(*E*/*Z*)-Equilibria, 19[◇]

Dimeric α-Lithio-2,6-dimethylstyrene☆

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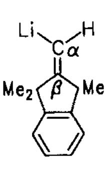
Improved preparations of 2,6-dimethylstyrene (**5**) and its α-bromo derivative (**10**) are described. The Br/Li exchange reaction of **10** provides single crystals of the title compounds **11** or **12**, which were characterized as disolvated dimers by X-ray analyses. A similar dimer persists in diethyl ether, *tert*-butyl methyl ether, and toluene at all accessible temperatures, with significant lithiation NMR shifts (relative to **5**) partially due to charge delocalization from the sp^2-carbanionic center. Some NMR coupling constants are typical of the dimeric aggregate. The configurational (*E,Z*) lability is quantified in toluene solution.

One of the fundamental problems in organolithium chemistry concerns aggregation and its possible influence[1] on reactivity. Tetrameric, dimeric and monomeric structures have been reported for aryllithium compounds[2], and a similar complexity is to be expected for α-lithioalkenes as a related but less extensively studied[3] sub-class that is likewise characterized by an sp^2-hybridized carbanionic center. For example, the β,β-shielded vinyllithium derivative **1** crystallized as a *dimeric* ether complex that remained dimeric in *tert*-butyl methyl ether solution but formed an equilibrium mixture with the presumably trisolvated *monomer* in tetrahydrofuran (THF)[4]. With a closely similar constitution, **2** crystallized from pentane solution as a cyclic *trimer*[5] devoid of any Lewis base ligands. On the other hand, the parent compound vinyllithium (**3**) formed an S_4-symmetric, *tetrameric* THF solvate[6] in the solid state and in THF solution at room temperature, whilst 11%[6,7] of a structurally uncharacterized *dimer* was observed at −90 °C in THF.



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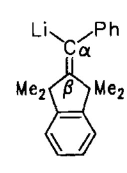

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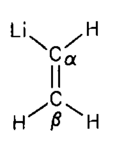

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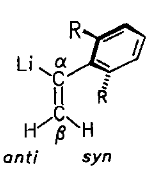

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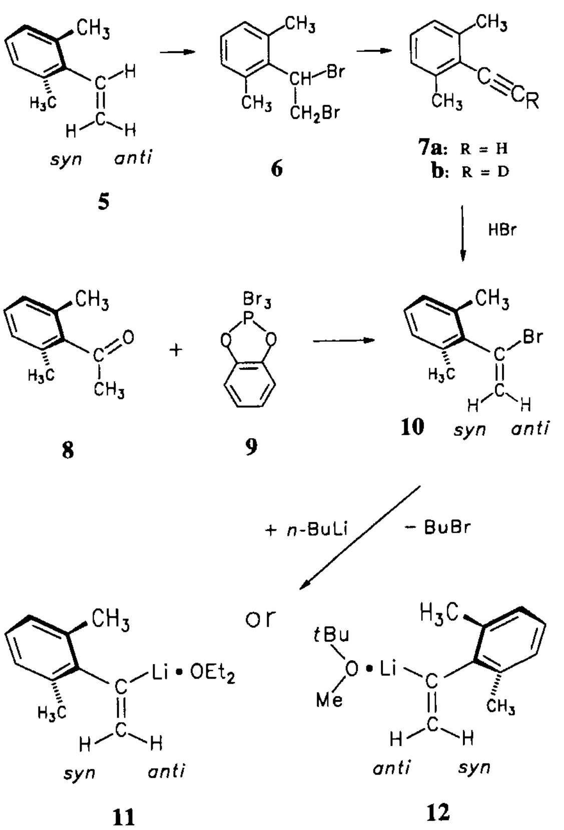
What kind of aggregates would then be formed by an α-aryl derivative such as **4** possessing an unsubstituted C-β-atom? Such α-lithiostyrenes had been found[8] to be configurationally labile in THF solution, unlike **1** or **3**, as revealed by the rapid (on the NMR time scale) *syn*/*anti* interchange of the diastereotopic β-protons. For the requisite structural characterization, we have chosen **4** with R = CH_3 because the 2,6-dimethylphenyl group is a slender substituent ("smaller"[9] than methyl) due to its inclination towards an orthogonal orientation at a double bond. This should avoid the conformational ambiguities expected with the possibly "larger"[9] α-phenyl group (R = H), but would not shield the carbanionic center C-α excessively.

A. Syntheses and Structures

2,6-Dimethylstyrene (**5**), required for spectral comparisons with **4** and for constitutional verification, was prepared in ca. 38% overall yield by modifications of the published route[10] from 2-bromo-1,3-dimethylbenzene. The Grignard addition to acetaldehyde proceeded as described[10,11] to give 1-(2,6-dimethylphenyl)ethanol, which was more easily dehydrated[12] by distillation from $KHSO_4$ and hydroquinone. Straightforward NMR assignments (^1H and ^{13}C) of the resulting olefin **5** were derived from the coupling constants. The dibromide[10] **6** showed diastereotopic methyl groups due to restricted aryl rotation, a phenomenon whose conformational analysis made it comprehensible why the treatment with ethanolic KOH gave (*E*)-β-bromo-2,6-dimethylstyrene[13] exclusively (rather than the α-bromide **10**). Therefore, **6** was transformed into the alkyne **7a**[14,15] which could be deuterated quantitatively to **7b** by deprotonation with *n*-butyllithium in ether followed by deuteriolysis. Hydrobromination of **7a** in acetic acid saturated with sodium bromide furnished the bromide **10** (72%), but it was difficult to obtain **10** rigorously pure in this way. Despite such unusual[16] conditions but in accord with previous[17,18] reports, **7b** afforded mainly the product of *cis* addition of HBr since (*E*)- and (*Z*)-[β-D_1]-**10** were isolated as a 3:1 mixture.

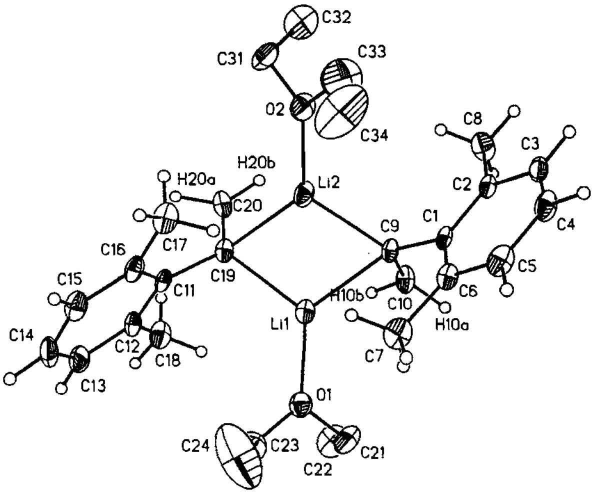
[◇] Part 18: Ref.[19]. – [+] X-ray structural analyses.



In a slightly shorter and much more convenient sequence, starting also from 2-bromo-1,3-dimethylbenzene, the ketone **8** was prepared via the aryl cyanide[19] and submitted to brominative deoxygenation[20,21] by reagent **9**, furnishing very pure α-bromo-2,6-dimethylstyrene (**10**) in a single step. The subsequent Br/Li interchange reaction with *n*-butyllithium was best performed in NMR tubes (5–12 mm diameter) because such vessels facilitate the spontaneous crystallization of ether complexes **11** (from diethyl ether solution) and **12** (from *tert*-butyl methyl ether, *t*BuOMe). It was not profitable to run this reaction in THF because the organolithium compound was very quickly destroyed in this solvent by its co-product 1-bromobutane. The crystals **11** or **12** were separated from any contaminants by washing with pentane, and then submitted to X-ray structural analyses or dissolved in an appropriate solvent for NMR spectroscopy.

The crystal structure of the ether complex **11** revealed a cyclic dimer possessing approximate C_2 symmetry and an almost planar (±0.12 Å) CLiCLi core with diagonal distances C9–C19 = 3.520 Å and Li1–Li2 = 2.51(1) Å. It is projected in Figure 1 along the quasi-C_2 axis which would interchange, for example, the two proximal methyl groups C7 and C17, or the two β-CH_2 moieties behind the projection plane. We admit that we had shared expectations[7] of either a *trans* (as in the dimer[4] of **1**) or a *cis* relationship between the two double bonds C9–C10 and C19–C20. However, the planes C1–C9–C10 and C11–C19–C20 include a dihedral angle of 103° (rather than 180° or 0°). They are also inclined against their associated aromatic planes by 76.4° and 78.5°, respectively, and hence they are practically non-conjugated with the 2,6-dimethylphenyl substituents. Li2 is situated 0.60 Å above the plane C1–C9–C10 and may be viewed as connected to C9 by a σ-like bond, whereas Li1 resides 1.38 Å below that plane; with respect to the other double-bond plane C11–C19–C20, the roles of the two Li cations are reversed. In accord with dimeric **1**[4] but again contrary to guesses[7] for a vinyllithium dimer, each one of the Li cations in **11** is "solvated" by *only one* ether molecule and has an almost perfectly planar (angular sum = 359.8°) primary coordination sphere. Positioned in front of the projection plane like the aryl substituents, the oxygen atoms are also roughly sp^2-hybridized (angular sum = 359.6°) but are not coplanar with the lithium planes.

Figure 1. Solid-state structure (ORTEP plot) of the dimeric Et_2O complex **11**, showing the crystallographic numbering; hydrogen atoms of the Et_2O ligands are omitted



Could the peculiar relative orientation (neither *cis* nor *trans*) of the two CC double bonds have been dictated by diethyl ether as a ligand? This suspicion appears unwarranted as the molecular structure (not depicted) of dimeric **12** with *t*BuOMe as the two Lewis base ligands was found to be virtually indistinguishable from that of **11**, excluding the alkyl substituents bonded to oxygen. For comparison, in Table 1 we have listed a selection[22] of the geometrical features for **11** and **12**; however, we shall discuss the averaged parameters of **11** alone because our crystal analysis of **12** was of inferior quality. Neither **11** nor **12** lost their ethereal Lewis base ligands under high-vacuum conditions, but *t*BuOMe could be pumped off from a THF solution of **12**.

The CC double bonds in **11** are as long as in ethylene (1.33 Å) and in **1** (1.32 Å)[4] and **2** (1.34 Å)[5], whereas the very unusual CC length (1.41 Å)[6] in tetrameric vinyllithium (**3**) was associated[7] with an "extraordinarily small π bond order". The suggestion[7] that dimeric **3** might have an even longer CC bond is thus not borne out by our dimers **11** and **12**. In contrast to **2**, the Li cations of **11** are not coordinated to the olefinic or the aromatic π systems nor to the methyl carbon (Table 1) or methyl hydrogen atoms (closest distance 2.755 Å). However, Li1 and Li2 attain formal tetracoordination by "agostic" interactions with

Table 1. Selected interatomic distances [Å] and angles [°] (at −60 °C) for dimeric **11** and dimeric **12**

	11	**12**		**11**	**12**
Li1-O1	1.920(8)	1.88(2)	Li2-O2	1.926(9)	1.91(1)
Li1-C9	2.205(9)	2.22(1)	Li2-C19	2.182(9)	2.21(1)
Li2-C9	2.150(8)	2.17(1)	Li1-C19	2.159(8)	2.17(2)
Li1-C7	3.273		Li2-C17	3.316	
Li1-C10	2.376(8)	2.42(1)	Li2-C20	2.379(8)	2.36(1)
Li2-C10	3.076		Li1-C20	3.147	
Li1-H10b	2.081(8)		Li2-H20b	2.175(9)	
C1-C9	1.493(6)	1.486(9)	C11-C19	1.476(6)	1.481(9)
C9-C10	1.324(6)	1.360(9)	C19-C20	1.326(6)	1.332(9)
C10-H10a	1.04	0.96	C20-H20a	1.13	0.96
C10-H10b	1.01	1.15	C20-H20b	0.99	1.09
Li1-Li2	2.51(1)	2.54(2)	H10b-H20b	3.489	
O1-Li1-C9	128.8(4)	131.2(7)	O2-Li2-C19	129.4(4)	128.7(7)
O1-Li1-C19	123.7(4)	124.7(7)	O2-Li2-C9	121.4(4)	126.5(6)
C9-Li1-C19	107.5(4)	103.8(6)	C9-Li2-C19	108.7(4)	104.3(5)
C21-O1-C23	110.8(4)	99 (1)	C31-O2-C33	111.5(5)	108.0(9)
Li1-O1-C23	128.9(4)	147 (1)	Li2-O2-C33	128.9(5)	135.2(9)
Li1-O1-C21	119.8(4)	113.0(9)	Li2-O2-C31	119.2(4)	115.4(8)
C2-C1-C6	119.3(4)	118.9(6)	C12-C11-C16	118.0(4)	119.3(6)
C2-C1-C9	121.3(4)	119.3(6)	C12-C11-C19	121.5(4)	120.5(6)
C6-C1-C9	119.0(4)	121.3(6)	C16-C11-C19	120.3(4)	120.0(6)
C1-C9-C10	118.2(4)	116.4(6)	C11-C19-C20	119.3(4)	118.3(6)
C1-C9-Li1	138.5(4)	139.8(6)	C11-C19-Li2	139.2(4)	141.5(5)
C1-C9-Li2	116.1(3)	116.5(5)	C11-C19-Li1	110.7(4)	116.4(6)
C10-C9-Li1	80.4(3)	81.1(5)	C20-C19-Li2	81.5(4)	79.3(5)
C10-C9-Li2	122.9(4)	123.7(6)	C20-C19-Li1	127.5(4)	121.4(6)
Li1-C9-Li2	70.3(3)	70.7(5)	Li1-C19-Li2	70.6(3)	70.8(5)
Li1-C10-C9	66.2(3)	65.1(5)	Li2-C20-C19	65.1(3)	67.0(5)
H10a-C10-H10b	110.1	118.2	H20a-C20-H20b	121.7	114.0

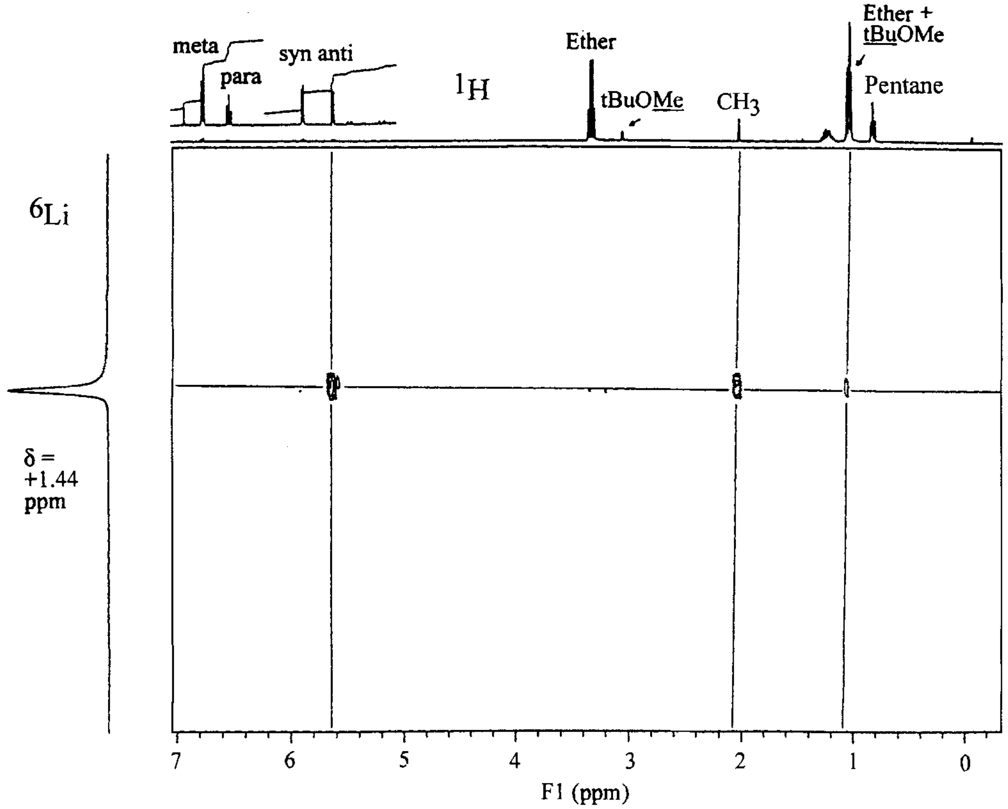
the olefinic *anti* C10−H10b and C20−H20b bonds, respectively, as shown by the averaged distances 2.378 Å to carbon and 2.13 Å to hydrogen atoms. The latter Li *cis* contacts are much shorter than the corresponding weighted parameter, 3 Å, inferred[6] from ^{6}Li,^{1}H-NMR correlation in tetrameric vinyllithium. Since the Li2−C10 and Li1−C20 distances average to 3.11 Å, they cannot contribute to bonding. The coordination in **11** and **12** of each Li to only one CH σ bond may be a reason for the peculiar orientation of CC double bonds mentioned above.

B. Dimeric 12 in Solution

The very simple preparation described above provides pure crystals of **11** or **12** free from interfering contaminants such as lithium bromide; hence one can be sure of the absence of mixed aggregates in solution. Only a single species was found for [^{6}Li]-labelled **12** in ether, as judged on the basis of concentration- and (for most nuclei) almost temperature-independent ^{1}H- and ^{13}C-NMR chemical shifts δ (see the Experimental Section) down to the solubility limit at −58 °C. It shares with crystalline **12** the aforementioned close contact of the cation with the *anti*-H and the looser contact with the methyl-hydrogen atoms, as shown in Figure 2 by strong correlation peaks of these nuclei in a two-dimensional (^{6}Li,^{1}H) HOESY[2] experiment. A weak interaction of ^{6}Li at δ = +1.44 is also seen with the methyl protons of the non-deuterated ether solvent but not with the OCH_3 of the formerly coordinated *t*BuOMe, now displaced by the solvent and observed with the normal δ values (^{1}H and ^{13}C) for free *t*BuOMe. Although we were unable to detect under any conditions of temperature and solvent the nonequivalence of the methyl groups expected from Figure 1, we attribute to the dissolved species a dimeric structure similar to that in the crystal, on account of the relationships presented below.

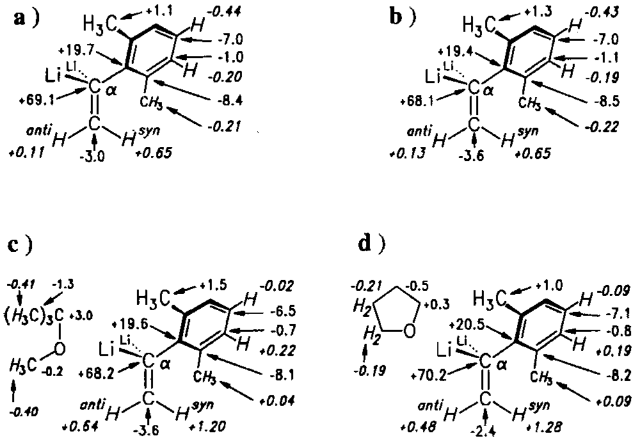
The NMR spectral consequences of lithiation may be defined for any H or C atom of **12** (or **11**) by reference to 2,6-dimethylstyrene (**5**). Since trace amounts of this parent olefin were detectable in most solvents, the comparisons could be made under identical conditions of solvent and temperature. For example, disturbing temperature effects had been eliminated for the previously[4] studied rigid sys-

Figure 2. Two-dimensional ^{6}Li,^{1}H-HOESY plot of dimeric **12** in Et_2O at +25 °C

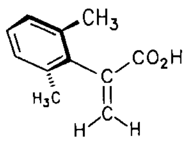


tem **1** by finding constant chemical shift differences Δδ. As the calculation of Δδ parameters at +25 °C is simply done by subtracting the δ values of olefin **5** (see the Experimental Section) from those of **12**, we present in Figure 3 the slightly different Δδ data found[22] at lower temperatures. Practically equal values in diethyl ether and in *t*BuOMe solutions, as shown in Figures 3a and 3b, characterize the same species already designated to be a dimer by the labels Li_2C. With due reservations, some of these lithiation shifts may be interpreted at least partially as measures of electrical charge modifications. Thus it appears safe to assume that the para position of **12** is charged predominantly by π-conjugation since proximity effects of the LiC bonds should be negligible over such a distance, while the perpendicular aryl orientation provides for the best possible quasi-π conjugation with the carbanionic sp^2-electron pair at C-α. Using the known factors 10.7 ppm/e[23] for ^{1}H and 156.3 ppm/e[24] for ^{13}C, we calculate from the Δδ values of *p*-H and *p*-C a consistent change of −0.043(2) π-charge units induced by the LiC bonds in Et_2O as well as in *t*BuOMe solutions. The qualitative features of a quasi-benzyl anion may also be gleaned from the Δδ data for the other aromatic carbon atoms. On the other hand, the very strong downfield lithiation shift of C-α, being typical of sp^2-hybridized carbanionic centres[2], cannot serve directly as a charge indicator. It would be even more difficult to interpret the upfield lithiation shift of C-β since its sign is opposed to that for **1**[4] and for vinyllithium[6,7]. Most of these parameters are considerably different for monomeric **12** in THF solution[22] (as they are for dimeric and monomeric **1**[4]) and will be reported later. To verify the chemical constitution of **12**, we carboxylated its *t*BuOMe solution and obtained **13** but did not find any halide in the aqueous extract.

Figure 3. Lithiation shifts Δδ [ppm] for dimeric **12** (rel. to **5**): (a) In Et_2O at −58 °C. – (b) In *t*BuOMe at −40 °C. – (c) With 1.3 equiv. of *t*BuOMe in [D_8]toluene at −84 °C. – (d) With 1.2 equiv. of THF in [D_8]toluene at −83 °C



Although **12** was insoluble in saturated hydrocarbons, it dissolved readily in toluene and exhibited slightly temperature-dependent NMR shifts for only some of its nuclei (see the Experimental Section). It is immediately evident from the lithiation shifts in Figure 3c that the (single) species was the same as in Et_2O or *t*BuOMe (Figure 3a and b). The Lewis base *t*BuOMe retained from the crystal was essential to generate this species and remained coordinated to lithium, as was evident from its peculiar coordination shifts $\Delta\delta$ referenced to free *t*BuOMe that had correspondingly differing chemical shifts at any temperature. In a HOESY[2] experiment performed at +25 °C (not depicted), ^{6}Li at $\delta = +1.40$ was again correlated with the *anti*-H and the methyl protons but this time also with either kind of protons in *t*BuOMe. When 1.2 equivalents of THF was added to a similar solution, *t*BuOMe became disconnected (as shown by its normal chemical shifts) from lithium and was replaced by THF which then exhibited the coordination shifts $\Delta\delta$ presented in Figure 3d, which were virtually temperature-independent. The accompanying lithiation shifts for THF-coordinating **12** are sufficiently similar to those in Figure 3c to infer again the same (single) species as before.



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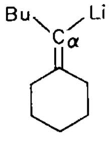

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If **12** under all of the preceding conditions does indeed have a dimeric structure similar to that in the crystal, its carbanionic centers C-α (or C9 and C19 in Figure 1) should be coupled magnetically to two ^{6}Li nuclei. For reasons of solubility, we could observe the expected ^{13}C-NMR quintet (1:2:3:2:1) with $^{1}J = 7.5$ Hz only in [D$_8$]toluene solutions below −34 °C. This coupling constant is somewhat different from those of dimeric vinyllithium (8.3 Hz at −100 °C)[6,7], of **14** (9.0 Hz at −112 °C in THF[25]) and of dimeric **1** (9.5 Hz up to +25 °C, as opposed to 15.9 Hz for monomeric **1**)[4]. A mixed aggregate can be excluded because the single crystals of **12** are not contaminated with other lithium compounds (e.g. LiBr), but the quintet splitting caused by two Li/C-α contacts would also be compatible with a higher cyclic oligomer under conditions of frozen *intra*aggregate exchange of lithium. However, on warming[26] the quintet should change to a septet splitting for a cyclic trimer with a 33% reduction in $^{1}J_{\text{CLi}}$ (and an even stronger reduction for a cyclic tetramer, etc.). In contrast, our $^{1}J_{\text{CLi}} = 7.5$ Hz remained unchanged from −84 to −35 °C, until the *inter*aggregate exchange of ^{6}Li became rapid on the NMR time scale. From the coalescence temperature, −18 (± 3) °C, and with $k_c \approx \pi \cdot J = 24\ s^{-1}$ as a rough empirical approximation of the rate constant at coalescence, we compute $\Delta G^{\ddagger}_{255} = 13.2\ (\pm\ 0.2)$ kcal/mol as the free enthalpy of activation. This rather high barrier would not be expected for the relatively open structure of a trimer as described[5] for the related trimer $(\mathbf{2})_3$.

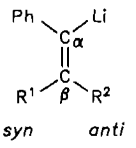
The combined evidence appears to be sufficiently convincing of the dimeric nature of **12** in the solvents studied above. Molecular mass determinations by isothermal distillation[2] were attempted without success due to the insufficient long-term stability of **12**. At +20 °C, the half-life times of **12** for decomposition to **5** were approximately 3 d in Et_2O and 12 d in *t*BuOMe solutions.

Some further NMR coupling constants of our dimer merit a comparative discussion. The apparent $^{1}J_{\text{CH}}$ values for the sp^2-hybridized carbon nuclei of 2,6-dimethylstyrene (**5**) are significantly reduced on lithiation (see the Experimental Section). The abnormal doublet splittings of C-α with $^{2}J_{\text{CH}} = 13.5$ (*anti*-H) and (−)7.8 Hz (*syn*-H) were resolved only in Et_2O solution and were completely absent in olefin **5** (sharp $^{1}J_{\text{CH}}$ doublet); they were assigned by analogy with tetrameric vinyllithium[7] and result from the electropositive nature of lithium. Finally, the geminal interproton coupling constant $^{2}J_{\text{HH}}$ of the olefinic CH_2 group is known to be a measure of σ-inductive effects and independent of π interactions on both theoretical and experimental grounds[27]. The positive sign of $^{2}J_{\text{HH}}$ established[27] for vinyllithium and confirmed[7] for the tetramer can be assigned confidently to **12** as well. Taking again the olefin **5** with $^{2}J_{\text{HH}} = 2.4$ Hz as a reference, this parameter as found for **12** is characteristic of the release of σ-electron density permitted by two Li cations in dimeric α-lithiostyrenes, with values of 6.0 Hz in Et_2O and *t*BuOMe, 5.8 Hz in toluene, and 6.3 Hz in toluene with 1.2 equivalent of THF. The latter value might indicate that the better donor THF caused a slightly enhanced σ-electron density at C-β. A stronger increase[22] of these properties will be reported later for monomeric **12** in THF.

C. Configurational Lability of 12 in Toluene Solution

The configuration (*E*/*Z*) of α-lithio-α-phenylalkenes **15** is rather unstable in solvents of a predominantly hydrocarbon nature[28–30]. For example, the half-life times for *E*/*Z* interconversions may be estimated from the crude literature data to be roughly 45 min for **15** (β,β-diaryl) at 25 °C in benzene containing 0.68% of Et_2O[28] and in pentane[30], or ca. 1 min for **15** (R^1 = Et, R^2 = H) at 22 °C with 10 equivalents of Et_2O in hexane[29]. We studied the corresponding *E*/*Z* diastereotopomerization **16a** $\rightleftharpoons$ **16b** of **12** (or **11**) in [D$_8$]toluene solution by recording expanded 80 MHz NMR spectra of the diastereotopic β-protons. These AB-type spectra became increasingly broad on heating from +88 up to +122 °C and reverted to doublets with $^{2}J = 5.7$ Hz (when OR_2 = *t*BuOMe in **16a**) on repeated cooling below +75 °C. The temperature-dependent rate constants *k* extracted by computer-assisted lineshape analyses did not depend on the diminishing formal concentrations (0.47–0.07 F) of **12** caused by slow decomposition. Although these analyses proved increasingly difficult because resonances of the decomposition products disturbed the AB spectra, we did not discover any deviation from a first-order dependence of the *syn*/*anti* interconversion rates with respect to the organolithium concentration. A possible (but not unique[31]) interpretation would describe this stereomutation as a monomolecular reaction of dimeric **12**.

These rate constants *k* (see the Experimental Section) determined in the presence of *t*BuOMe (0.40–0.55 M) did not change upon addition of ca. one equivalent of THF (0.32



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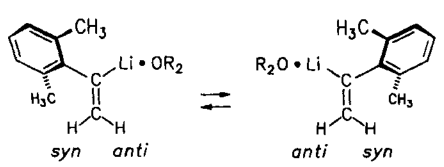

16a **16b**

M), giving rise to ^2J = 6.3 Hz in the static AB spectrum (since now OR_2 = THF in **16a**). Therefore, all k values could be described by a single set of activation parameters, $\Delta H^{\ne}$ = 20.8 (± 2.3) kcal/mol and $\Delta S^{\ne}$ = +0.5 (± 5.8) cal mol^{-1} K^{-1}. While a vanishing entropy $\Delta S^{\ne}$ of activation would be consistent with a monomolecular stereomutation process of dimeric **16a/b**, some other explanations[31] cannot be excluded and a mechanistic discussion would appear improper at present. In any event, our results are comparable to those for 3,3-dimethylbutyllithium in diethyl ether[32] and for 2-methylbutyllithium in pentane[33] with respect to $\Delta S^{\ne}$, to the first-order behaviour and even to the difficulty of approaching coalescence at higher temperatures; however, carbanion inversion of these aggregated primary *alkyl*lithium compounds occurred more easily by ca. 6 kcal/mol in $\Delta H^{\ne}$. On the other hand, our activation parameters are applicable over the realm of the donor-stabilized dimer, as delineated in Section B. They may be utilized to extrapolate free activation enthalpies $\Delta G^{\ne}$ and half-life times $t_{1/2}$ of configurational lability: At +25 °C, $\Delta G^{\ne}_{298}$ = 20.6 (± 0.5) kcal/mol, hence $t_{1/2} \approx$ 3 min, in accord with the literature evaluation given above; at −25 °C, a $t_{1/2}$ of the order of days would be expected and may serve as a guide for synthetic work aiming at the retention of configuration in compounds of type **15** in hydrocarbon solvents.

For a final contrast, we mention an expected value of $t_{1/2} \approx$ 20 s for **12** at −25 °C in THF solution[8] and an extrapolated $\Delta G^{\ne}_{373} \approx$ 18.3 kcal/mol. At the latter temperature of +100 °C, the observed $\Delta G^{\ne}_{373}$ was 19.6 (± 0.1) kcal/mol for **12** in [D_8]toluene containing a larger amount of THF (1.43 M, or 12% by volume). However, such conditions are beyond the domain of exclusively dimeric **12**, and the implied (ca. fourfold) acceleration with respect to the dimer would be explainable if at +100 °C ca. 13% of the material was present as the configurationally more labile species already encountered[8] in bulk THF. Clearly, a more extensive investigation of **12** is due in order to arrive at a more complete understanding of this system.

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Experimental Section

^{1}H NMR: Varian VXR-400S, HA-60-IL, A-60; Bruker WP-80-CW, AW-80-CW. – ^{13}C NMR: Varian VXR-400S; internal standard TMS; coupling constants (absolute magnitudes only) obtained by gated or selective decoupling, multiplicities by DEPT. – ^{6}Li NMR: Varian VXR-400S; ext. standard ^{6}LiBr in THF; (^{6}Li,^{1}H)-HOESY experiments at +25 °C with a mix time of 4 s. The labelled specimens (>91% ^{6}Li) of **12** were prepared with [^{6}Li]butyllithium made as described previously[4]. – NMR tubes and solvents were dried as previously[4], but [D_8]toluene was used as received.

[D_{12}]Cyclohexane (0.08 ml) was added to NMR samples in nondeuterated solvents (0.5 ml) and used for locking to the magnetic field. Temperatures during the NMR experiments were controlled by the usual routine tests with methanol or glycol samples. The actual formal concentrations (F) as defined per $C_{10}H_{11}Li$ unit were measured against the ^{1}H-NMR integral of a calibrated capillary.

1-(2,6-Dimethylphenyl)ethanol: The crude material[10,11] was distilled at 112–116 °C/12 Torr (ref.[10] 112–117 °C/10 Torr) and then crystallized from petroleum ether to give 49% of colourless cubes with m.p. 66–67.5 °C (ref.[11] 66–67 °C, ref.[10] 68.5–69.5 °C). – ^{1}H NMR (CCl_4): δ = 1.31 (d, ^3J = 6.7 Hz, CH_3), 2.30 (s, 2-/6-CH_3), 3.06 (br. s, OH), 5.15 (q, ^3J = 6.7 Hz, 1-H), 6.82 (quasi-s, 3 H); different from ref.[11].

2,6-Dimethylstyrene (**5**): The aforesaid aryl ethanol (17.2 g, 114 mmol), hydroquinone (0.5 g) and $KHSO_4$ (0.5 g)[12] were heated gradually up to 180 °C in a distillation apparatus under 120 Torr. The condensed mixture of water and olefin **5** was separated with ether and dried with $CaCl_2$. Redistillation at 92.5–93 °C/36 Torr (ref.[10] 65.8–66 °C/10 Torr) provided 12.65 g (84%) of pure liquid **5**. – ^{1}H NMR (CCl_4, cyclopentane, *t*BuOMe, Et_2O or THF): δ = 2.25 (s, 2 *o*-CH_3), 5.20 (dd, ^3J = 17.8, ^2J = 2.4 Hz, *syn*-H), 5.48 (dd, ^3J = 11.7, ^2J = 2.4 Hz, *anti*-H), 6.66 (dd, ^3J = 17.8 and 11.7 Hz, α-H), 6.94 (s, 3 H); in [D_8]toluene δ = 2.18, 5.08, 5.34, 6.50, 6.91 (2 *m*-H), 6.95 (*p*-H); compare $CDCl_3$ in ref.[34]. – ^{13}C NMR ($CDCl_3$): δ = 20.8 (q, ^1J = 126 Hz, 2 CH_3), 119.4 (dd, ^1J = 158 and 155.5 Hz, C-β), 126.7 (d, ^1J = 159 Hz, *p*-C), 127.8 (dqi, ^1J = 157, ^3J = 4.5 Hz, 2 *m*-C), 135.2 (d, ^1J = 153 Hz, C-α), 135.8 (br., 2 *o*-C), 137.8 (br., *i*-C); different from ref.[35]. – ^{13}C NMR ([D_8]toluene, cyclopentane, *t*BuOMe, Et_2O or THF): δ = 21.0, 119.3, 127.1, 128.2, 135.7, 136.0, 138.0. – All NMR data showed little temperature dependency[22].

2-(1,2-Dibromoethyl)-1,3-dimethylbenzene (**6**): From **5** as described[10] in 96% crude yield. – ^{1}H NMR (CCl_4): δ = 2.33 and 2.48 (2 s, 2 CH_3), 3.92 and 4.20 (AB part of ABX system, ^2J = 10.5 Hz, CH_2Br), 5.65 (dd, ^3J = 10.5 and 6.5 Hz, CHBr), 6.93 (quasi-s, 3 H); CH_3 coalescence at +57 °C (60 MHz).

(2,6-Dimethylphenyl)acetylene (**7a**): In a deviation from the published methods[13,15], crude dibromide **6** (24.7 g, 84.6 mmol) and ca. 400 mmol of sodium amide (toluene suspension) in 190 ml of anhydrous THF were refluxed for 18 h. Cautious hydrolysis with saturated aqueous ammonium chloride, acidification, extraction with ether and distillation of the dried extracts gave 5.52 g (50%) of liquid **7a** with b.p. 88–89 °C/32 Torr (ref.[13] 95–100 °C/15 Torr, ref.[15] 200–202 °C). – ^{1}H NMR (CCl_4): As in refs.[13,14].

2,6-Dimethylacetophenone (**8**): The crude ketone **8** required no purification if prepared with the following slight modifications to the most convenient procedure[20]. After the addition of methylmagnesium iodide (76 mmol) to 2,6-dimethylbenzonitrile[19,20] (5.00 g, 38.1 mmol) in refluxing xylene (3 h), the imine[20] of **8** was extracted into aqueous acid and recovered by making the extracts alkaline with conc. aqueous ammonia solution. This totally uncontaminated crude material was refluxed at 130 °C in 50 ml of 2 N H_2SO_4 for at least 3.7 d and then worked up[20] to give 3.49 g (62%) of pure and stable[36] **8**. – ^{1}H NMR (CCl_4): δ = 2.19 (s, 2 *o*-CH_3), 2.34 (s, CH_3), 6.85 and 7.00 (A_2B system, C_6H_3).

2-(1-Bromoethenyl)-1,3-dimethylbenzene (**10**): The published[20] conditions were applied with in situ generation of reagent **9** from 2-bromo-1,3,2-benzodioxaphosphole (5.34 ml, 42.2 mmol) and bromine (1.95 ml, 38.1 mmol) in 10 ml of anhydrous chloroform. After addition of ketone **8** (5.00 g, 33.7 mmol), heating to 80°C for 4 h and workup[21], the crude product (5.65 g) contained residual **8** and its α-bromo derivative. Chromatography on 30 g of silica gel with 150 ml of petroleum ether furnished the pure[20] liquid **10** (3.44 g, 48%) without distillation[36]. – ^{1}H NMR: See below and refs.[13,14,20]. – ^{13}C NMR (CDCl$_3$): δ = 19.7 (2 CH$_3$), 121.0 (CBr), 121.7 (CH$_2$-β), 127.4 (2 *m*-C), 128.4 (*p*-C), 135.6 (2 *o*-C), 139.8 (*i*-C)[37].

(E)- and (Z)-[β-D$_1$]-2-(1-Bromoethenyl)-1,3-dimethylbenzene ([D$_1$]-**10**): The methodically safer but more involved anhydrous conditions[13,14,17,18] were not necessary in this case (although they were so with other alkynes). Instead, aqueous hydrobromic acid (48%, 5 ml) was decolourized with a little sodium sulfite and added to an intimately mixed suspension of sodium bromide (5 g) in glacial acetic acid (25 ml). The deuterated alkyne **7b** (2.22 g, 16.9 mmol) was introduced and heated under reflux for 30 min on a steam bath. The cooled mixture was taken up in water (125 ml) and extracted with ether (3 ×). The combined extracts were shaken with 2 N aqueous NaOH, washed neutral, dried with Na$_2$SO$_4$, and distilled at 90–110°C (bath temp.)/12 Torr to give 2.48 g (69%) of ([D$_1$]**10**) (ref.[13] b.p. 86–91°C/0.1 Torr, ref.[20] 97.5–99°C/11 Torr). – ^{1}H NMR (CCl$_4$): δ = 2.34 (s, 2 *o*-CH$_3$), 5.60 (s, 0.24 H, *syn*-β of (*Z*)-isomer), 5.87 (s, 0.75 H, *anti*-β of (*E*) isomer), 6.96 (quasi-s, C$_6$H$_3$)[37]; compare refs.[13,14,17].

2-(α-Lithioethenyl)-1,3-dimethylbenzene Ether Complex (**11**): A 5-mm NMR tube was heated at 120°C overnight, cooled under Ar, charged with 100 mg (0.47 mmol) of bromide **10** in 0.5 ml of anhydrous diethyl ether, and cooled to –30°C under a stream of Ar. A hexane solution (0.414 ml) of *n*-butyllithium (0.52 mmol) was added at once, and the tube was sealed with a soft stopper. After cautious mixing by gentle shaking, the single crystals of **11** were grown at –30°C and washed at this temperature with pentane (3 × 0.3 ml) from a syringe, then dried in a stream of dry Ar for a few seconds and mounted in the diffractometer.

tBuOMe Complex (**12**) *of 2-(1-Lithioethenyl)-1,3-dimethylbenzene, and* [^{6}Li]-**12**: The bromide **10** (40 mg, 0.19 mmol) in 0.5 ml of anhydrous *t*BuOMe was treated with 0.165 ml (0.21 mmol) of *n*-butyllithium as described above for **11**. The single crystals of **12** were washed and dried in the same manner for X-ray analysis.

Samples for NMR studies were prepared by the same techniques from 60 mg (0.28 mmol) of bromide **10** in 0.4 ml of anhydrous *t*BuOMe at –30°C, but with 0.208 ml of a cyclopentane solution of [^{6}Li]*n*-butyllithium (0.312 mmol). In order to grow larger crystals (1 mm), the mixture was warmed to room temperature for 10 min, cooled at –20°C for 30 min, and moved gently to induce crystallization. If **12** formed a microcrystalline precipitate, the NMR tube was warmed to +50°C in a water bath for complete dissolution and recooled slowly to –20°C. When precipitation was complete, after 1–2 h at –78°C, the NMR tube was opened under Ar and the supernatant was removed by syringe. The crystals were washed at –78°C by swirling with (cyclo)pentane (4 × 0.3 ml) and withdrawal of the liquid from the settled crystals (maximal yield 60–70%). After drying in a stream of Ar for a few sec, anhydrous Et$_2$O or *t*BuOMe (0.4 ml) and 0.08 ml of [D$_{12}$]cyclohexane as well as TMS (0.005 ml) were introduced with slight cooling, or [D$_8$]toluene (0.5 ml) and TMS were added. The rubber stopper was then replaced tightly and wrapped externally with Parafilm®.

*Selection[22] of ^{1}H-NMR Data for [^{6}Li]-**12** at 400 MHz:* (a) Ca. 0.09–0.16 F in Et$_2$O/[D$_{12}$]cyclohexane (7:1) at +25°C: δ = 2.07 (s, 2 CH$_3$), 5.62 (*anti*-H) and 5.89 (AB system, ^2J = 6.0 Hz, *syn*-H), 6.54 (t, ^3J = 7.5 Hz, *p*-H), 6.77 (d, ^3J = 7.5 Hz, 2 *m*-H); at –40°C: δ = 2.05, 5.62, 5.87, 6.53, 6.77. – (b) In *t*BuOMe/[D$_{12}$]cyclohexane (7:1) at +25°C: δ = 2.06 (s, 2 CH$_3$), 5.61 (*anti*-H) and 5.85 (AB system, ^2J = 6.0 Hz, *syn*-H), 6.52 (t, ^3J = 7.5 Hz, *p*-H), 6.76 (d, ^3J = 7.5 Hz, 2 *m*-H); at –40°C: δ = 2.03, 5.63 (br.), 5.85, 6.53, 6.77. – (c) Ca. 0.25 F in [D$_8$]toluene at +25°C: δ = 2.23 (s, 2 CH$_3$), 5.85 (*anti*-H) and 6.17 (AB system, ^2J = 5.7 Hz, *syn*-H), 6.84 (t, ^3J = 7.5 Hz, *p*-H), 7.02 (d, ^3J = 7.5 Hz, 2 *m*-H); at –84°C: δ = 2.23, 5.98 and 6.28 (^2J = 5.8 Hz), 7.00, 7.15. – (d) Ca. 0.54 F in [D$_8$]toluene with 0.68 M THF at +25°C: δ = 2.23 (s, 2 CH$_3$), 5.75 (*anti*-H) and 6.19 (AB system, ^2J = 6.2 Hz, *syn*-H), 6.78 (t, ^3J = 7.5 Hz, *p*-H), 6.99 (d, ^3J = 7.5 Hz, 2 *m*-H); at –83°C: δ = 2.28, 5.82 and 6.36 (^2J = 6.4 Hz), 6.93, 7.12.

*Selection[22] of ^{13}C-NMR Data for [^{6}Li]-**12** at 100.6 MHz:* (a) Ca. 0.09–0.16 F in Et$_2$O/[D$_{12}$]cyclohexane (7:1) at +25°C: δ = 22.1 (qd, ^1J = 125, ^3J = 5.5 Hz, 2 CH$_3$), 117.3 (quasi-t, ^1J = 147 Hz, CH$_2$-β), 120.5 (dd, ^1J = 155.3, ^2J = 2.3 Hz, *p*-C), 127.6 (dm, ^1J = 152 Hz, 2 *m*-C), 128.1 (m, 2 *o*-C), 157.5 (m, *i*-C), 204.3 (dd, ^2J = 13.5 and 7.8 Hz, C-α); at –40°C: δ = 22.3, 116.6 (br.), 120.3, 127.3, 127.6, 157.2, 204.5 (br.). – (b) In *t*BuOMe/[D$_{12}$]cyclohexane (7:1) at +25°C: δ = 22.3 (2 CH$_3$), 116.5 (CH$_2$-β), 120.3 (*p*-C), 127.4 (2 *m*-C), 127.8 (2 *o*-C), 157.8 (*i*-C), 203.8 (br., C-α); at –40°C: δ = 22.4, 115.8 (br.), 120.1, 127.1, 127.3, 157.2, 203.6. – (c) Ca. 0.25 F in [D$_8$]toluene at +25°C: δ = 22.4 (qd, ^1J = 124.9, ^3J = 5.5 Hz, 2 CH$_3$), 117.2 (quasi-t, ^1J = 147 Hz, CH$_2$-β), 120.7 (d, ^1J = 158.0 Hz, *p*-C), 127.6 (dm, ^1J = 156 Hz, 2 *m*-C), 128.0 (m, 2 *o*-C), 157.3 (m, *i*-C), 203.4 (m, C-α); at –84°C: δ = 22.8, 115.8, 120.5, 127.4, 127.5, 157.3, 203.5 (qi, $^1J_{\mathrm{CLi}}$ = 7.5 Hz, C-α). – (d) Ca. 0.54 F in [D$_8$]toluene with 0.68 M THF at +25°C: δ = 22.0, 117.4, 120.4, 127.5, 128.0, 157.7, 204.6; at –83°C: δ = 22.3, 117.0, 119.9, 127.3, 127.4, 158.2, 205.5 (br.).

X-Ray Crystal Structure Analyses: A Siemens P4/V automated four-circle diffractometer operating with MoK_α radiation and a graphite monochromator was used for all measurements. Colourless cubes of **11** (0.4 × 0.3 × 0.25 mm) and **12** (0.4 × 0.4 × 0.3 mm) were mounted in glass capillaries in poly(fluoroether) oil and cooled to 213 K. Cell dimensions were calculated from 17 (**11**) and 20 (**12**) centred reflections. Background measurement: Stationary crystal and stationary counter at the beginning and end of scan, each 12.5% of total scan time. Data reduction used Lorentz and polarization corrections. Both structures were solved by direct methods, using the program XS (Siemens), and refined by full-matrix least-squares on F^2 with the program SHELXT2 (Sheldrick 1993). Non-hydrogen atoms were refined in anisotropic description. Hydrogen atoms, although largely found in the difference Fourier synthesis, were placed in calculated positions and refined as a riding model with fixed U_i[38]. The weighting scheme used was $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$ where $P = (F_o^2 + 2F_c^2)/3$.

11: (C$_{14}$H$_{21}$LiO)$_2$, M = 424.50, triclinic, space group P$\bar{1}$, a = 8.727(5), b = 12.475(7), c = 14.935(9) Å, α = 66.33(4)°, β = 73.99(2)°, γ = 74.60(2)°, V = 1409(1) Å^3, Z = 2, $d_{\mathrm{calc.}}$ = 1.000 g/cm^3, μ = 0.059 mm^{-1}, F(000) = 464. – 2Θ range = 3.04–47.00° for $-1 \leq h \leq 9$, $-12 \leq k \leq 12$, $-15 \leq l \leq 16$; ω scans, scan speed 4.0–60.0°/min, scan range = 1.8°, reflections collected = 3803, unique reflections = 3510 (R_{int} = 8.54%), observed reflections = 2004 [$F > 4\sigma(F)$]; 297 variables, R = 0.083 and $wR2$ = 0.230 [for $4\sigma(F)$]; $R1$ = 0.130 and $wR2$ = 0.260 for all data; GOF = 1.015, largest difference peak = 0.384 e/Å^3; weighting scheme: x = 0.1660, y = 0.

12: (C$_{15}$H$_{23}$LiO)$_2$, M = 452.55, triclinic, space group = P$\bar{1}$, a = 7.151(2), b = 13.696(3), c = 16.468(4) Å, α = 74.89(2)°, β = 81.78(1)°, γ = 79.53(1)°, V = 1523.4(7) Å^3, Z = 2, $d_{\mathrm{calc.}}$ = 0.987 g/cm^3, μ = 0.058 mm^{-1}, F(000) = 496. – 2Θ range = 2.58–50° in $0 \leq h \leq 8$, $-15 \leq k \leq 15$, $-19 \leq l \leq 19$, ω scans, scan range = 1.3°, scan speed = 3.4–60°/min, reflections collected = 5680, unique reflections = 5289 (R_{int} = 0.215), observed reflections = 2476

$[F \geqslant 4\sigma(F)]$; variables = 319, GOF = 1.072; R = 0.139 and $wR2$ = 0.364 for $4\sigma(F)$; R = 0.288 for all data; weighting scheme: x = 0.2342, y = 4.1799, largest residual peak = 1.197 e/Å^3. – Atom O1, as well as C21 and C31, showed anomalously large thermal parameters, and refinement in split positions did not improve the results singificantly. As shown by the large R_{int} value, the crystal quality was obviously not satisfactory.

2-(2,6-Dimethylphenyl)-2-propenoic acid (**13**): The bromide **10** (148 mg, 0.70 mmol) in 0.7 ml of *t*BuOMe was cooled at −30°C under Ar and treated with 0.77 mmol of *n*-butyllithium in 0.61 ml of hexane. After 30 min at room temperature, the mixture was poured onto dry-ice, warmed up again, and taken up in diethyl ether and 2 N NaOH (3 × 1.5 ml). The combined aqueous layers were acidified and extracted with ether (3 × 2 ml) to yield 79 mg of crude acids, which were crystallized from pentane to give 34 mg (28%) of pure **13**. Its m.p. was 102–104°C after recrystallization from cyclohexane. – IR (KBr): $\tilde{\nu}$ = 3200–2500 cm^{-1} (CO_2H), 1688 (vs), 1620, 1214, 978, 775. – ^{1}H NMR ($CDCl_3$): δ = 2.19 (s, 2 CH_3), 5.76 and 6.76 (AB system, ^2J = 1.7 Hz, CH_2), 7.05 and 7.14 (A_2B system, ^3J = 7.6 Hz, *m-/p*-H), 10.6 (br., CO_2H); similar in CCl_4. – ^{13}C NMR ($CDCl_3$): δ = 20.3 (2 CH_3), 127.3 (2 *m*-C), 127.9 (*p*-C), 131.5 (CH_2), 135.9 (C-α), 136.2 (2 *o*-C), 139.4 (*i*-C), 171.6 (CO_2H). $C_{11}H_{12}O_2$ (176.2): calcd. C 74.98, H 6.86; found C 74.62, H 6.73.

Diastereotopomerization Rate Constants (**16a** ⇌ **16b**) *in [D$_8$]Toluene:* For formal concentrations 0.07–0.47 F in the presence of *t*BuOMe (0.40 and 0.55 M), with or without THF (0.32 M), the rate constants k (temp. ±1 K) = 30 ± 3 s^{-1} (+121.5°C), 32 ± 3 (119.0°C), 13 ± 2 (110.5°C), 7 ± 2 (99.5°C), 6 ± 2 (98.0°C) were used for activation parameters, but 3 ± 1 (89.0°C) and 2 ± 1 (88.5°C) were not used. – With THF (1.43 M), k = 31 ± 2 s^{-1} (100.5°C) and 11 ± 1 (89.5°C).

☆ Dedicated to Prof. *Joseph Klein* on the occasion of his 80th birthday.

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[36] Compare ref.[20] for data and citations.

[37] Assigned by comparison with 2-(1-bromopropenyl)-1,3-dimethylbenzene[19].

[38] Further details[22] of the crystallographic and structural data are available on request from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK, on quoting the depository number CSD 10058 for **11** and for **12**, the names of the authors, and the journal citation.

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