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A "Conducted Tour" Migration of Li^+ during the cis/trans Stereoinversion of α-Arylvinyllithiums

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Dedicated to the memory of Professor Donald J. Cram

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Supporting information for this article includes lithiation shifts $\Delta\delta$, preparation of **15**, tabulated primary NMR data, and diastereotopomerization rate constants; it is given via a link at the end of the document.

Key words. conformational analysis • cis,trans configurational lability • reaction mechanisms • sp^2-carbanion inversion • structural elucidation

Abstract. A "conducted tour" migration keeps a mobile client on a profitable route even though an occasional side-step may seem attractive. A stereochemical manifestation of such a migration had been suggested by Donald J. Cram (1964), and we present now a different example that concerns the cis/trans stereoinversion of monomeric $H_2C=C(Li)$–aryl compounds: Upon THF-assisted heterolysis of the Li–C bond with formation of a solvent-separated ion pair (SSIP), the unchained "mobile client" $Li^+(THF)_4$ is proposed to surmount the rim of the electronically fixed aryl group and to disdain the less encumbered pathways across the $H_2C=C$ region (see Scheme 1). This interpretation is based on knowledge from a previously published series of monomeric α-arylalkenyllithiums in combination with two new members: 4-(α-lithiovinyl)-2,2-dimethylbenz[f]indane (**1**) revealed both a barrier against α-aryl rotation and a route-distinguishing retardation as compared with the correspondingly migration-dependent cis/trans stereoinversion rate constant of 1-(α-lithiovinyl)naphthalene (**2**). Monomeric and dimeric ground states of **1** and **2** and their microsolvation numbers were determined by means of recently developed primary and secondary NMR criteria.

Introduction

The pseudomonomolecular, ionic mechanism[1,2] of cis/trans interconversion (configurational lability) of α-arylvinyllithiums in tetrahydrofuran (THF) as a solvent depends on three kinds of motion: Heterolytic cleavage of the Li–C(α) bond, followed by migration of the Li cation, and a transitory rehybridization of the charge-bearing, quasi-sp^2 hybridized center C(α) that inverts its configuration. The whole process is illustrated in Scheme 1 for the imagined 4-(α-lithiovinyl)-2,2-dimetrhylbenz[f]indane (**1**), whose stereoinversion ("diastereotopomerization") would interconvert the NMR chemical shifts δ of the two diastereotopic β-H atoms. The trisolvated ground state of **1** (to be disclosed in this work) is a contact ion pair **1**-CIP and is expected to demand a high concentration of THF for the immobilization of a fourth THF ligand at lithium with formation of the THF-separated ion pair **1**-SSIP as a highly reactive intermediate. The increased distance of $Li^+(THF)_4$ from the carbanionic center C(α) in **1**-SSIP would enable the charge-carrying, quasi-sp^2 orbital at C(α) to change into a transitory p_x orbital (Scheme 1) in the proposed[1] transition state of stereoinversion. The ensuing descent from the transition state would transform p_x into the quasi-sp^2 orbital of the stereoinverted intermediate **1´**-SSIP. However, **1´**-SSIP cannot be formed without a suitable migration of $Li^+(THF)_4$: Since ionic dissociation of an SSIP intermediate into the free ions had been excluded for related α-arylalkenyllithiums through the observation of concentration-independent rate constants k_ψ,[1–5] such a migration must occur within the THF-solvated ion pairs on the way from **1**-SSIP to **1´**-SSIP. The subsequent loss of one THF ligand from **1´**-SSIP would form the final product **1´**-CIP, so that the transitory immobilization of one additional THF ligand at Li implies the whole process to be catalyzed by THF and hence to run with a pseudomonomolecular rate constant k_ψ that depends on the THF concentration.

A seemingly facile migration pathway (β-route in Scheme 1) would conduct the cation $Li^+(THF)_4$ across the olefinic CH_2-β region. Favorable electrostatic interactions might make it more attractive for $Li^+(THF)_4$ to migrate across the still charge-bearing, temporarily sp-hybridized C(α) center (α-route). The π-route had been proposed previously[1–5] to proceed as a "conducted tour"[6] along the charge gradients that resulted through delocalization of negative electric charge from the Li–C(α) bond into the α-aryl π-electron system: Such a delocalization is at its maximum in the depicted transition state with a lateral overlap

(Scheme 1) of the two p_x orbitals at C(α) and C(4) which are situated within the C(α)=C(β) double-bond plane; this confers a partial double-bond character to the C(4)–C(α) bond (quasi-benzyl-anion resonance[7]) and creates an electronic barrier against deviation from the close to perpendicular orientation of the α-aryl plane with respect to the double-bond plane. Such a rotational barrier would disfavor the possibility of a transport of $Li^+(THF)_4$ riding on a π face of a rotating α-aryl group. The energetic stabilization against α-aryl rotation and the concomitant accumulation of delocalized negative π-charge in the *para* position (at C-9) are stronger in the linear transition state than in the non-linear ground state **1**-CIP; this had been established[1] through the Hammett reaction constant $\rho = +5.2$ for the stereoinversion rate constants as determined for a related familiy of α-arylalkenyllithiums (*para*-substituted derivatives of **7a** in Scheme 2).

The new α-arylvinyllithium **1** was designed to provide more direct evidence for Li^+ migration on the π-route across the α-aryl part: Steric or electronic hindrance by its 2,2-dimethylpropan-1,3-diyl side-chain (Scheme 1) might raise the cis/trans stereoinversion barrier compared with that of the less encumbered 1-(α-lithiovinyl)naphthalene (**2**); the envisioned barriers would be obtained from the cis/trans interconversion rates of the olefinic CH_2-β protons in **1** and **2**. In order to minimize steric differences, **1** was also designed to resemble the known[2] α-(2,6-dimethylphenyl)vinyllithium (**4**) sterically in the neighbourhood of the Li–C(α) bond: The 2-/6-CH_3 substituents of **4** correspond to CH_2-3 and CH-5 of **1** wherein they are fixed as members of a cyclopentene and a phenyl ring, respectively. Since the single unsubstituted *ortho*-position might influence the barrier of **2**, we searched for a more general answer to this question through rate comparisons of the α-(2-alkylphenyl)vinyllithiums[7] **3** and **5** with the published data of α-(2,6-dialkylphenyl)alkenyllithiums **4**[2] and **6**.[4] As a basic requirement, **1** and **2** should be monomeric in THF (as are **3**–**7**). The design of **1** was also thought to reveal the rapidity of α-aryl rotation in the ground state of **1** by means of NMR coalescences (averaging of the δ values) within the signal pairs of geminal protons in CH_2-1 and in CH_2-3 and of the 2-CH_3 substituents in **1**. The resulting rotational barriers were expected to keep the aromatic ring plane in a perpendicular orientation with respect to the C(α)=C(β) double-bond plane in **1**-CIP.

Our first task will consist in identifying the monomeric and dimeric species of **1** and **2** (ground states in Section 1), followed by Section 2 with measurements of the cis/trans stereointerconversion rates and evaluation of the corresponding stereoinversion barriers in search of evidence for the "conducted tour" migration of $Li^+(THF)_4$ on the π-route.

Results and Discussion

1. Ground States of the Alkenyllithiums

The carboxylic acid **10** was prepared from 4-bromo-2,2-dimethylbenz[f]indane[8] (**8**) via the lithio derivative **9** and its carboxylation (Scheme 3); it was important to realize that **10** was weakly soluble in both Et_2O and aqueous NaOH. The ensuing formation of the 4-acetyl derivative **11** from **10** with methyllithium (3 equiv) was terminated through quenching with $ClSiMe_3$ before aqueous workup, so that remnant methyllithium was destroyed before the ketone **11** was liberated through hydrolysis.[9] Brominative deoxygenation[10] with the reagent **12** converted **11** into 4-(α-bromovinyl)-2,2-dimethylbenz[f]indane (**13**). The temperature-dependent NMR spectra of some diastereotopic nuclei in **13** (2-CH_3 and CH_2-3 in Scheme 3 and Tables[11] S1) disclosed a barrier of $\Delta G^{\ddagger}$(35 and 48 °C) = 15.9(2) kcal mol^{-1} against α-aryl (half-)rotation with passage through a possibly coplanar conformation of the α-aryl and the C(α)=C(β) double-bond planes: The responsible obstacle was the α-Br atom, since the corresponding α-aryl rotations could not be "frozen" on the ^{1}H and ^{13}C NMR time scales with 4-CO_2H in **10**, 4-acetyl in **11** (down to −103 °C), and 4-vinyl in the alkene **14**. The assignments of all ^{1}H and ^{13}C NMR signals of **14** agreed satisfactorily with the known[12] assignments for 1-vinylnaphthalene (**15**) which were needed further below. Preparation of the polymerization-prone **15** through dehydration of 1-(1-naphthyl)ethanol by a reagent generated from *N*,*N*-dimethylformamide with oxalyl chloride can be recommended.

The Br/Li interchange reaction (Scheme 3) of the 4-(α-bromovinyl) derivative **13** with *n*-butyllithium (*n*BuLi) in cyclopentane or hexane occurred smoothly at room temperature (rt) in the absence of electron-pair donor substances (such as Et_2O). This caused an initial confusion because the quickly emerging $BrCH_2$ ^{1}H NMR triplet of the co-product 1-bromobutane (*n*BuBr) was not accompanied by the expected signals of the $=CH_2$ part of **1** in the olefinic spectral region that displayed only a very broad yet shallow baseline elevation. But when this clear solution was treated with *tert*-butyl methyl ether (*t*BuOMe) in a slight excess over **13**, the missing $=CH_2$ part of **1** appeared with a the expected intensity of the two doublets and

with a mutual two-bond coupling constant of $^{2}J_{H,H}$ = 6.0 Hz; as a constitutional proof, protolysis with a little *tert*-butyl alcohol generated the "parent" alkene **14**. This behavior made it clear that we would not be able to investigate donor-free **1**, perhaps due to the formation of a spectroscopically unresolved mixture of highly aggregated species of **1** in the absence of donor ligands. Unfortunately, this unsolvated **1** did not precipitate from these hydrocarbon solvents, so that it could not be purified by the usually applied washing with pentane. Unlike **4**,[13] **1** did also not precipitate during its preparation in *t*BuOMe as the solvent; thus, we had to remove *n*BuBr and all other volatiles by evaporation at rt in a high vacuum. The solid residue, containing some *t*BuOMe that was coordinated to **1** (and possibly to some LiBr), dissolved readily in hydrocarbons or ethereal solvents; these solutions had to be stored at –20 °C under argon gas cover till the ensuing NMR determinations of the (non)aggregation and microsolvation states could be carried out. Thus, we investigated always samples with at least one equivalent of *t*BuOMe.

An orange-colored solution of isotope-labeled [^{6}Li]**1** in [D_8]toluene displayed a ^{13}C-α NMR quintet at –55 °C. The intensity ratio of 1:2:3:2:1 of the five quintet components is characteristic of a $^{13}C^{6}Li_2$ motif since it results through magnetic coupling of the observed ^{13}C nucleus with n = 2 ^{6}Li nuclei;[14] it can be detected only if the intermolecular Li scrambling is sufficiently slow to preserve the intramolecular $^{13}C,^{6}Li$ spin coherence on the NMR time scale. This primary NMR criterion of aggregation pointed to the four-membered ring core (C_2Li_2) of a dimeric structure, as known for the established[13] dimers of **4**. The frequency intervals of the quintet components furnished the one-bond NMR coupling constant $^{1}J(^{13}C,^{6}Li)$ = 7.5 Hz; by means of the empirical[15] Equation (1), this value revealed microsolvation at **1** by d = 1 *t*BuOMe ligand per Li, since a = 2 ^{13}C-α centers have contacts with each ^{6}Li nucleus in the proposed $^{13}C_2{}^{6}Li_2$ core of **1**. Thus, the [D_8]toluene solution contained the disolvated dimer, namely, (**1**&*t*BuOMe)$_2$, in analogy with the known[13] solid-state structure of (**4**&*t*BuOMe)$_2$. This dimer remained the only species of **1** at all temperatures from 25 to –90 °C, as shown by the practically constant ^{13}C chemical shifts δ (Table[11] S2a). As a secondary NMR criterion, the two-bond interproton coupling constant $^{2}J_{H,H}$ = 5.8 Hz of the $=CH_2$ moiety remained also unchanged from –55 up to 25 °C (Table[11] S2b), which provided two important pieces of evidence: By means of the empirical[16] Equation (2), it confirmed that the microsolvation number of d = 1 in (**1**&*t*BuOMe)$_2$ remained valid at least up to 25 °C and not only at –55 °C as deduced above

through ^{13}C splitting. Second, it established that the rapid stereoinversion process to be described in Section 2 was less rapid (namely, below coalescence) here in toluene at 25 °C.

$$d = 46\ \text{Hz} \times (n \times {}^{1}J_{C,Li})^{-1} - a \quad (1)$$

$$d = ({}^{2}J_{H,H} - 3.9\ \text{Hz})/1.67 \quad (2)$$

Quite similar NMR spectral features were observed for **1** in its orange-colored *t*BuOMe solutions: Most of the ^{13}C (Table[11] S3a) and ^{1}H (Table S3b) chemical shifts δ were numerically close to the above data in toluene and did not depend on the temperature between 25 and –103 °C, so that the same disolvated dimer (**1**&*t*BuOMe)$_2$ as above appeared to be the only species of **1** also in *t*BuOMe. In spite of the abundant solvent, the well-resolved $^{2}J_{H,H}$ = 6.0 Hz coupling confirmed [by Eq. (2)] microsolvation by only d = 1 *t*BuOMe ligand per Li. All ^{13}C and ^{1}H chemical shifts of this species were assigned through selective decoupling experiments and the two-dimensional $^{1}H,^{6}Li$ (HOESY) correlations (short distances) of ^{6}Li with both 5-H and the upfield olefinic β-H (trans to α-aryl). These data and the above assignments for the "parent" alkene **14** were required for calculations of lithiation NMR shifts $\Delta\delta = \delta(\text{RLi}) - \delta(\text{RH})$ which can purge δ(RLi = **1**) from special effects that are also present in δ(RH = **14**), making the effects of lithiation more clearly visible. We use them as another secondary NMR criterion of (non)aggregation: Despite substantially different chemical shifts δ,[11] the characteristic $\Delta\delta$ data of constitutionally comparable positions in **1**&*t*BuOMe and **4**&*t*BuOMe were sufficiently similar (Table 1) to conclude that these two systems responded similarly to lithiation: These dimers of **1** and **4** have almost equal $\Delta\delta$(C-*para*) values in *t*BuOMe (entries 2 and 5) or in toluene (entries 1 and 4), including also cyclopentane (entry 3 and Table[11] S4). Such upfield lithiation NMR shifts are partially[7] caused by the delocalization of electric charge from the Li–C(α) bond to the *para* position (as detailed in references [2] and [7]), so that their similar magnitudes indicated similar interplanar angles between the α-aryl and the C(α)=C(β) double-bond planes in dimeric **1** and **4**. These magnitudes revealed close to perpendicular conformations that provide for a close to maximum overlap of the charge-carrying Li–C(α) bond (quasi-sp^2) orbital and the p_x orbital at C-*ipso* in the C(α)=C(β) double-bond plane (quasi-benzyl-anion resonance). The small deviation of $\Delta\delta$(C-*para*) of monomethyl-bearing, dimeric **3** (entry 6) may be due to a slightly

different conformational preference. Complete sets of $\Delta\delta$ values are collected in Figure S1.[11]

Comparison of the ^{13}C NMR spectrum of dimeric **1** in *t*BuOMe (Figure 1a) with that in Figure 1b established that **1** cannot be dimeric in THF solution. The dark-green color of THF solutions of **1** seemed to be due to traces of contaminants that did not disturb the NMR properties of **1**; this followed from the well-resolved ^{13}C and ^{1}H NMR spectra at and below –30 °C, whose chemical shift values did not depend on the temperature (Tables[11] S5a and S5b). Accordingly, protolytic quenching led to decolorization and afforded the parent alkene **14**. Adventitiously generated **14** in small amounts vanished soon through polymerization (in contrast to the stable solutions of **14** with **1** in the non-THF solvents). Since ^{13}C-α splitting by ^{6}Li (as mentioned above) could not be detected down to –103 °C, we took again recourse to the secondary criterion of lithiation shifts $\Delta\delta$: The strongly downfield-shifted, practically equal $\Delta\delta$(C-α) = +76.3(1) ppm of both **1** and **4** (entries 7 and 8 in Table 1) suggested that **1** was also a trisolvated monomer in THF. In fact, microsolvation by d = 3 THF ligands was confirmed through Equation (2) by the interproton coupling constant of $^{2}J_{H,H}$ = 8.9 Hz (entry 7). The almost equal magnitudes of both $\Delta\delta$(C-*para*) = –11.3(3) ppm and $\Delta\delta$(*para*-H) = –0.74(2) ppm for **1**&3THF (entry 7) and **4**&3THF (entry 8) were typically greater than those of dimeric **1** in entries 1–3 and bear witness to the characteristically increased π delocalization in the ground states of our monomeric, trisolvated alkenyllithiums. As a consequence of this strengthened quasi-benzyl-anion resonance, the barrier against rotation about the C(α)–C(*ipso*) bond must be higher for the monomers than for the dimers. This expectation was experimentally verified through observation of separate NMR signals of the diastereotopic protons (Scheme 3) in CH_2-1, CH_2-3, and 2,2-$(CH_3)_2$ at 400 MHz between –85 and –103 °C (Table[11] S5b) for monomeric but not for dimeric **1**. The pairwise averaging of these signals occurred through sufficiently rapid α-aryl rotation in monomeric **1** at individual coalescence temperatures and furnished the rotational barrier of $\Delta G^{\ddagger}$(–60 and –66 °C) = 9.9(2) kcal mol^{-1}, as detailed for **1** in the Experimental Section. Since deviations from the close to perpendicular conformations against such barriers would generally diminish[7] the π delocalization and hence sacrifice part of the appertaining energetic stabilization, even the monomers of the two α-(2-alkylphenyl)vinyllithiums **3** and **5** tended to preserve such a conformation in spite of their unsubstituted 6-positions. This may be visualized by the known[17] lithiation shifts $\Delta\delta$(C-*para*) = –10.5(1) ppm of **3** and **5** in THF (entries 10 and 11)

whose slightly diminished magnitudes may be due to a low tendency to populate a dimeric equilibrium component, in accord with their slightly reduced coupling of $^2J_{H,H}$ = 8.0 Hz.

1-(α-Lithiovinyl)naphthalene (**2**) precipitated after its generation through a Br/Li interchange reaction in pentane and could be purified through washing with pentane. Its constitution was established through protolysis which gave the parent alkene **15** with the same ^{1}H NMR spectrum as that obtained with the initially mentioned, independently synthesized[11] sample. In THF as the solvent, **2** displayed interproton CH_2-β coupling constants of $^2J_{H,H}$ = 9.0 Hz at and below rt (Table S6[11] and entry 9 of Table 1), which was translated by means of eq (2) into the microsolvation number d = 3 THF ligands per Li. This trisolvated ground state of **2**&3THF is monomeric, as shown by its magnitude of $\Delta\delta$(C-α) = +76.2 ppm which equals that of the trisolvated monomer of **1**&3THF (entries 9 and 7). In spite of its single unsubstituted *ortho* position, **2**&3THF appeared to maintain the close to perpendicular α-aryl conformation in analogy with **1**&3THF, judged by $\Delta\delta$(C-*para*) = –11.3 ppm. Many of the further $\Delta\delta$ values (Figure[11] S1) were also similar for **1**&3THF and **2**&3THF, which suggested that π delocalization toward the *para* position was hardly influenced by the 2,2-dimethylpropan-1,3-diyl side-chain in **1**.

This section demonstrated that the ground states of **1** and **2** are trisolvated monomers in THF and that close to perpendicular conformations are common for their monomers and for the dimer of **1**. The α-aryl group of monomeric **1**-CIP rotates across a barrier of $\Delta G^{\ddagger}$(–63 °C) = 9.9(2) kcal mol^{-1} that includes the transitory sacrification of electron delocalization from the Li–C(α) bond into the naphthyl π system. The corresponding rotational barrier of dimeric **1** is lower (albeit unknown) due to the generally weaker π-electron delocalization in dimers; quantitative information on such an effect was reported[4] for the ground states of monomeric and dimeric **6**. The dimeric species of **1**, **3**, and **4** showed no ^{1}H NMR evidence for the cis/trans stereoinversion that is described for the monomers in the followin section.

2. A "Conducted Tour" Migration of $Li^+(THF)_4$ on the π-Route

Due to severe obstruction of the α- and β-routes, the π-route across an α-phenyl group was the most reasonable possibility of Li^+ migration in the derivatives of 2-(α-lithiobenzylidene)-1,1,3,3-tetramethylindane (**7a** in Scheme 2), which was the original system that provided the discovery[15] of Equation (1) and the deduction[1] of the ionic stereoinversion mechanism as

illustrated in Scheme 1. For the planned search for migration-impeding substituents, however, this system was unsuitable because two *ortho*-methyl substituents in **7b** accelerated the stereoinversion process instead of impeding it: The free pseudoactivation enthalpy barrier at 0 °C, $\Delta G_{\psi}^{\ddagger}$(0 °C), of **7b** (entry 2 of Table 2) was lower by 0.9 kcal mol^{-1} than that of **7a** (entry 1). This resulted through intramolecular repulsive interactions[1] by the 1,1,3,3-tetramethyl substituents (energetic elevation of the ground state) and was also perceptible by the bigger barrier reduction from 16.3 kcal mol^{-1} (entry 8) in α-(2,6-dimethylphenyl)vinyllithium (**4**) to 13.35 kcal mol^{-1} for **7a** (entry 1). A comparable inversion-accelerating effect (3 – 5 kcal mol^{-1}) of the bulky 1,1,3,3-tetramethyl armament had previously[18] been noted with *N*-phenyl imines that are sterically equivalent and isoelectronic models of the inverting carbanionic moieties in **4** and **7a**. Therefore, it became necessary to get rid of the accelerating front strain in **7a**,**b** and to use barriers of the less encumbered vinyllithiums such as **4** as references for the wanted substituent effects at the α-aryl groups. This choice restricted our NMR-based rate measurements to the cis and trans β-H atoms that are constitutionally equivalent but stereochemically different (namely, "diastereotopic"): With increasingly rapid cis/trans interconversion ("diastereotopomerization"), the four absorption lines of this $H_2C{=}C$ ^{1}H NMR spectrum will first suffer increasing line broadening and then "coalesce" into a singlet at the averaged resonance position of $(\delta_{cis} + \delta_{trans})/2$.[19] Computer-aided simulations[20] of these rate-dependent line shapes can furnish the pseudo-first-order rate constants k_{ψ} of the pseudomonomolecular (namely, THF-catalyzed) cis/trans stereoinversion. These k_{ψ} values were used for obtaining linear plots of $\ln k_{\psi}$ versus 1000/T, as exemplified for **2**&3THF in Figure 2, and furnished the pseudoactivation parameters $\Delta G_{\psi}^{\ddagger} = \Delta H_{\psi}^{\ddagger} - T\Delta S_{\psi}^{\ddagger}$ of this stereoinversion process as listed in Table 2.

Internal repulsion was indeed much less of a problem in the ground states of our α-arylvinyllithiums **1** – **6**, as shown by the hardly lower barrier (entry 5: 15.79 kcal mol^{-1})[4] of α-(2,6-diisopropylphenyl)vinyllithium (**6**) in comparison with that of **4** (entry 8). Internal repulsion was not totally absent, however, as revealed by a substantially lower barrier[5] of α-(2,6-di-*tert*-butylphenyl)vinyllithium. In spite of the significant differences of **1** – **7b** in their structural details and barriers, the pseudoactivation entropies in entries 1 – 3 and 5 – 8 fall into the narrow range of $\Delta S_{\psi}^{\ddagger} = -23 \pm 3$ cal mol^{-1} K^{-1}, which is characteristic of the ionic mechanism and includes a contribution from the transitory immobilization of the fourth THF ligand that is required for the two THF-separated ion pair intermediates (SSIP) and the

transition state in analogy with Scheme 1. The $\Delta S_{\psi}^{\ddagger}$ value of **1** was also strongly negative, but it was not included in entry 4 because it was numerically less reliable due to the competing decomposition of **1** in THF. Nevertheless, the magnitude of $\Delta G_{\psi}^{\ddagger}$(0 °C) of **1** was reliable since not extrapolated but calculated directly from the k_{ψ} value[11] measured at 0 °C (Table S5c). Comparison of **4** with its 2-methyl congener **3** (entries 8 and 7, Table[11] S7) established that the presence of the second *ortho*-methyl substituent in **4** hardly changed the barrier. This appeared to apply also to the presence of the second *ortho*-isopropyl substituent in **6** (entries 5 and 6) since it must be admitted that the mono-isopropyl congener **5** apparently began to dimerize in THF at the exceptionally high temperatures of up to 92 °C (a common trend of the usually[21] endothermic dimerizations). This became visible for **5** in THF through the published[22] concentration dependence of the rate constants k_{ψ} at 88 °C and the extrapolated, apparent $\Delta G_{\psi}^{\ddagger}$(0 °C) values that increased with increasing concentrations of **5** (footnotes "b" in Tables[11] S8–S10). Although measured with the most dilute (most deaggregated) THF solution of **5** (0.3 M), the barrier denoted in entry 6 is probably still a little too high, so that the second *ortho*-isopropyl group in **6** hardly changed the barrier observed for **5**. On the basis of such an insignificant influence of additional *ortho*-alkyl substituents, the 0.93 kcal mol^{-1} *higher* barrier of **1** (entry 4) relative to that of 1-(α-lithiovinyl)naphthalene (**2** in entry 3) cannot be due to the *ortho*-positioned CH_2-3 group in **1**. This left the *meta*-positioned CH_2-1 group as the responsible obstacle that impeded Li^+ migration; analogously, a preferred passage across the *meta*-position around *ortho*-positioned *tert*-butyl groups was already suspected previously.[23] As outlined in Section 1 and shown by the $\Delta\delta$(*para*) values in entries 7 – 9 of Table 1, the 2,2-dimethylpropan-1,3-diyl side chain appeared to have almost no electronic influence on the relevant charge gradient toward the *para* position. Therefore, this barrier difference between **1** and **2** is ascribed to a steric effect of the CH_2-1 part of that side chain. Such a retardation by a *meta*-positioned substituent would not be expected on the α- or β-routes, which leaves the π-route as an unrefuted possibility.[24]

This section demonstrated the possibility of $Li^+(THF)_4$ migration on the π-route in 1-(α-lithiovinyl)naphthalene (**2**) during cis/trans stereoinversion by the pseudomonomolecular, ionic mechanism: Even without the β-route-obstructing 1,1,3,3-tetramethyl substituents of **7a**,**b** and despite an inviting unobstructed β-route in **2**, the migrating cation preferred to be

conducted along the charge gradients on the π-route, presumably with the aim of surmounting the aryl rim in the *meta*/*para* region.

Conclusion

The thermal ground state of 4-(α-lithiovinyl)-2,2-dimethylbenz[f]indane (**1**) is a disolvated dimer in *t*BuOMe and other non-THF solvents but a trisolvated monomer in THF. The delocalization of electric charge from the Li–C(α) bond into the α-aryl part of the monomer provides for a close to perpendicular orientation of the aryl and the C(α)=C(β) double-bond planes with a 9.9(2) kcal mol^{-1} barrier against aryl rotation about the C(α)–C(4) bond. These properties qualified **1** to serve for the following investigations.

The stereoinversion barriers of $\Delta G_{\psi}^{\ddagger}(0\ °C) \approx 16$ kcal mol^{-1} in THF are almost equal (Table 2) for α-arylvinyllithiums with 2,6-dimethylphenyl (**4**), 2-methylphenyl (**3**), 2,6-diisopropylphenyl (**6**), and 2-diisopropylphenyl (**5**) groups. Thus, one unsubstituted *ortho* position (in **3** and **5**) did not lower the $\Delta G_{\psi}^{\ddagger}(0\ °C)$ barrier as far as the ground states were truly monomeric. (**5** tended perceptively[22] to populate its dimeric species at the higher temperatures and concentrations.) At first sight, this might be taken as evidence for the α- or β-route of $Li^{+}(THF)_4$ migration and would then imply that these routes were hardly sensitive to a second small *ortho*-alkyl substituent and certainly even less so to small *meta*-alkyl groups. If so, the increase from $\Delta G_{\psi}^{\ddagger}(0\ °C) = 12.94(1)$ kcal mol^{-1} for **2** to 13.87(1) kcal mol^{-1} for **1** would be unexpected. On the other hand, a π-route may also be hardly sensitive to a second small *ortho*-alkyl group but can of course be expected to sense obstruction by a small *meta*-positioned alkyl substituent, as observed for **1**. We conclude that the π-route is an appropriate stereoinversion pathway for **2** (as it was for **7a** and **7b**); there appears to be no evidence against the π-route along the similar π-charge gradients ("conducted tour") in other α-arylvinyllithiums.

However, a corresponding deduction for **1** would expect that an even more migration-impeding derivative of **1** should exhibit a still higher stereoinversion barrier; if not, both **1** and its prospective derivative might be suspected to have changed over to $Li^{+}(THF)_4$ migration across the α- or β-regions.

Experimental Section

General. The utilized techniques and spectrometers were desribed previously.[15] α-Arylvinyllithiums **1** – **5** were studied either in commercial [D_8]toluene or in nondeuteriated, anhydrous ethereal solvents containing up to ca. 15% (v/v) of dry [D_{12}]cyclohexane. ^{1}H and ^{13}C NMR shifts were referenced to internal $SiMe_4$. NMR abbreviations were d = doublet, m = multiplet, q = quartet, qi = quintet, quat = quaternary, sept = septet, t = triplet.

4-(α-Lithiovinyl)-2,2-dimethylbenz[f]indane (1&*t*BuOMe). A dry NMR tube (5 mm) was charged with the bromoalkene **13** (50 mg, 0.17 mmol) and anhydrous *t*BuOMe (0.5 mL). This solution was cooled under argon gas cover to –30 °C and treated with *n*Bu^{6}Li (0.18 mmol) in cyclopentane (0.122 mL) or with unlabelled *n*BuLi (0.18 mmol) in hexane (0.079 mL). The open NMR tube with the yellow solution was warmed up to rt and immediately placed in a large Schlenk flask (still and always unter argon gas) and fixed in a tilted position for the cautious, very slow evaporation of the solvent and all volatiles at rt down to a pressure of ca. 0.01 mbar. After the slow admission of dry argon gas, the non-volatile residue was cooled and dissolved in the chosen solvent with a trace of $SiMe_4$ (and [D_{12}]cyclohexane, if necessary), then stored at –20 °C and kept only briefly at higher temperatures. ^{1}H NMR of *dimeric* **1** ([D_8]toluene, 400 MHz, 25 °C) δ 1.21 (s, 6H, 2 × 2-CH_3), 2.82 (s, 2H, CH_2-3), 2.85 (s, 2H, CH_2-1), 6.20 (broadened d, ^2J = 5.8 Hz, 1H, β-H trans to α-aryl), 6.50 (d, ^2J = 5.8 Hz, 1H, β-H cis), 7.24 (s, 1H, 9-H), 7.24 (obscured t, 1H, 6-H), 7.29 (t, ^3J = 7.3 Hz, 1H, 7-H), 7.71 (d, ^3J = 7.8 Hz, 1H, 8-H), 8.34 (d, ^3J = 8.0 Hz, 1H, 5-H) ppm, assigned through decoupling (see ^{13}C) and comparison with **1** in *t*BuOMe; ^{1}H NMR of *dimeric* **1** (*t*BuOMe, 400 MHz, 25 °C) δ ca. 1.14 (obscured s, 2 × 2-CH_3), 2.70 (s, 2H, CH_2-3), 2.77 (d, $^4J \leq 1.0$ Hz, CH_2-1), 5.89 (broadened d, ^2J = 6.0 Hz, 1H, β-H trans to α-aryl), 6.14 (d, ^2J = 6.0 Hz, 1H, β-H cis), 7.06 (s, 1H, 9-H), 7.08 (td, ^3J = 8.1 Hz, ^4J = 1.1 Hz, 1H, 6-H), 7.14 (td, ^3J = 8.1 Hz, ^4J = 1.1 Hz, 1H, 7-H), 7.52 (d, ^3J = 7.5 Hz, 1H, 8-H), 8.07 (d, ^3J = 8.1 Hz, 1H, 5-H) ppm, assigned through HOESY cross peaks of ^{6}Li with 5-H and trans-H (and also with both solvent signals) and confirmed through selective {^{1}H} decoupling as follows: {5-H} → 6-H as a d ca. 8 Hz, and {8-H} → 7-H as a d ca. 7 Hz; ^{1}H NMR of *monomeric* **1** (THF, 400 MHz, –85 °C) δ 1.01 and 1.18 (2 × br s, 3+3H, 2 × 2-CH_3), 2.44 and 2.68 (AB system, 2 × d, ^2J = 15 Hz, 1+1H, CH_2-3), 2.62 and 2.76 (AB system, 2 × d, ^2J = 14 Hz, 1+1H, CH_2-1), 5.32 (d, ^2J = 8.9 Hz, 1H, β-H trans to aryl), 5.75 (d, ^2J = 8.9 Hz, 1H, β-H cis), 6.75 (s, 1H, 9-H), 6.93 (t, ^3J = 7.4 Hz, 1H, 6-H), 7.04 (t, ^3J = 7.4 Hz, 1H, 7-H), 7.40 (d, ^3J = 7.5 Hz, 1H, 8-H), 8.00 (d, ^3J =

7.6 Hz, 1H, 5-H) ppm, compare Table 5b for the temperature dependence; ^{13}C NMR of *dimeric* **1** ([D$_8$]toluene, 100.6 MHz, 25 °C) δ 29.4 (qm, ^1J = 125 Hz, 2 × 2-CH$_3$), 39.8 (unresolved, C-2), 48.5 (t, ^1J = 128 Hz, CH$_2$-3), 48.6 (t, ^1J = 128 Hz, CH$_2$-1), 116.2 (ddm, ^1J = 156 Hz, C-9), 120.5 (broadened t, ^1J = 147 Hz, CH$_2$-β), 122.7 (dd, ^1J = 158 Hz, ^3J = 8 Hz, C-6), 124.1 (obscured dd, ^3J = 8 Hz, C-7), 127.1 (obscured dd, ^3J = 6 Hz, C-5), 128.1 (obscured dt, ^3J = 6 Hz, C-8), 129.3 (q, ^3J = 6 Hz, C-4a), 130.6 (dm, ^3J = 6 Hz, C-3a), 134.8 (t, ^3J = ca. 6 Hz, C-8a), 142.4 (broad, C-9a), 151.6 (dm, ^3J = 15 Hz, C-4 coupling with β-H trans), 201.1 (unresolved, C-α, at –55 °C as a qi 1:2:3:2:1 with $^1J_{C,Li}$ = 7.5 Hz) ppm, assigned through the $J_{C,H}$ coupling patterns and selective {^{1}H} decoupling as follows: {2-CH$_3$} → C-2 as a qi with ^2J = ca. 2 Hz; {CH$_2$-1/-3} → C-3a as a d with ^3J = 6 Hz, C-9 as a dd with ^3J = 5 Hz, C-9a as a s; {β-H trans} → C-4 and C-α narrowed; {β-H cis} → C-4 as a d with ^3J = 14 Hz; {6-/7-/9-H} → C-4a as a s, C-8a as a d with ^3J = 4.5 Hz; {8-H} → C-4a and C-8a narrowed, C-6 as a ^1J d; {5-H} → C-7 as a ^1J d, C-8a as a d with ^3J = 6 Hz; ^{13}C NMR of *dimeric* **1** (*t*BuOMe, 100.6 MHz, 25 °C) δ 29.5 (qm, ^1J = 125 Hz, > qi with ^3J = 4.5 Hz, 2 × 2-CH$_3$), 40.0 (m, ^2J = 3 Hz, C-2), 48.5 (obscured, CH$_2$-3), 48.8 (obscured, CH$_2$-1), 115.7 (dm, ^1J = 156 Hz, C-9), 119.6 (t, ^1J = 148 Hz, CH$_2$-β), 122.4 (dd, ^1J = 158 Hz, ^3J = 8.5 Hz, C-6), 124.0 (dd, ^1J = 158 Hz, ^3J = 8.8 Hz, C-7), 127.2 (dd, ^1J = 157 Hz, ^3J = 7.0 Hz, C-5), 127.9 (dt, ^1J = 156 Hz, ^3J = 6.0 Hz, C-8), 129.3 (q, ^3J = 6.1 Hz, C-4a), 130.2 (unresolved, C-3a), 134.8 (dd, ^3J = 7.5 Hz and ca. 5 Hz, C-8a), 142.3 (m, apparent J = 4.3 Hz, C-9a), 152.0 (tm, ^3J = 12.8 Hz, C-4), 201.3 (unresolved, C-α) ppm, assigned through the $J_{C,H}$ coupling patterns and selective {^{1}H} decoupling as follows: {CH$_2$-1/-3} → C-3a as a ^3J d, C-9a as a sharp s; {β-H trans} → C-4 and C-α narrowed; {β-H cis} → C-α narrowed, C-4 less narrowed; {6-/7-/9-H} → C-4a narrowed, C-5 as a sharp ^1J d, C-8a as a ^3J d; {8-H} → C-4a narrowed, C-6 as a sharp ^1J d; {5-H} → C-7 as a sharp ^1J d, C-8a as a broad ^3J d; ^{13}C NMR of *monomeric* **1** (THF, 100.6 MHz, –55 °C) δ 29.5 (q, 2 × 2-CH$_3$), 39.9 (quat, C-2), 48.0 (t, CH$_2$-3), 48.9 (t, CH$_2$-1), 111.2 (d, CH-9), 111.4 (t, CH$_2$-β), 120.6 (d, C-6), 123.4 (d, CH-7), 126.1 (quat, C-4a), 127.2 (d, CH-5), 128.4 (d, CH-8), 128.6 (quat, C-3a), 134.6 (quat, C-8a), 142.2 (quat, C-9a), 157.3 (quat,C-4), 210.9 (quat, C-α) ppm, assigned through DEPT and comparisons with **1** in *t*BuOMe, compare Table 5a for the temperature dependence; α-aryl rotation of *monomeric* **1** in THF: The pairwise geminal protons of CH$_2$-1 and CH$_2$-3 and the diastereotopic 2-C*H*$_3$ groups displayed separate chemical shifts at –85, –94, and –103 °C (Table S5b). These 400

MHz spectra of CH_2-1 with $\Delta\nu$ = 60 Hz and ^2J = 14 Hz, of CH_2-3 with $\Delta\nu$ = 96 Hz and ^2J = 15 Hz, and of 2-CH_3 with $\Delta\nu$ = 72 Hz and ^2J = 0 Hz coalesced at estimated temperatures of –66(3), –60(5), and –66(3) °C, respectively. The rate constants k_c at these temperatures were calculated from $k_c = \pi(\Delta\nu^2 + 6J^2)^{0.5}/2^{0.5}$, yielding the rotational ΔG barriers of 9.9(2), 9.9(2), and 10.0(3) kcal mol^{-1}, respectively.

1-(α-Lithiovinyl)naphthalene (2). 1-(α-Bromovinyl)naphthalene[25] (4.45 g, 19.1 mmol) and pentane (5 mL) were stirred in a Schlenk flask at –78 °C under argon gas cover during the slow introduction of *n*Bu^{6}Li (22.9 mmol) in pentane (18.4 mL). The Br/Li interchange reaction was almost complete after 25 min at rt, whereupon the product **2** began to precipitate completely within less than 4 hours. The supernatant was withdrawn by pipette, and the precipitate was washed with dry pentane (2×), then evaporated to dryness at rt in vacuo: yield, 2.0 g (66%). ^{1}H NMR (THF, 80 MHz, –62 °C) δ 5.20 (d, ^2J = 9.0 Hz, 1H, β-H trans to α-aryl), 5.75 (d, ^2J = 9.0 Hz, 1H, β-H cis), 6.37 (dd, ^3J = 6 Hz, ^4J = 1.2 Hz, 1H, 2-H), ca. 7.0 and ca. 7.3 (2 × obscured m, 3-/4-/5-/6-/7-H), 8.09 (m, 1H, 8-H) ppm, assigned through comparison with **1**, **3** and **5**, see Table S6 for the temperature dependence; ^{13}C NMR (THF, 25.15 MHz, –47 °C) δ 112.0 (t, CH_2-β), 113.3 (d, C-2), 116.7 (d, C-4), 121.6 (dd, C-7), 124.3 (d, C-6), ca. 126.2 (d, C-3), 126.7 (d, C-8), 127.2 (d, C-5), 130.2 (quat, C-8a), 134.2 (quat, C-4a), 163.2 (quat, C-1), 210.5 (quat, C-α) ppm, assigned through gated and off-resonance decoupling and comparison with **1**; no temperature and concentration dependence detected between –38 and –96 °C.

2,2-Dimethylbenz[f]indan-4-carboxylic Acid (10). *n*BuLi (12.2 mmol) in hexane (4.4 mL) was added dropwise to a stirred solution of 4-bromo-2,2-dimethylbenz[f]indane[8] (**8**, 3.28 g, 11.9 mmol) in anhydrous Et_2O (20 mL) at –30 °C under inert gas cover. The mixture change its color from green to yellow, then orange-red during the addition. After 10 min at rt, the solution was poured onto solid CO_2 and warmed up to rt. The yellow mixture was completely dissolved in Et_2O and a sufficient amount of conc. (6 M!) aqueous NaOH. The aqueous layer was washed with Et_2O (to be discarded), then acidified with conc. HCl, and extracted with CH_2Cl_2 (3 ×; not Et_2O!). The combined CH_2Cl_2 extracts were washed with distilled water until neutral, dried over Na_2SO_4, filtered, and evaporated to yield the crude acid **10** (2.30 g, 80%). The analytically pure sample was obtained through recrystallization first from chloroform, then from toluene, and a final sublimation at 150–170 °C (bath temp.)/0.15 mbar; mp 188–190 °C. ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.20 (s, 6H, 2 × 2-CH_3),

2.88 (s, 2H, CH_2-3), 3.20 (s, 2H, CH_2-1), 7.60 (m, 2H, 7-/6-H), 7.71 (s, 1H, 9-H), ca. 7.78 (m, 1H, 8-H), 8.60 (m, 1H, 5-H), 11.90 (broad s, 1H, CO_2H) ppm, assigned through comparison with the alkene **14**; IR (KBr) ν 3300–2400 (broad O–H), 3056, 2961, 2899, 2866, 1689 (s), 1631 (w), 1425, 1248, 1217, 746 cm^{-1}. Anal. calcd for $C_{16}H_{16}O_2$ (240.30): C, 79.97; H, 6.71. Found: C, 80.65; H, 6.62.

4-Acetyl-2,2-dimethylbenz[f]indane (11). Methyllithium (12.5 mmol) in Et_2O (8.67 mL) was added dropwise to a stirred suspension of the acid **10** (1.00 g, 4.16 mmol) in anhydrous Et_2O (7.0 mL) at –20 °C under argon gas cover. As expected, the brisk evolution of CH_4 ceased after the addition of the initial third (1 equiv) of methyllithium. The finally orange-colored solution became red during one hour of refluxing at 40 °C, whereafter it was re-cooled to –10 °C and treated with $ClSiMe_3$ (0.63 mL, 5.00 mmol) and then stirred at rt for one hour. The resultant, colorless suspension was cooled in ice during the addition of water and Et_2O (40 mL). The Et_2O layer was shaken with aqueous NaOH (2 M, 15 mL), then distilled water (2 × 10 mL), and then kept waiting for further workup. The combined aqueous extracts were shaken with Et_2O (15 mL, also kept waiting), acidified with conc. HCl and shaken with Et_2O (3 ×). The latter three Et_2O phases were combined, washed with distilled water until neutral, dried over $MgSO_4$, filtered, and evaporated to leave the unconsumed portion of the acid **10** (130 mg, 13%). The two waiting Et_2O layers were combined, dried over $MgSO_4$, filtered, and concentrated to yield the non-acidic product fraction (830 mg, < 84%). Pure **11** crystallized from low-boiling petroleum ether (2 ×) with mp 58–60 °C (486 mg, 49%). ^{1}H NMR ($CDCl_3$ + CH_2Cl_2 1:2, 400 MHz, 25 °C) δ 1.16 (s, 6H, 2 × 2-CH_3), 2.60 (s, 3H, acetyl-CH_3), 2.85 (s, 2H, CH_2-3), 2.86 (d, ^2J = 1.3 Hz to 9-H, 2H, CH_2-1), 7.42 (m, 2H, 6-/7-H), 7.66 (unresolved, 1H, 9-H), 7.77 (m, 2H, 5-/8-H) ppm, assigned through the ^4J splitting of CH_2-1 and comparison with the alkene **14**; at –103 °C: δ 1.15, 2.69, 2.88, 2.91, 7.49,7.74, 7.84 (8-H) and 7.88 (d, 1H, 5-H) ppm; ^{13}C NMR ($CDCl_3$ + CH_2Cl_2 1:2, 100.6 MHz, 25 °C) δ 28.3 (q of octets, ^1J = 125 Hz, ^3J = 4.3 Hz, 2 × 2-CH_3), 32.3 (sharp q, ^1J = 128 Hz, acetyl-CH_3), 41.0 (> sept, ^2J = 3.7 Hz, C-2), 47.07 (tm, ^1J = 130 Hz, CH_2-1), 47.13 (tm, ^1J = 130 Hz, CH_2-3), 124.6 (dm, ^1J = 158 Hz, C-5), 124.9 (ddt, ^1J = 159 Hz, ^3J = 5.0 and 2.5 Hz, C-9), 125.5 (dd, ^1J = 160 Hz, ^3J = 8.5 Hz, C-7), 126.1 (dd, ^1J = 160 Hz, ^3J = 8.5 Hz, C-6), 128.2 (dm, ^1J = 158 Hz, C-8), 128.7 (m, ^3J = ca. 5 Hz, C-4), 133.4 (m, C-4a), 135.5 (m, C-8a), 139.8 (dtm, ^3J = 7.5 and 5.5 Hz, C-3a), 143.1 (tt, ^3J = 5.5 Hz, ^2J = 3.5 Hz, C-9a), 205.9 (q, ^2J = 5.8 Hz, CO) ppm; at –103 °C: δ 28.1, 32.7, 41.3, 46.3, 47.0, 124.4,

125.3, 125.5, 126.2, 128.0, 128.1, 132.7, 134.2, 140.6, 143.1, 207.2 ppm, assigned through comparison with the alkene **14**, the $J_{C,H}$ coupling patterns, and the following selective {^{1}H} decoupling experiments: {2-CH_3} → 2-CH$_3$ as a qi with ^3J = ca. 4 Hz to both CH$_2$; {CO–CH_3} → CO as a s; {CH$_2$-1/-3} → 2-CH$_3$ as a qq with ^3J = 4.5 Hz, C-2 as a septet with ^2J = 4 Hz, C-3a as a d with ^3J = 7.5 Hz, C-9 as a dd with ^3J = 5.2 Hz to 8-H, C-9a as a s; {6-/7-H} → C-8 as a dd (^3J to 9-H); {9-H} → C-3a as a t with ^3J = 5 Hz, C-4a narrowed; {5-/8-H} → C-3a as a t, C-4a narrowed, C-5 and C-8 as two narrow ^3J t; IR (KBr) ν 3051 (w), 2954, 2929, 2864, 1683, 1464, 1423, 1364, 1220, 1204, 1154, 774, 753 cm^{-1}. Anal. calcd for C$_{17}$H$_{18}$O (238.33): C, 85.67; H, 7.61. Found: C, 85.84; H, 7.65.

4-(α-Bromovinyl)-2,2-dimethylbenz[f]indanen (13). A solution of 2-bromo-1,3,2-benzodioxaphosphole[10] (0.882 mL, 6.97 mmol) in anhydrous chloroform (1.5 mL) was cooled in an ice bath under inert gas cover and stirred during the dropwise addition of elemental bromine (0.321 mL, 6.27 mmol). After further stirring at rt for ca. 25 min, the resultant solution of 2,2,2-tribromo-1,3,2-benzodioxaphosphole (**12**) was stirred in an ice bath and treated dropwise with a solution of 4-acetyl-2,2-dimethylbenzo[f]indane (**11**, 830 mg, 3.48 mmol) in anhydrous chloroform (0.5 mL). The mixture was stirred at rt for at least 15 min for the complete consumption of ketone **11**, then diluted with pentane (4 mL) and poured into ice-cold aqueous NaOH (2 M, 15 mL). After not more than 15 min at rt (so to avoid the hydrolysis of **13** that would regenerate ketone **11**), the aqueous layer was extracted with pentane (2 × 5 mL) and then discarded. The three pentane phases were combined and shaken with aqueous NaOH (3 × 5 mL, to be discarded) and then washed with distilled water until neutral, dried over MgSO$_4$, filtered, and concentrated. The crude material (857 mg) was filtered through a column of silica gel (6 cm, 10 g) with petroleum ether (80 mL) to give almost pure **13** (411 mg, 39%) that crystallized from low-boiling petroleum ether with mp 71–73 °C. ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C, Table S1b) δ 1.17 (s, 6H, 2 × 2-CH$_3$), 2.83 and 2.88 (AB system, ^2J = 16 Hz, 2H, CH$_2$-3), 2.87 (d, ^4J = 1.2 Hz, 2H, CH$_2$-1), 5.83 (d, ^2J = 1.4 Hz, 1H, β-H cis to α-aryl), 6.10 (d, ^2J = 1.4 Hz, 1H, β-H trans), 7.40 (ddd, ^3J = 8.1 and 6.9 Hz, ^4J = 1.5 Hz, 1H, 7-H), 7.46 (ddd, ^3J = 8.3 and 6.9 Hz, ^4J = 1.5 Hz, 1H, 6-H), 7.59 (unresolved, 9-H), 7.75 (d, ^3J = 8.1 Hz, 1H, 8-H), 8.04 (d, ^3J = 8.3 Hz, 1H, 5-H) ppm, assigned through the ^4J coupling of CH$_2$-1 with 9-H, the coupling of trans-H with C-4 (see below), and comparison with the alkene **14**; ^{13}C NMR (CDCl$_3$, 100.6 MHz, 25 °C, Table S1a) δ 28.32 and 28.44 (2 × qm, ^1J = 125 Hz, ^3J = ca. 4 Hz, 2 × 2-CH$_3$), 40.3 (> nonet, ^2J =

3.6 Hz, C-2), 46.6 (tm, ^1J = 130 Hz, CH_2-1), 47.6 (t, ^1J = 129 Hz, CH_2-3), 122.2 (sharp dd, apparent ^1J = 159 and 165 Hz, CH_2-β), 123.8 (dm, ^1J = 158 Hz, C-9), 124.8 (dd, ^1J = 159 Hz, ^3J = 6.9 Hz, C-5), 125.2 (dd, ^1J = 160 Hz, ^3J = 8.4 Hz, C-7), 125.4 (dd, ^1J = 160 Hz, ^3J = 8.2 Hz, C-6), 126.6 (t, ^2J = 6.5 Hz, C-α), 127.7 (dt, ^1J = 158 Hz, ^3J = 6.0 Hz, C-8), 129.7 (q, ^3J = 6.7 Hz, C-4a), 133.1 (unresolved, C-4 and C-8a, separated at –55 °C), 141.4 (unresolved, C-3a), 142.5 (tt, ^3J = ca. 5 Hz, ^2J = ca. 3.5 Hz, C-9a) ppm, assigned through comparison with the alkene **14** and selective {^{1}H} decoupling as follows: {2-CH_3} → C-2 as a qi with ^2J = 3.2 Hz, CH_2-1 as a tq with ^3J = 3.0 Hz but CH_2-3 as a tt with ^3J = 2.6 Hz; {CH_2-1/-3} → C-2 as a septet with ^2J = 3.7 Hz, C-3a as a d with ^3J = 7.4 Hz, C-9 as a dd with ^3J = ca. 4.8 Hz, C-9a as a s, CH_2-1 as an octet with ^3J = 4.0 Hz but CH_2-3 as septet with ^3J = 4.3 Hz; {β -H trans} → C-4 narrowed, C-α as a d wih ^2J = 4.8 Hz; {β-H cis} → C-α as a d with ^2J = 5.5 Hz; {6-/7-/8-/9-H} → C-4a as a s, C-8a as a d with ^3J = ca. 5.5 Hz to 5-H; {8-H} → off-resonance decoupling increased in the sequence of 5-/8-/9-/6-/7-H; {5-H} → C-6 as a dd, C-7 as a sharp d, C-8a as a d with ^3J = ca. 5 Hz, off-resonance decoupling decreased in the sequence of 5-/8-/9-/6-/7-H; IR (KBr) ν 3060 (w), 2954, 2927, 1629, 1423, 1363, 1107, 895, 741 (s) cm^{-1}. Anal. calcd for $C_{17}H_{17}Br$ (301.23): C, 67.78; H, 5.69; Br, 26.53. Found: C, 67.73; H, 5.52; Br, 27.38. α-Aryl rotation in $CDCl_3$: The diastereotopic protons of CH_2-3 only displayed the anticipated two doublets with Δν = 21.5 Hz and ^2J = 16 Hz at rt under 400 MHz; this AB system coalesced at 48(3) °C. The 2-CH_3 groups showed only the expected ^{13}C nonequivalence (Δν = 13.4 Hz at 100.6 MHz) that coalesced at 35(3) °C. The rate constants k_c at 48 and 35 °C were calculated from $k_c = \pi(\Delta\nu^2 + 6J^2)^{0.5}/2^{0.5}$, yielding the rotational $\Delta G^{\ddagger}$ barriers of 15.9(2) and 16.0(1) kcal mol^{-1}, respectively.

4-Vinyl-2,2-dimethylbenz[f]indane (14). The crude protolysis products of several samples of **1** were combined and prepurified through distillation at 85–100 °C (bath temp.)/0.01 mbar, followed by adsorption on a column (5 cm) of silica gel (2 g, 100–200 μm) and elution with low-boiling petroleum ether (forerun of 7 mL discarded). The eluate (67 mg) was crystallized from EtOH at –70 °C to yield pure **14** (53 mg) with mp 27–28 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 1.16 (s, 6H, 2 × 2-CH_3), 2.86 (d, ^4J = 1.1 Hz, 2H, CH_2-1), 2.91 (s, 2H, CH_2-3), 5.51 (dd, ^3J = 17.8 Hz, ^2J = 1.9 Hz, 1H, β-H cis to α-aryl), 5.67 (dd, ^3J = 11.5 Hz, ^2J = 1.9 Hz, 1H, β-H trans), 7.19 (dd, ^3J = 17.8 Hz, ^3J = 11.5 Hz, 1H, α-H), 7.38 (m, 1H, 7-H), 7.40 (m, 1H, 6-H), 7.54 (s, 1H, 9-H), 7.74 (m, 1H, 8-H), 8.06 (m, 1H, 5-H) ppm, at –65 °C δ

1.15, 2.88, 2.93, 5.53, 5.72, 7.28, 7.46, 7.47, 7.60, 7.81, 8.08, assigned through the ^4J coupling of CH_2-1 with 9-H, DQCOSY, and the following NOESY correlations: 1-H ↔ 9-H ↔ 8-H ↔ 7-H, 3-H ↔ α-H ↔ 5-H ↔ 6-H; ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25 °C) δ 28.5 (q of octets, ^1J = 125 Hz, ^3J = 4.5 Hz, 2 × 2-CH_3), 40.3 (> septet, ^2J = 3.6 Hz, C-2), 47.6 (tm, ^1J = 129 Hz, CH_2-1), 47.9 (tm, ^1J = 129 Hz, CH_2-3), 119.8 (sharp t, ^1J = 158 Hz, CH_2-β), 122.3 (dm, ^1J = 158 Hz, C-9), 124.3 (dm, ^1J = 159 Hz, C-5), 124.7 (dd, ^1J = 159 Hz, ^3J = 8.5 Hz, C-7), 124.9 (dd, ^1J = 159 Hz, ^3J = 8.5 Hz, C-6), 127.9 (dm, ^1J = 157 Hz, C-8), 130.8 (unresoved, C-4a), 130.9 (unresolved, C-4), 133.2 (m, C-8a), 133.7 (sharp d, ^1J = 153 Hz, C-α), 140.8 (unresolved, C-3a), 142.9 (sharp t, ^3J = 4.5 Hz, C-9a) ppm, at –65 °C δ 28.2, 40.4, 47.1, 47.6, 120.1, 122.1, 123.9, 124.7, 124.8, 127.7, 130.1, 130.2, 132.5, 133.2, 140.8, 143.0 ppm, assigned through HETCOR and the following ^2J and ^3J COLOCS (7 Hz) cross-peaks. ^2J: C-α ↔ β-*H* cis, C-2 ↔ 2-C*H*$_3$ and both C*H*$_2$-1/-3, C-3a ↔ C*H*$_2$-3, C-5 ↔ 6-*H*, C-9a ↔ C*H*$_2$-1; ^3J: 2-C*H*$_3$ ↔ C-1/-3 and 2-*C*H$_3$, C*H*$_2$-1 ↔ C-3/-9 and 2-*C*H$_3$, C*H*$_2$-3 ↔ C-1 and 2-*C*H$_3$, β-*H* trans ↔ C-4, 5-*H* ↔ C-7/-8a, 6-*H* ↔ C-4a/-8, 7-*H* ↔C-5 and C-8a, 8-*H* ↔ C-4a/-6/-9, 9-*H* ↔ C-3a/-4a/-8; IR (film) ν 3067 (w), 2953, 2925, 2865, 2833, 1506, 1465, 1425, 1366, 996, 920, 872, 777, 746 (s), 699 cm^{-1}. Anal. calcd for $C_{17}H_{18}$ (222.33): C, 91.84; H, 8.16. Found: C, 91.67; H, 7.97.

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[16] See p 6318 and Figure 1 in Ref. [2].

[17] Formulas **15** and **16** in Figure 1 of Ref. [7].

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[19] An example of such temperature-dependent line shapes and their simulations may be viewed in Section C and Figure 5 on pp 1042–1043 of reference [4].

[20] For references to pertinent programs, see p 2526 of reference [5].

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[23] On p 2527 of reference [5].

[24] Further arguments against alternative migration modes were presented in reference [1] and on pp 6319–6320 of reference [2].

[25] Compound **11s** in Ref. [10].

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Scheme 1. Possibilities (α-, β-, and π-route) of $Li^{+}(THF)_4$ migration in the ionic stereoinversion mechanism of **1** in THF; aryl = 2,2-dimethylbenz[f]indan-4-yl.

Scheme 2. The known α-arylalkenyllithiums **3** – **7** to be compared with **1** and **2**.

Scheme 3. Preparations of the Precursors and Derivatives of **1**.

Figure 1. Partial ^{13}C NMR spectra of 4-(α-lithiovinyl)-2,2-dimethylbenz[f]indane (**1**): a) In *t*BuOMe at –70 °C, o = alkene **14**; b) in THF at –85 °C (alkene **14** polymerized).

Figure 2. Temperature dependence of the natural logarithms (ln) of the pseudo-first-order stereoinversion rate constants k_ψ (s^{-1}) of 1-(α-lithiovinyl)naphthalene (**2**&3THF) in THF.

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Table 1. Microsolvation numbers *d*, NMR coupling constants $^2J_{H,H}$ [Hz] of CH_2-β, and lithiation shifts $\Delta\delta = \delta(RLi) - \delta(RH)$ of the α-arylalkenyllithiums **1**–**5** in five solvents.

Entry No.	Com-pound	α-Aryl Group	Solvent (equiv of B)[a]	Agg [b]	*d*	$^2J_{H,H}$ (at °C) [c]	Lithiation shifts $\Delta\delta$ [ppm]					Temp. °C [d]	Ref.
							C-α	C-β	C-*ipso*	C-*para*	*para*-H		
1	**1**	benzindane	toluene (2)	D	1	5.8 (≤ +25)	+66.5 [e]	+0.9	+20.0	–6.7	–0.12 [f]	+25	[g]
2	**1**	benzindane	*t*BuOMe	D	1	6.0 (≤ +25)	+66.8	–0.1	+20.3	–7.2	–0.40	+25	[g]
3	**1**	benzindane	c-C_5H_{10} (1)	D	1	–	+66.1	+1.0	+19.9	–6.7	–0.34	+25	[g]
4	**4**	2,6-$(CH_3)_2$	toluene (1.3)	D	1	5.7 (≤ +25)	+68.2	–3.6	+19.6	–6.5	–0.02 [f]	–84	[2]
5	**4**	2,6-$(CH_3)_2$	*t*BuOMe	D	1	5.7 (≤ –7)	+68.1	–3.6	+19.4	–7.0	–0.43	–40	[2]
6	**3**	2-CH_3	Et_2O	D	1	–	+67.9	+5.0	+21.8	–6.1	–	–70	[7]
7	**1**	benzindane	THF	M	3	8.9 (≤ –40)	+76.2	–8.2	+25.6	–11.6	–0.72	–30	[g]
8	**4**	2,6-$(CH_3)_2$	THF	M	3	8.8 (≤ +2)	+76.4	–10.9	+24.2	–11.0	–0.76	–89	[2]
9	**2**	naphthyl-1	THF	M	3	9.0 (≤ +28)	+76.2	–5.0	+27.7	–11.3	–	–47	[g]
10	**3**	2-CH_3	THF	M	3	8.0 (+25)	+77.3	–4.7	+.8	–10.4	–0.61	–38	[7]
11	**5**	2-$CH(CH_3)_2$	THF	M	3	8.0 (+25)	+75.1	–3.9	+26.7	–10.6	–0.60	–60	[7]

[a] Equivalents of B = *t*BuOMe present. [b] "M" = monomer, "D" = dimer. [c] Temperature of this $^2J_{H,H}$ value. [d] Temperature of determinations of $\Delta\delta = \delta(RLi) - \delta(RH)$. [e] Quintet (1:2:3:2:1) at –55 °C with $^1J(^{13}C,^6Li) = 7.5$ Hz. [f] Special effect of toluene. [g] This work. …

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Table 2. Pseudoactivation parameters $\Delta G_{\psi}^{\ddagger}$ (kcal mol^{-1} at 0 °C), $\Delta H_{\psi}^{\ddagger}$ (kcal mol^{-1}), and $\Delta S_{\psi}^{\ddagger}$ (cal mol^{-1} K^{-1}) of the cis/trans diastereotopomerization rates of monomeric alkenyllithiums **1** – **7** in THF.

Entry	Compd.	Aryl group[a]	$\Delta G_{\psi}^{\ddagger}$(0 °C)	$\Delta H_{\psi}^{\ddagger}$	$\Delta S_{\psi}^{\ddagger}$	HT[b]	Ref.
1	**7a**	phenyl[c]	13.35 (±0.03)	6.63 (±0.24)	–24.6 (±1.0)	0.0	[1]
2	**7b**	2,6-Me_2Ph[d]	12.47 (±0.01)	6.77 (±0.18)	–20.8 (±0.7)	+5	[1]
3	**2**	naphthyl-1	12.94 (±0.01)	6.9 (±0.1)	–22.3 (±0.4)	+28	[e]
4	**1**	benzindane	13.87 (±0.01)	–	–	+15	[e]
5	**6**	2,6-ipr$_2$Ph	15.79 (±0.07)	9.3 (±0.4)	–23.6 (±1.2)	+71	[4]
6	**5**	2-iprPh	16.1 (±0.1)	9.0 (±0.4)	–25.9 (±1.2)	+92	[e]
7	**3**	2-MePh	16.14 (±0.05)	10.6 (±0.3)	–20.2 (±0.8)	+74	[e]
8	**4**	2,6-Me_2Ph	16.3 (±0.1)	10.2 (±0.7)	–22.2 (±2.2)	+63	[2]

[a] ipr = isopropyl, Me = methyl, Ph = phenyl. [b] HT = highest temperature (°C) of the rate measurements. [c] **7a** = 2-(α-Lithiobenzylidene)-1,1,3,3-tetramethylindane. [d] **7b** = 2-(α-Lithio-2´,6´-dimethylbenzylidene)-1,1,3,3-tetramethylindane. [e] This work.

[TOC-Graphic:]

Separation and migration; no digressions.

Quasi-benzyl-anion resonance is stronger in the linear transition state (see the Graphic) than in the two trivolvated, angular groundstates (CIP and CIP´), because immobilization of the fourth THF ligand at Li increases the charge delocalization from C(α) to C(4). The excess negative charge (∂^-) at C(4) appeared to favor the migration of $Li^+(THF)_4$ across the C(3)/C(4) region of the conformationally fixed α-aryl group.

Keywords: conformational analysis • *E,Z* configurational lability• reaction mechanisms • sp^2-carbanion inversion • structural elucidation