 132.37, 133.22, 133.98, 141.12 ppm ($6\times C_{arom}$); IR (film): $\nu=3061$, 3035, 3021, 2948, 2866, 1485, 1469, 1449, 1429, 1378, 908, 817, 762, 734 cm^{-1}; MS: *m*/*z* (%): 315 (0.10) $[M+3H]^+$, 314 (1.21) $[M+2H]^+$, 313 (9.58) $[M+1H]^+$, 312 (36.83) $[M]^+$, 230 (19), 229 (100), 228 (43), 226 (11); HR-MS: *m*/*z* calcd for $C_{24}H_{24}$: 312.1878; found 312.1882.

The synthesis of fluorinated starting materials and full description of the remaining compounds **1a–c** to **12a** can be found in the Supporting Information.

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