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Ring expansion and vinylic nucleophilic substitution competing for (*tert*-alkyl)$_2$C=C(Li)–Cl in carbenoid chain processes☆

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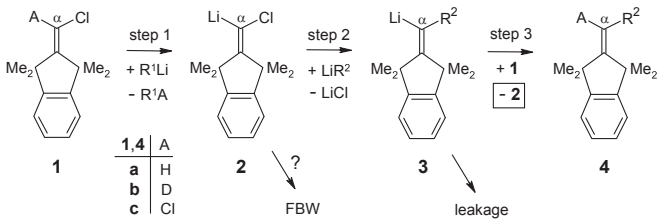
ABSTRACT

Vinylic nucleophilic substitution (S_NV) reactions of unactivated, cyclic α,α-dichloroalkenes [(*tert*-alkyl)$_2$C=CCl$_2$] with aryllithiums (RLi) to give (*tert*-alkyl)$_2$C=C(Cl)–R are presented to be carbenoid chain reactions, which involve the unsaturated Cl,Li-carbenoids (*tert*-alkyl)$_2$C=C(Li)–Cl as transient intermediates. The chains are longer and the overall reactions much slower in *tert*-butyl methyl ether (*t*-BuOMe) than in THF as the solvent. In competition with the fast S_NV step of these Cl,Li-carbenoids, the Fritsch–Buttenberg–Wiechell (FBW) ring expansion in *t*-BuOMe (but less so in THF) generates short-lived cyclohexyne species, which are trapped by the accompanying RLi species to yield chlorocyclohexene derivatives [(*tert*-alkyl)–(Cl)C=C(R)–(*tert*-alkyl)] as the FBW chain products.

1. Introduction

Two different types of carbenoid chain reactions were independently identified in the last decade. The type-1 chain (Scheme 1) looks like a simple vinylic nucleophilic substitution (S_NV) reaction that produces **4** from **1**. However, a significantly retarding kinetic deuterium isotope effect (**1b** reacting slower than **1a**) established that **1a** was consumed through an initial scission of the A–C(α) bond (step 1) by a strong base R^{1}Li with formation of the unsaturated Cl,Li-carbenoid **2**.[1,2] A sufficiently reactive nucleophile R^{2}Li (which may be identical with R^{1}Li) will usually intercept **2** very quickly[3] (step 2) before **2** decays.[4] The resultant alkenyllithiums **3** are sufficiently basic to perform the final transfer (step 3) of particles A (=H or D) from **1a** or **1b**, producing **4a** or **4b** along with the chain carrier **2**. An unintentional trapping of **3** by side-reactions ('leakage') may interrupt a running chain reaction. For the α,α-dichloride **1c**, this mechanism was established in a different manner with methyllithium (the usual tetramer) as a strongly basic but weakly nucleophilic reagent R^{1}Li in competition with PhC≡CLi as a weakly basic but strongly nucleophilic reagent R^{2}Li as follows. No conversion of **1c** took place with PhC≡CLi alone, whereas the expected product **4c** (R^2 = C≡CPh) emerged as soon as substantially less than 1 equiv of methyllithium was added as the initiator R^{1}Li (step 1) that was unable to compete with PhC≡CLi for the intermediate **2** (step 2). This established for **1c** that the initiating step 1 (performed by methyllithium) is different from a step 2 in which R^{2}Li generates the precursor **3** of product **4c**, so that at least one intermediate (namely, **2**) must occur in between these steps during the conversion of **1c** to **4c**. In the general protocol[1,2] with R^{2}Li = R^{1}Li, the total consumption of **1a**–**c** often required only little more than 1 equiv (instead of 2) of a sufficiently basic nucleophile R^{2}Li, as demanded if the uninterrupted carbenoid chain mechanism obtains.



Scheme 1. The type-1 carbenoid chain reaction.

The Fritsch–Buttenberg–Wiechell (FBW) reaction[3,5] will eliminate LiHal from a short-lived carbenoid R^{3}R^{4}C=C(Li)–Hal with formation of an alkyne R^{3}C≡CR^4. For the R^{3}R^{4}C part embedded in a cyclic arrangement, this means ring expansion with formation of a cycloalkyne[6] and deviation from the usual course of the above type-1 carbenoid chain reaction if an interception of a carbenoid

☆ Sterically congested molecules, Part 28. For Part 27, see Ref. 25.

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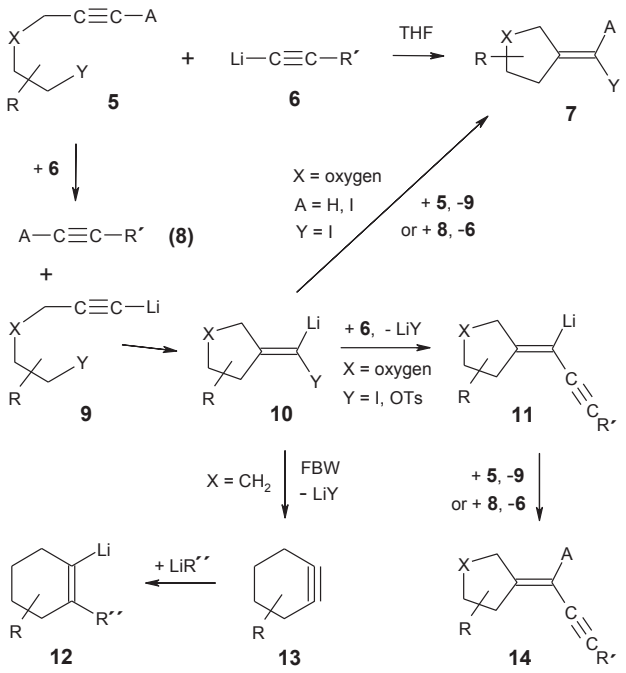
such as **2** by R^2Li in step 2 is too slow. A similar kind of deviation by FBW ring expansion was recently detected[7] in connection with the carbenoid chain reaction type-2[8,9] that explained the THF-dependent conversion of the acyclic starting material **5** into cyclic isomers **7** (Scheme 2) in the following way. The weak basicity of LiC≡CR′ (**6**) sufficed for an initial activation of **5** by the transfer of particles A (=H, D, I, or Br)[7] with formation of AC≡CR′ (**8**) and the Li acetylide **9**. The increased nucleophilicity of the LiC≡C function in **9** (compared to **5**) facilitated the intramolecular S_N2 reaction of its C-β center with stereoinversion[7] of the attacked carbon center of the C–Y bond, remarkably accompanied by the fixation of Y=iodine in the developing Li,Y-carbenoid **10**.[7,9] With Y=iodine in **10**, mono- or di-iodides **7** may result through the final transfer of A (=H or I, respectively) in two ways: (i) delivery of A *from the coproduct* AC≡CR′ (**8**) will regenerate LiC≡CR′ (**6**) as the catalyst[8] of the process; for A=deuterium in the substrate **5** and LiN(*i*-Pr)$_2$ (LDA) as the catalyzing base,[7] a corresponding transfer of A=D may occur from the byproduct DN(*i*-Pr)$_2$. (These catalytic modes are unavailable for our carbenoid chain type-1 in Scheme 1 where R^1A with A=H or D cannot regenerate the necessary strong base R^1Li). (ii) Alternatively, a transfer of A (=H or I) *directly from the starting material* **5** to carbenoid **10** with formation of product **7** and the chain carrier **9** will maintain a carbenoid chain process. Both of these processes may be outrun by the following deviating choices made by carbenoid **10**.



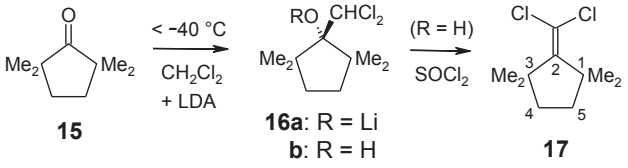
Scheme 2. Examples of the type-2 carbenoid chain reaction.

With X=CH_2 in **10** (Y=I or O_3S–aryl),[7,10] the cyclohexyne derivatives **13** were generated through FBW ring expansion.[7,9] These short-lived intermediates **13** were intercepted through cycloaddition[10] to 1,3-diphenylisobenzofuran or through nucleophilic addition of R″Li (=**6** or **9** or *n*-butyllithium);[7,10] the latter additions afforded cyclohexenyllithiums **12**, which may reimburse the catalyst **6** (from **8**) or the chain carrier **9** (from **5**) through the A transfer reactions as above. With the FBW process retarded by X=oxygen, carbenoid **10** may choose to be trapped by nucleophiles such as reagent LiC≡CR′ (**6**); the resultant alkenyllithium **11** can likewise undergo the A transfer reaction to create product **14** along with the catalyst **6** or the chain carrier **9**. Using our carbenoid chain reaction type 1, we will now examine sterically encumbered, unsaturated Li,Cl-carbenoids such as **2** for their propensity to FBW ring expansion and for the rate-limiting chain steps.

2. Results and discussion

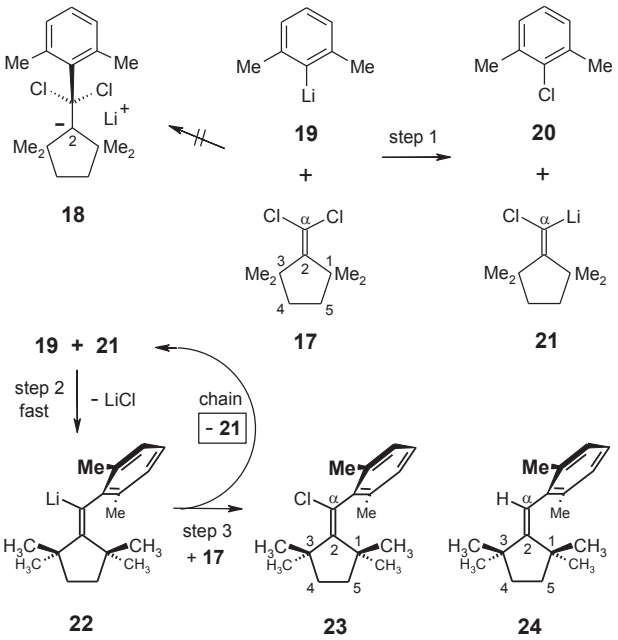
2.1. Syntheses and FBW ring expansion in the cyclopentylidene series

The rather unstable carbenoid $LiCHCl_2$ was generated in THF (Scheme 3) at −70 °C from an excess of dichloromethane with LDA in the presence of 2,2,5,5-tetramethylcyclopentanone[11] (**15**), producing the lithium alkoxide **16a**. This primary product must be kept and finally protonated at internal temperatures well below −40 °C to give **16b**, because **16a** is prone to eliminate LiCl with formation of an α-chlorooxirane and thence an α-chloroaldehyde, as exemplified[12] previously with the related alkoxide *t*-$Bu_2C(OLi)$–$CHCl_2$ that is burdened with even stronger internal strain. The ensuing dehydration of **16b** with $SOCl_2$ furnished purer (namely, crystalline) samples of the α,α-dichloroalkene **17** than had been obtained previously[13] by a different procedure.



Scheme 3. Synthesis of substrate **17**.

The vinylic nucleophilic substitution (S_NV) reaction (Scheme 4) of the unactivated dichloroalkene **17** by 2,6-dimethylphenyllithium (**19**), devised to produce the chloroalkene **23**, should not be expected to proceed via an addition–rotation–elimination (ARE)[14] mechanism with elimination of LiCl from the intermediate **18**, because the negative charge at C-2 of **18** would be strongly destabilized by the two flanking *tert*-alkyl substituents that shield C-2



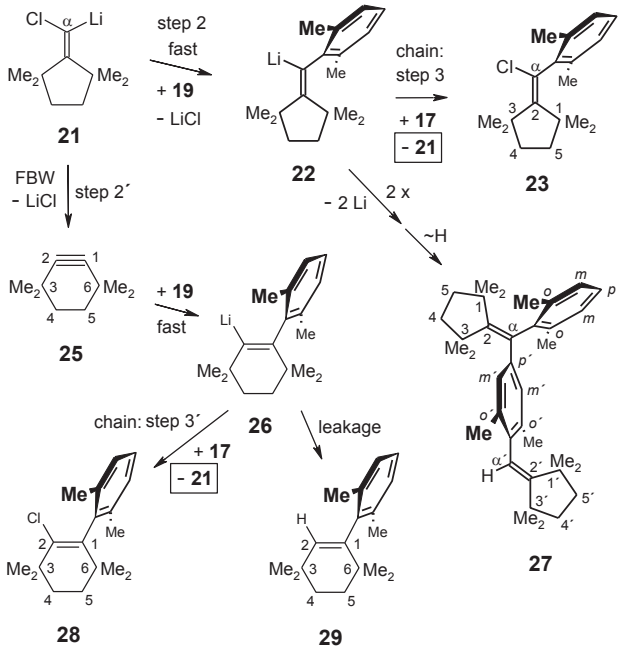
Scheme 4. The carbenoid chain reaction *in THF* as the solvent.

against stabilizing solvation. Instead, a Cl/Li interchange reaction (step 1) will initiate a carbenoid chain reaction (type 1) by the transfer of A=chlorine from **17** to **19** with formation of the Cl,Li-carbenoid **21**, as witnessed by the detection of chloro-2,6-dimethylbenzene (**20**) as a coproduct. S_NV reactions at Li,Hal-carbenoids usually[1,3] are very rapid, so that **19** can intercept (step 2) the short-lived carbenoid **21** before it decays. The resultant, strongly basic alkenyllithium **22** can propagate the chain (step 3) through acceptance of a chlorine particle from the substrate dichloroalkene **17**, creating the product **23** and the chain carrier **21** (The coproduct **20** did not transfer its chlorine to **22** and survived, therefore.). Clearly, step 3 rather than the much faster[1,3] step 2 will limit the velocity of running carbenoid chain cycles.

An undisturbed carbenoid chain reaction in Scheme 4 would require steps 2 and 3 to be much faster than step 1, so that only slightly more than 1 equiv of reagent **19** would suffice[1] for the total conversion of dichloroalkene **17** into product **23** (chain steps 2 and 3) along with merely a trace of coproduct **20** (step 1). In contrast, a reverse rate sequence (steps 1 and 2 being faster than step 3) would lead to the consumption of up to 2 equiv of reagent **19** per mol of **17** (steps 1 and 2) and an accumulation of the intermediate alkenyllithium **22** along with one entire equivalent of **20**: product **23** would then not be obtained from **22** unless a residual amount of **17** was available for a delayed step 3. Hence, the observation of substantially more product **23** than coproduct **20** can provide evidence for the carbenoid chain mechanism (faster step 3).

In THF as the solvent, the dichloroalkene **17** was consumed by reagent **19** (1.4 equiv) at room temperature (rt) within less than 40 min. The crude mixture of nonacidic products was shown by ^{1}H NMR to contain **20**, **23**, and **24** in a ca. 2:6:1 ratio. The olefin **24** arose through chain terminations by the slow proton transfer (within ca. 1 h at rt) from THF to **22** in the aprotic milieu maintained by reagent **19**; it did not arise during the aqueous workup, as confirmed through final quenching with solid CO_2, which served to detect residual portions of reagent **19** in the form of 2,6-dimethylbenzoic acid but uncovered only small portions of the carboxylic acid that derived from the equally small amounts of surviving **22**. Therefore, the main product **23** revealed the operation of a carbenoid chain type 1 process with a rather slow chain-propagating step 3 that was disturbed through competition by step 1 (coproduct **20** augmented) and by slow chain termination ('leakage').

The carbenoid chain mechanism developed in Scheme 4 remained valid in *tert*-butyl methyl ether (*t*-BuOMe) as the solvent, using the dichloroalkene **17** and 2 equiv of 2,6-dimethylphenyllithium (**19**): the chloroalkene **23** was the main product and again accompanied by some chloro-2,6-dimethylbenzene (**20**) as an indicator of step 1. However, warming to 42 °C during at least 23 h was now necessary for the complete consumption of **17**. One of the reasons for this substantial retardation in *t*-BuOMe may be seen in the differing aggregational states of reagent **19**: since **19** in THF is known to be monomeric[15] at −125 °C and dimeric[16] at −60 °C with both forms in a mobile equilibrium, one can expect **19** in the weaker donor solvent *t*-BuOMe to be more extensively aggregated and hence presumably less reactive in steps 1 (initiation) and 2 (S_NV), which depend on the reactivity of **19**. Such a deceleration of step 2 apparently encouraged an FBW ring expansion (step 2′ in Scheme 5) of **21**, which created the strained 3,3,6,6-tetramethylcyclohexyne (**25**). Nevertheless, step 2 must still be very fast so as to trap a portion of the short-lived carbenoid **21** before it expands to give **25**. Although more shielded than the 'parent' cyclohexyne (**13** if R=H in Scheme 2), **25** was intercepted by **19** to afford the alkenyllithium **26** at a high rate, as judged from our failure to find the ring-opened 'dimer'[17] of **25** that was reported[18] to be formed from **25** in a matrix milieu even at −228 °C. The extended (FBW) carbenoid chain cycle



Scheme 5. The carbenoid chain reaction (steps 2 and 3) competing *in t-BuOMe* as the solvent with FBW ring expansion (step 2′) whose chain is propagated in step 3′.

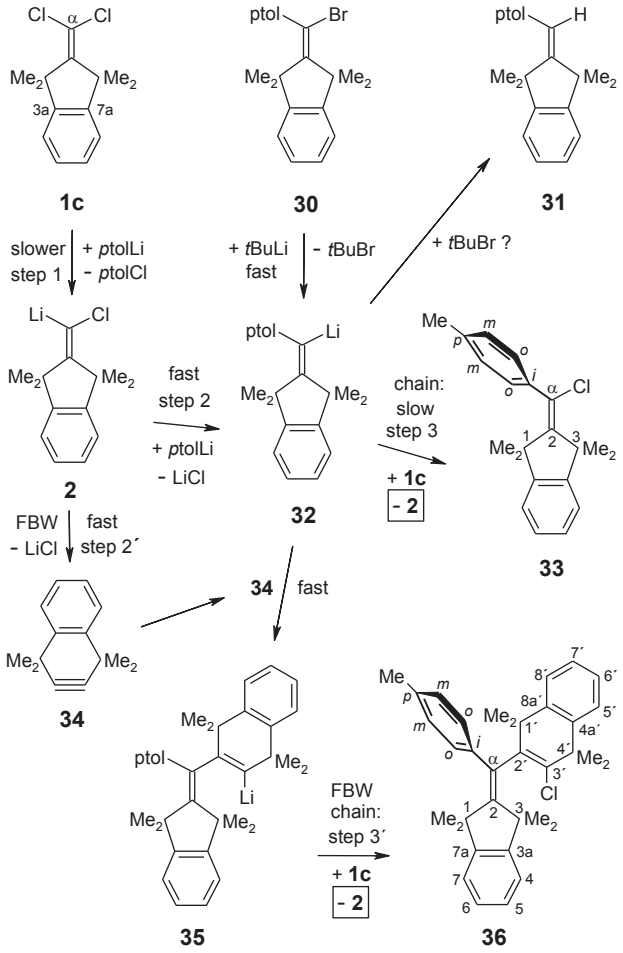
was then closed through a chlorine particle transfer from **17** to **26** (step 3′), which furnished the FBW product **28** and the chain carrier **21**. Step 3′ occurred in close competition with a proton transfer ('leakage') that afforded the ring-expanded olefin **29**, as shown by the product ratio of ca. 1:6:2:1 for **20**, **23**, **28**, and **29** (Control experiments confirmed that **29** was not formed from the chloroalkene **28** in an organolithium milieu.). Due to its poor yield, **29** could not be purified but was identified in the mixtures by means of its NMR spectra. The structural discrimination of the isomeric chloroalkenes **28** and **23** was simple on the basis of ^{1}H and complete ^{13}C NMR signal assignments: selective proton decoupling by irradiation of 3-CH_3 simplified the ^{13}C multiplet of C-2 in **28** to a triplet with a $^3J_{C,H}$=4.5 Hz coupling to CH_2-4 (Scheme 5), whereas the chlorine-bearing C-α in **23** cannot have and did not show such a $^3J_{C,H}$ splitting. The small amount of coproduct **20** permitted to conclude that both **23** and **28** were formed via carbenoid chain pathways, which implies that steps 3 (**23**) and 3′ (**28**) were faster than step 1 (coproduct **20**) in their competition for the substrate **17**. This demonstrates a relative rate sequence of step 2 ≫ (steps 3 and 3′) > step 1.

Is step 1 the only kinetic 'bottleneck' in Scheme 4 (and in the prelude to Scheme 5)? The above-mentioned (6+2):1 ratio of chlorine-bearing products (**23** and **28**) and the leakage product **29** points to short reaction chains whose termination occurred on leakage of the intermediate **26** and implied a corresponding loss of the possibility to propagate the chains via step 3′ with regeneration of the chain carrier **21** for further passes through both steps 2 and 2′. Without such occasional withdrawal of **26** from the circulation, the parallel reaction chains of intermediate **22** would have been substantially longer: Because **22** is persistent in *t*-BuOMe and only a very small amount of the nonexpanded olefin **24** was detected during experiments in the spirit of Scheme 5, **22** in *t*-BuOMe obviously can wait for the substrate **17** with which to generate **23** in step 3. In such a situation of an undisturbed chain reaction, we would have been allowed to conclude that an observed sluggish overall rate was codetermined by a slow step 3 as a second kinetic 'bottleneck'. Regrettably, the withdrawal of **26** impaired a correct assessment of step 3; but direct evidence for a slow step 3 in a similar system will be presented below in Section 2.2. In the

meantime, a certain accumulation of **22** (caused presumably by a retarded step 3) may be inferred from the detection of a small amount of the hydrocarbon **27** that can be thought to arise through an oxidative dimerization of accumulated **22**, followed by a formal p'-to-α' hydrogen shift.[19] The molecular formula ($C_{36}H_{50}$) of **27** became evident through its prominent M^+ mass spectral peak, which was accompanied by an M^++1 satellite (^2H plus ^{13}C) of 40.8% intensity (calculated 40.35%). Starting with the only olefinic proton NMR resonance (α'-H), all 12 proton signals of **27** were assigned; on this basis, the constitution of **27** followed from complete structural assignments of all 26 ^{13}C resonance positions (6×CH_3, 4×CH_2, 4×quaternary sp^3, 4×sp^2-CH, and 8×quaternary sp^2).

2.2. FBW ring expansion in the indan-2-ylidene series

Here we are completing the description of a previous[20] experiment (steps 1, 2, and 3 in Scheme 6) that produced the chloroalkene **33** from dichloroalkene **1c** (1.5 equiv) with the reagent *p*-methylphenyllithium (*p*tolLi) via the Cl,Li-carbenoid **2**. This consumption of *p*-tolLi in *t*-BuOMe as the solvent took 2–4 h at 37 °C,[20] which reaction period is practically equal to that of 2,6-dimethylphenyllithium (**19**) with **1c**, namely,[21] 3 h at 33 °C with production of the benzo derivative[21] of **23**. Comparison with the sluggish conversion of substrate **17** in *t*-BuOMe, as reported in the preceding section, reveals **1c** to be more reactive than **17**, perhaps due to stronger steric shielding of C-α by the methyl groups, which are more inclined toward C-α because of the longer C-4/C-5 bond in **17** as compared to the shorter C-3a/C-7a bond in **1c** (Scheme 6).



Scheme 6. Dichloroalkene **1c** (step 3) and cycloalkyne **34** reacting with the alkenyllithium **32** *in t-BuOMe* as the solvent (*p*-tol=*p*-methylphenyl).

The crude product acquired from **1c** with *p*-tolLi contained the chloroalkene **33** (isolated yield 29%)[22] and residual **1c** but no 'leakage' olefin[23] **31**, which points to barely disturbed chain reactions. In addition, the ring-expanded FBW product (**36**) (yield 4%) was detected in the previously[20] ignored last chromatographic fractions; it is now analyzed and shown in the sequel to be generated with the help of a slow step 3 of the carbenoid chain reaction type 1. An X-ray diffraction analysis at 23 °C revealed the solid-state topology of **36** (but not the mode of its formation) as displayed in Fig. 1: The plane of the central double-bond C2/C14 (C-2/C-α) encloses interplanar angles of 69° and 73° with its two substituents at C14 (*p*-tolyl and the 2-naphthyl-derived chloroalkene, respectively). Internal strain created through repulsion of these two C-α substituents by the 1,1- and 3,3-dimethyl groups (C10–13) may be read from the shrinked sp^2-angle C15/C14/C23 (C-*ipso*/C-α/C-2′=112.0°) and from the unequal angular distortions of the two 3-CH_3 groups (C12 and C13) from local tetrahedral symmetry. Dissolved **36** maintains its chirality (Fig. 1) on the 400-MHz NMR timescale, as shown by the nonequivalence of all nine methyl groups in the fully assigned ^1H and ^{13}C NMR spectra.

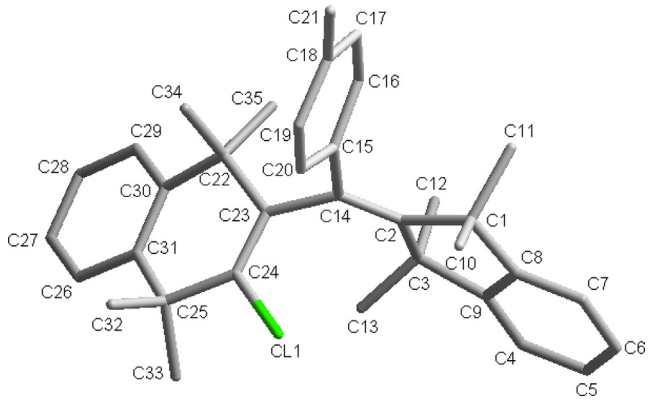


Fig. 1. X-ray structure of **36** whose nonhydrogen atoms are shown with their crystallographic numbering.

Scheme 6 depicts the route from **1c** to the FBW product **36** (steps 1, 2′, and 3′). In contrast to the interception of cyclohexyne derivative **25** (Scheme 5) by **19**, the similarly shielded cycloalkyne **34** was not trapped by the aryllithium reagent *p*-tolLi. This may be due to a retarded ring expansion of the indanylidene carbenoid **2** (step 2′) as compared with the more flexible cyclopentylidene carbenoid **21**. The alternative possibility of an accelerated carbenoid S_NV reaction (step 2) with the sterically unencumbered *p*-tolLi appears less obvious in consideration of the higher aggregation states[16] of *p*-tolLi in THF (dimeric) or in Et_2O (tetrameric), as compared with **19**,[16] so that *p*-tolLi might be expected to be more highly aggregated (and perhaps less reactive) than **19** also in the present solvent *t*-BuOMe. With *p*-tolLi concentrations dwindling anyway in later reaction stages, however, step 2 will slow down so that step 2′ can begin to compete: The emerging, short-lived cycloalkyne **34** added quickly to the meanwhile accumulated alkenyllithium **32**,[24] creating the strongly basic intermediate **35** that completed (step 3′) the deviating FBW chain cycle through a chlorine particle transfer from the surplus dichloroalkene **1c** to **32** with formation of **36** and the chain carrier **2**. This pathway was confirmed through an independent generation of the intermediate **32** from the known[25] bromoalkene **30** with *t*-BuLi (2 equiv) in *t*-BuOMe, followed by addition of **1c** (1 equiv) and observation of the consumption of **32** in situ[26] for 2 h. After quenching with solid CO_2 and aqueous workup, the crude material (no carboxylic acids

detected) was a mixture of **1c**, **31**, **33**, and **36** (ca. 44:30:22:4) in rough agreement with the **33**/**36** ratio of 29:4 cited above. The unexpected olefin[23] **31** is thought to have resulted through proton transfer to **32** from part of the coproduct *t*-BuBr (Scheme 6). We estimated the first half-reaction time of this separated step 3 to be in the order of 20 min at rt in *t*-BuOMe; the corresponding overall reaction period resembles that of the above-mentioned overall reaction (120–240 min at 37 °C) of *p*-tolLi with **1c**. Hence, this chain-propagating step 3 was not fast and had limited the rate of the overall process in (partial) cooperation with the slower step 1. Of course, the addition reaction of **32** to the short-lived cycloalkyne **34** must be fast; but this cannot suppress the slow step 3 because of the low concentration of **34**. Comparably slow steps 3 were previously[27] encountered for the carbenoid chain reactions of **1c** with an excess of several other aryllithiums in *t*-BuOMe or Et_2O as the solvents, where alkenyllithium intermediates (corresponding to **32**) were also observed (^{1}H NMR in situ) but did not permit an unequivocal interpretation.

3. Conclusion

The unactivated, cyclic α,α-dichloroalkenes (*tert*-alkyl)$_2$C=CCl$_2$ (**1c** and **17**) can react with organolithiums via unsaturated Cl,Li-carbenoids (*tert*-alkyl)$_2$C=C(Li)Cl (**2** and **21**) in carbenoid chain cycles of alternating S_NV (very fast[3] step 2) and Cl/Li interchange (slower step 3) events. The solvent-dependent velocity of step 3 appears to be at least partially determinative for the preparative productiveness and the overall reaction periods: the primary S_NV products (*tert*-alkyl)$_2$C=C(Li)–aryl (**22** and **32**) in the solvent THF were labile ('leakage') but sufficiently reactive toward the substrates (**17** and **1c**, respectively) despite steric shielding, whereas they were durable in *t*-BuOMe and revealed that product formation by the chain-propagating step 3 can be a strikingly sluggish process. There may even be other cases in which the initiating carbenoid formation (step 1) remains competitive with (or faster than) step 3, so that it may partially (or totally) thwart the chain mechanism by means of an exhaustive consumption of the substrate (*tert*-alkyl)$_2$C=CCl$_2$ that should have carried out step 3. For preparative purposes, this nonchain carbenoid possibility (steps 1 and 2 only) may be either ameliorated by an excess of the dichloroalkene substrate or made productive through quenching with another finally introduced external organic chlorine supplier.

Ring expansions are the main reaction mode of unsaturated Hal,K-carbenoids that were generated from (halogenomethylidene) cyclobutane derivatives[3,28] in a nonpolar milieu. We have presented here an example of our indan-2-ylidene Cl,Li-carbenoids as being reasonably resistant against this undesired FBW reaction. In contrast, one of our cyclopentylidene Cl,Li-carbenoids revealed that the very facile S_NV step can be partially disturbed by competing FBW ring expansion in *t*-BuOMe (but less so in THF) as the solvent. The FBW products can result from trapping of the cycloalkynes by the organolithium reagent (ca. 20% of **28**) or by the chain-propagating (or an independently generated) alkenyllithium such as **32** (ca. 4% of **36**). It follows that substantially less reactive nucleophiles than aryllithiums may not always undergo clean S_NV reactions (namely, avoiding the FBW complication) with our unsaturated Hal,Li-carbenoids; examples were already described[29] for the corresponding Cl,K-carbenoids (*tert*-alkyl)$_2$C=C(K)–Cl.

4. Experimental section

4.1. General information

All organometallic procedures were carried out under a cover of slowly streaming, dry argon gas. The in situ experiments were performed in dried NMR tubes (5 mm) that were charged under argon gas cover, then tightly closed with a solvent-stable soft rubber stopper, sealed with Parafilm® that was wrapped around the stopper, and stored at −18 °C in a large Schlenk tube filled with argon. ^{1}H and ^{13}C NMR chemical shifts δ were referenced to tetramethylsilane as an internal standard. Chromatographic separations used silicagel (60 Å, 100–200 μm). Combustion analyses were carried out in the departmental service unit.

4.2. 1-(Dichloromethyl)-2,2,5,5-tetramethylcyclopentanol (16b)

A freshly prepared solution of lithium *N*,*N*-diisopropylamide (LDA, 214 mmol) in anhydrous THF (35 mL) was added dropwise within 35 min to the stirred solution of dichloromethane (18.3 mL, 285 mmol) and 2,2,5,5-tetramethylcyclopentanone[11] (**15**, 10.00 g, 71.3 mmol) in anhydrous THF (50 mL) at −70 °C. The orange-brownish mixture was stirred for another 60 min at up to −40 °C internal temperature and then quenched at −40 °C by the slow addition of glacial acetic acid (25 mL) in THF (25 mL). On warming up to 0 °C, the mixture deposited a crystalline precipitate was poured into ice-cold aqueous hydrochloric acid (2 M, 500 mL), and was shaken with Et_2O (4×100 mL). The combined aqueous layers were washed with distilled water until neutral, dried over Na_2SO_4, and concentrated to leave a brown liquid (14.86 g) containing **16b** together with the corresponding spirocyclic α-chlorooxirane (11%) (The latter side-product would have been avoided through working at less than −40 °C and with a shorter dwell time). Distillation at 35–52 °C (bath temp 75–95 °C)/0.015 mbar furnished **16b** as a yellowish liquid (10.85 g, 68%) that contained a trace of the corresponding 1-chloro-1-formyl-2,2,5,5-tetramethylcyclopentane and crystallized slowly. Mp 38.5–41 °C (from pentane at −70 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.19 and 1.21 (2s, 2×6H, 2×CH_3), 1.48 and 1.72 (2m, 2×2H, CH_2–CH_2), 2.34 (s, 1H, OH), 6.07 (s, 1H, $CHCl_2$) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 25.77 (qm, ^1J 126 Hz, apparent ^3J 2.5 Hz, 2×CH_3), 25.92 (qm, ^1J 126 Hz, ^3J unresolved, 2×CH_3), 40.03 (tsept, ^1J 130 Hz, ^3J 4.5 Hz, 2×CH_2), 48.41 (unresolved, C-2/-5), 79.80 (sharp d, ^1J 174 Hz, $CHCl_2$), 85.44 (unresolved, C-1) ppm; IR (KBr) ν 3589 and 3568 (2 sharp O–H), 2951, 2878, 1469, 1382, 1123, 1028, 992, 771, 747, 735, 718 cm^{-1}. Anal. Calcd for $C_{10}H_{18}Cl_2O$ (225.16): C, 53.35; H, 8.06; Cl, 31.49. Found: C, 53.61; H, 8.15; Cl, 31.75.

4.3. 2-(Dichloromethylidene)-1,1,3,3-tetramethylcyclopentane (17)

A solution of the alcohol **16b** (15.0 g, 66.6 mmol) in distilled pyridine (75 mL) was stirred in an ice-bath during the slow, dropwise addition of thionyl chloride (13.10 mL, 180 mmol). After stirring at rt overnight, the dark brown suspension was poured into ice-cold aqueous HCl (2 M, 450 mL) and shaken with Et_2O (4×150 mL). The combined organic layers were washed with aqueous HCl (2 M, 2×100 mL) and then with distilled water until neutral, dried over Na_2SO_4, and concentrated at rt to afford almost pure **17** (8.91 g, 65%). This orange-brown, volatile liquid was filtered through silicagel (80 g) with low-boiling petroleum ether/Et_2O (98:2) and concentrated at rt to leave a colorless liquid (7.41 g, 54%) that crystallized slowly in a refrigerator: colorless needles with mp 23.5–26 °C (pentane at −70 °C; Ref. 13: no mp); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.27 (s, 12H, 4×CH_3), 1.62 (s, 4H, CH_2–CH_2) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 26.13 (4×CH_3), 41.01 (2×CH_2), 46.99 (C-1/-3), 113.57 (CCl_2), 155.06 (C-2) ppm, assigned through comparison with 2-(dichloromethylidene)-1,1,3,3-tetramethylindane (**1c**, which is compound **2c** in Ref. 1), but in disagreement with the eight (rather than five) ^{13}C signals reported[13] previously for **17**; IR (film) ν 2958, 2869, 1605, 1591, 1460, 1366, 908, 849 cm^{-1}. Anal. Calcd for $C_{10}H_{16}Cl_2$ (207.14): C, 57.98; H, 7.79; Cl, 34.23. Found: C, 58.04; H, 7.74; Cl, 33.80.

4.4. 2-(α-Chloro-*o*,*o*-dimethylbenzylidene)-1,1,3,3-tetramethyl cyclopentane (23)

A solution of pure bromo-2,6-dimethylbenzene (4.50 mL, 34.5 mmol) in anhydrous THF (75 mL) was stirred at −70 °C during the slow addition of *tert*-butyllithium (*t*-BuLi, 68 mmol) in hexane (39.8 mL). The solution was stirred at rt for 30 min so as to destroy the byproduct *t*-BuBr[30] and then recooled to −70 °C for the dropwise addition of dichloroalkene **17** (5.00 g, 24.1 mmol) dissolved in anhydrous THF (25 mL). The black solution was stirred at rt for 40 min and poured onto solid CO_2. The warmed-up mixture was treated with aqueous NaOH (2 M, 500 mL) and shaken with Et_2O (4×75 mL). The combined organic layers were washed with distilled water until neutral, dried over Na_2SO_4, and concentrated at rt to afford a yellow liquid (6.65 g) containing **23**, the olefin **24**, and chloro-2,6-dimethylbenzene (**20**, δ_H 2.37 ppm, boiling at ca. 30 °C/0.02 mbar) in a molar ratio of 6:1:2 together with a tiny trace of **29** as the only products. Distillation at 76–92 °C (bath temp 95–145 °C)/0.05 mbar furnished a mixture of **23** (49%) and **24** (11%), which was redistilled to provide pure **23** as a yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.78 (s, 6H, 2×1-CH_3), 1.48 (s, 6H, 2×3-CH_3), 1.53 (t, ^3J 7 Hz, 2H, CH_2-5), 1.66 (t, ^3J 7 Hz, 2H, CH_2-4), 2.33 (s, 6H, 2×*o*-CH_3), 7.05 and 7.10 (AA′B system, ^3J 7.5 Hz, 2H+1H, 2×*m*-H and *p*-H) ppm, assigned through the following {^{1}H} decoupled NOE difference spectra: {1-CH_3}→CH_2-5 and *o*-CH_3, {3-CH_3}→CH_2-4 only; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.97 (qm with reduced intensity, ^1J 126.5 Hz, 2×*o*-CH_3), 26.85 (qsext, ^1J 126 Hz, ^3J 4.5 Hz, 2×1-/3-CH_3), 41.08 (tm, ^1J 129 Hz, CH_2-4), 41.52 (tm, ^1J 129 Hz, CH_2-5), 46.54 (m, apparent *J* 3.8 Hz, C-3), 46.58 (m, apparent *J* 3.8 Hz, C-1), 123.53 (sharp s, C-α), 127.30 (ddq, ^1J 157.5 Hz, ^3J 7.5 Hz, ^3J 4.8 Hz, 2×C-*m*), 127.86 (sharp d, ^1J 159 Hz, C-*p*), 136.49 (dq, ^3J 7.4 Hz, ^2J 6.2 Hz, 2×C-*o*), 139.41 (m, C-*ipso*), 152.94 (m, ^3J 3.3 Hz, C-2) ppm, assigned through the following selective {^{1}H} decoupling experiments: {1-CH_3}→1-CH_3 simplified; {3-CH_3 and CH_2-4/-5}→3-CH_3 simplified, CH_2-4 decoupled from 3-CH_3, CH_2-5 as a narrow m, and C-3 as a sharp s; IR (film) ν 2954, 2868, 1635 (w), 1461, 1363, 770, 723 cm^{-1}. Anal. Calcd for $C_{18}H_{25}Cl$ (276.85): C, 78.09; H, 9.10; Cl, 12.81. Found: C, 78.59; H, 9.16; Cl, 11.39.

4.5. 2-(2,6-Dimethylbenzylidene)-1,1,3,3-tetramethylcyclo pentane (24)

A crude sample of the α-chloroalkene **23** (450 mg, ca. 1.6 mmol) in *tert*-butyl alcohol (20 mL) was refluxed with elemental Li° (2×140 mg, 2×20 mmol) for 2 h (all Li° dissolved). The mixture was diluted with Et_2O (60 mL) and water (30 mL), and the aqueous layer was extracted with more Et_2O (10 mL). The combined Et_2O layers were washed with distilled water until neutral, dried over Na_2SO_4, and concentrated to yield the crude liquid **24** (330 mg, ca. 1.36 mmol); bp 75–85 °C (bath temp)/0.002 mbar. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.87 (s, 6H, 2×1-CH_3), 1.22 (s, 6H, 2×3-CH_3), 1.52 (AA′ part of an AA′BB′ system, 2H, CH_2-5), 1.57 (BB′ part, 2H, CH_2-4), 2.20 (s, 6H, 2×*o*-CH_3), 6.05 (s, 1H, α-H), 6.98 and 7.04 (AA′B system, ^3J 7.3 Hz, 3H, 2×*m*-H and *p*-H) ppm, assigned through comparison with compound **38** in Ref. 31; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.79 (qm, see the {^{1}H} decoupling and the computer-simulated multiplets further below, 2×*o*-CH_3), 27.65 (qsext, ^1J 125.3 Hz, ^3J 4.2 Hz to 1-CH_3 and CH_2-5, 2×1-CH_3), 30.53 (qsext, ^1J 125.3 Hz, ^3J 4.2 Hz to 3-CH_3 and CH_2-4, 2×3-CH_3), 38.47 (tm, ^1J 128.7 Hz, apparent *J* 4.8 Hz, CH_2-4), 40.78 (tm, ^1J 128.7 Hz, apparent *J* 4.8 Hz, CH_2-5), 43.37 (m, for ^2J and ^3J see {^{1}H}, C-1), 44.77 (m, for ^2J and ^3J see {^{1}H}, C-3), 118.47 (sharp d, ^1J 149.2 Hz, C-α), 126.05 (sharp d, ^1J 158.0 Hz, C-*p*), 126.72 (ddq, see {^{1}H}, 2×C-*m*), 136.29 (m, see {^{1}H}, 2×C-*o*), 137.91 (m, see {^{1}H}, C-*ipso*), 159.64 (m, apparent *J* 3.4 Hz, C-2) ppm, assigned as above and through selective {^{1}H} decoupling as follows: {*o*-CH_3}→*o*-CH_3 as a disturbed q with d ^3J 4.1 Hz, C-*m* as a sharp dd with ^1J 156 and ^3J 7.6 Hz, C-*ipso* as a td with ^3J 6.6 and ^2J 1 Hz, C-*o* simplified to a peculiar dm (doublet next to a dt) that was successfully simulated with the following set of coupling constants: d ^3J 7.6 Hz to *p*-H, d ^3J 2.5 Hz to α-H, d ^2J 0.9 Hz to one of the *m*-H, d ^4J −1.2 Hz to the other *m*-H, $^3J_{H,H}$ 7.3 Hz, $^4J_{H,H}$ +1.5 Hz; {1-CH_3}→t (ca. 4 Hz) coupling of 1-CH_3 with CH_2-5, C-1 as a dm with ^3J 8.6 Hz trans to α-H, CH_2-5 simplified; {3-CH_3}→t (ca. 4 Hz) coupling of 3-CH_3 with CH_2-4, C-3 as a dm with ^3J 5.5 Hz cis to α-H, CH_2-4 simplified; {α-H}→C-*o* as a pseudo-qi that could be simulated with the above set of $J_{C,H}$ and $J_{H,H}$ values, but including ^2J 5.8 Hz to *o*-CH_3 and excluding α-H; {all aryl-H}→*o*-CH_3 as a sharp q, C-*o* as a broadened q with ^2J 5.8 Hz to *o*-CH_3, C-*ipso* as an m with ^3J 4.2 Hz. The unusual appearance of several proton-coupled ^{13}C NMR resonances was confirmed by simulations with the following appropriate coupling constants: for C-*o* with the above set of $J_{C,H}$ and $J_{H,H}$ values and again including ^2J 5.8 Hz to *o*-CH_3; for *o*-CH_3, ^1J 126.2 Hz, ^3J 4.1 Hz to one of the *m*-H, ^5J +0.7 Hz to the other *m*-H, ^4J +0.3 Hz to *p*-H, $^3J_{H,H}$ 7.3 Hz, $^4J_{H,H}$ +1.4 Hz; for C-*m*, d ^1J 156.0 Hz, d ^3J 7.6 Hz, q ^3J 4.9 Hz to one of the two *o*-CH_3, ^2J 1.2 Hz, $^4J_{H,H}$ +1.4 Hz; for C-*ipso*, t ^3J 6.6 Hz, sept ^3J 4.3 Hz, d ^2J 1 Hz, ^4J 0 Hz, $^3J_{H,H}$ 7.3 Hz; IR (film) ν 3062 (w), 2954, 2865, 1459, 1362, 767 cm^{-1}. Anal. Calcd for $C_{18}H_{26}$ (242.41): C, 89.19; H, 10.81. Found: C, 88.64; H, 11.19.

4.6. 2′-{*o*′,*o*′-Dimethyl-*p*′-[*o*,*o*-dimethyl-α-(1,1,3,3-tetramethyl cyclopent-2-ylidene)benzyl]benzylidene}-1′,1,′3′,3′-tetramethylcyclopentane (27)

Although this product of an oxidative dimerization of **22** was not visible by ^{1}H NMR in the crude product mixture described further below, it was traced down as follows. The pot residue that remained after a distillation of the chloroalkene **28** was prepurified by chromatography on silicagel with low-boiling petroleum ether, affording a mixture (82 mg) of **23**, **28**, and **27** that deposited small needles (30 mg, 1%) of **27** from hot methanol (5 mL): mp 213–214 °C (3× from methanol); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.88 (s, 6H, 2×1′-CH_3), 0.91 (s, 6H, 2×1-CH_3), 0.99 (s, 6H, 2×3-CH_3), 1.19 (s, 6H, 2×3′-CH_3), 1.51 (m, 4H, CH_2-4 and CH_2-5′), 1.54 (m, 4H, CH_2-4′ and CH_2-5), 2.13 (s, 6H, 2×*o*′-CH_3), 2.45 (s, 6H, 2×*o*-CH_3), 5.98 (s, 1H, α′-H), 6.95 (s, 2H, 2×*m*′-H), 6.96 and 6.98 (AA′B system, 3H, 2×*m*-H and *p*-H) ppm, assigned through the NOESY correlations α′-H↔3′-CH_3↔CH_2-4′, α′-H↔*o*′-CH_3↔1′-CH_3↔CH_2-5′, *o*′-CH_3↔*m*′-H↔3-CH_3↔CH_2-4, and *m*′-H↔*o*-CH_3↔1-CH_3↔CH_2-5; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.97 (qm, ^1J 126 Hz, 2×*o*′-CH_3), 22.56 (qm, ^1J 126 Hz, 2×*o*-CH_3), 27.69 (qsext, ^1J 125.2 Hz, 2×1′-CH_3), 28.28 (qsext, ^1J 125.2 Hz, 2×1-CH_3), 30.31 (qm, ^1J 125.2 Hz, 2×3-CH_3), 30.45 (qm, ^1J 125.2 Hz, 2×3′-CH_3), 38.48 (tsept, ^1J 128.4 Hz, CH_2-4′), 40.85 (tsept, ^1J 128.4 Hz, CH_2-5′), 41.64 (tsept, ^1J 128.4 Hz, CH_2-5), 42.58 (tsept, ^1J 128.4 Hz, CH_2-4), 43.33 (unresolved, C-1′), 44.81 (unresolved, C-3′), 45.00 (unresolved, C-1), 45.79 (unresolved, C-3), 118.51 (sharp d, ^1J 149 Hz, C-α′), 125.90 (sharp d, ^1J 158.5 Hz, C-*p*), 127.44 (ddq, ^1J 155 Hz, 2×C-*m*), 128.46 (ddq, ^1J 155.5 Hz, 2×C-*m*′), 133.75 (t, ^2J 3.5 Hz, C-*p*′), 134.65 (qd, ^2J 5.4 Hz, ^2J 2.3 Hz to *m*′-H, 2×C-*o*′), 135.73 (overlaid m, C-*ipso*′), 135.90 (apparent qi, 2×C-*o*), 141.02 (sharp s, C-α), 142.69 (m, C-*ipso*), 154.24 (unresolved, C-2), 159.65 (unresolved, C-2′) ppm, assigned through HETCOR and the following selective {^{1}H} decoupling experiments: {3-CH_3}→CH_2-4 as a t 126 Hz, C-3 and C-2 sharpened; {1-CH_3}→CH_2-5 as a t 128 Hz, C-1 and C-2 sharpened; {3′-CH_3}→CH_2-4′ as a t 123 Hz, C-3′ narrowed; {*o*′-CH_3}→C-*m*′ as a dd with ^1J 155.5 Hz and ^3J 6.8 Hz, C-*o*′ as a d ^2J 2.3 Hz, C-*ipso* as a t ^3J 6.7 Hz; {*o*-CH_3}→C-*m* as a ddd with ^1J ca. 155 Hz, ^3J 7 Hz, and ^2J 1.1 Hz, C-*o* as a d ^3J 6.9 Hz, C-*ipso* as a sharp t; {all tetramethylcyclopentylidene protons}→C-1′ as a d ^3J 9.3 Hz (trans to α′-H), C-3′ as a d ^3J 5.8 Hz (cis to α′-H), C-1/-2/-3 as three

sharp s, C-2′ as a d ^2J 3.8 Hz to α′-H; {all aromatic H}→*o*-CH_3 and *o*′-CH_3 as two sharp q with ^1J 126 Hz, C-*m*′ as a q ^3J 4.5 Hz, C-*o* as a q ^2J 5.7 Hz, C-*p*′ as a sharp s, C-*ipso* and C-*ipso*′ simplified; EIMS (70 eV) *m*/*z*=482.79 (M^+) with ($^1H+^{13}C$) satellite 40.8% (calcd 40.35% for $C_{36}H_{50}$). Anal. Calcd for $C_{36}H_{50}$ (482.80): C, 89.56; H, 10.44. Found: C, 89.01; H, 10.83.

4.7. 2-Chloro-1-(*o*,*o*-dimethylphenyl)-3,3,6,6-tetramethylcyclohexene (28)

A solution of pure bromo-2,6-dimethylbenzene (3.22 mL, 24.1 mmol) in anhydrous *t*-BuOMe (41 mL) was stirred at −70 °C during the slow addition of *t*-BuLi (48.3 mmol) in hexane (28.4 mL), then kept at rt for 30 min so as to destroy the byproduct *t*-BuBr,[30] and stirred at −70 °C during the dropwise addition of the dichloroalkene **17** (2.50 g, 12.1 mmol) in *t*-BuOMe (8 mL) within 20 min. The mixture was warmed at 40–45 °C for ≥23 h, poured onto solid CO_2, warmed up, treated with aqueous NaOH (2 M, 150 mL), and shaken with Et_2O (3×50 mL). The combined organic layers were extracted with NaOH (2×), washed with distilled water until neutral, dried over Na_2SO_4, and concentrated to yield a yellow liquid (2.41 g) that contained a roughly 1:6:2:1 mixture of **20**, **23**, **28**, and **29** accompanied by traces of further products. Column chromatography on silicagel with low-boiling petroleum ether afforded first **23** (1535 mg, ca. 46% containing some **29**), followed by the isomer **28** (490 mg, ca. 15%), which crystallized slowly from pentane at −70 °C or from methanol at rt: transparent rods, mp 58–59.5 °C; bp 80–85 °C/0.04 mbar. ^1H NMR of **28** ($CDCl_3$, 400 MHz) δ 0.98 (s, 6H, 2×6-CH_3), 1.25 (s, 6H, 2×3-CH_3), 1.67 and 1.84 (AA′MM′ system, 2H+2H, CH_2-5 and CH_2-4), 2.18 (s, 6H, 2×*o*-CH_3), 7.03 and 7.07 (AA′B system, 2H+1H, 2×*m*-H and *p*-H) ppm, assigned through the NOESY correlations *m*-H↔*o*-CH_3↔6-CH_3↔CH_2-5↔CH_2-4↔3-CH_3; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.66 (qm, ^1J 126.0 Hz, 2×*o*-CH_3), 28.35 (qsext, ^1J 126.6 Hz, ^3J 4.4 Hz, 2×3-CH_3), 28.80 (qqt, ^1J 126.3 Hz, ^3J 4.8 Hz, ^3J 4.5 Hz, 2×6-CH_3), 35.75 (tm, ^1J 123 Hz, CH_2-4), 36.00 (tm, ^1J 123 Hz, CH_2-5), 37.98 (m, C-3), 39.86 (m, C-6), 126.19 (sharp d, ^1J 158.5 Hz, C-*p*), 127.28 (ddq, ^1J 156.5 Hz, ^3J 7.5 Hz, ^3J 5 Hz, 2×C-*m*), 136.19 (apparent qi, $^3J=^2J$=6.0 Hz, 2×C-*o* with reduced intensity due to the prolonged relaxation time T_1=12±3 s), 138.67 (m, C-*ipso*), 139.35 (tm, ^3J 3.5 Hz, C-1), 140.21 (tm, ^3J 4.5 Hz, C-2) ppm, assigned through HETCOR and the following selective {^1H} decoupling experiments: {6-CH_3}→C-1 as a t ^3J 3.5 Hz, C-6 sharpened, CH_2-5 simplified; {3-CH_3}→C-2 as a t ^3J 4.5 Hz, C-3 sharpened, CH_2-4 simplified; {CH_2-5}→6-CH_3 as a qq, C-6 sharpened; confirmed through HMBC experiments showing the $^3J_{C,H}$ correlations 6-CH_3↔C-1↔CH_2-5↔C-3, 3-CH_3↔C-2↔CH_2-4↔C-6, C-4↔3-CH_3↔3-CH_3↔CH_2-4, C-5↔6-CH_3↔6-CH_3↔CH_2-5, *m*-H↔C-*m*↔*o*-CH_3↔C-*ipso*↔*m*-H↔*o*-CH_3, *p*-H↔C-*o*, and the $^2J_{C,H}$ correlations 6-CH_3↔C-6↔CH_2-5, 3-CH_3↔C-3↔CH_2-4, and *o*-CH_3↔C-*o*. Anal. Calcd for $C_{18}H_{25}Cl$ (276.85): C, 78.09; H, 9.10. Found: C, 78.20; H, 9.00.

4.8. 1-(*o*,*o*-Dimethylphenyl)-3,3,6,6-tetramethylcyclohexene (29)

This ring-expanded olefin was measured as an enriched component in an inseparable mixture as obtained from preparations of **23** and **28**. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.96 (s, 6H, 2×6-CH_3), 1.05 (s, 6H, 2×3-CH_3), 1.64 (quasi-s, 4H, CH_2-4/-5), 2.23 (s, 6H, 2×*o*-CH_3), 5.07 (s, 1H, 2-H), ca. 7.01 (overlaid, 2×*m*-H and *p*-H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.4 (2×*o*-CH_3), 28.9 (2×6-CH_3), 29.8 (2×3-CH_3), 37.2 and 39.0 (CH_2-4/-5), C-3/-6 not assigned, 125.7 (*C*H-*p*), 127.2 (2×*C*H-*m*), 136.8 (2×C-*o*), 137.4 (*C*H-2), 141.2 and 141.5 (2×quart., C-*ipso* and C-1) ppm, assigned through HETCOR and comparison with **24**.

4.9. 2-[α-(3′-Chloro-1′,4′-dihydro-1′,1′,4′,4′-tetramethylnaphth-2′-yl)-4-methylbenzylidene]-1,1,3,3-tetramethylindane (36)

This ring-expanded side-product was obtained[20] from the carbenoid chain reaction of dichloroalkene **1c** (1.5 equiv) with 4-methylphenyllithium (**19**) in *t*-BuOMe (not in THF) as the solvent. After column chromatography on silicagel had afforded the expected α-chloroalkene **33**,[22] further elution of the column with Et_2O furnished an oily mixture (918 mg) that deposited cotton-like needles of **36** (138 mg, yield 4%) from ethanol (25 mL); mp 228–229 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.63 (s, 3H, 1′a-CH_3), 1.13 (s, 3H, 1a-CH_3), 1.42 (s, 3H, 3a-CH_3), 1.50 (s, 3H, 4′a-CH_3), 1.52 (s, 3H, 1b-CH_3), 1.61 (s, 3H, 3b-CH_3), 1.67 (s, 3H, 4′b-CH_3), 1.85 (s, 3H, 1′b-CH_3), 2.36 (s, 3H, *p*-CH_3), 7.08 (m, 2H, 4-/7-H), 7.11 (broadened d, ^3J 7.8 Hz, 2H, 2×*m*-H), 7.18 (m, 2H, 5-/6-H), 7.22 (m, 2H, 6′-/7′-H), 7.33 (m, 1H, 8′-H), 7.36 (br, 1H, 1×*o*-H), 7.40 (m, 1H, 5′-H), 7.74 (br, 1H, 1×*o*-H) ppm, assigned through HETCOR and COLOCS correlations (see below); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.24 (qt, ^1J 126 Hz, ^3J 4.4 Hz, *p*-CH_3), [28.06 (3b-CH_3), 28.22 (1′b-CH_3), 29.41 (1a-CH_3), 29.80 (4′b-CH_3), 30.32 (4′a-CH_3), 34.09 (3a-CH_3), 35.42 (1b-CH_3), 38.75 (1′a-CH_3), altogether 8×qq with ^1J ca. 126 and ^3J ca. 4.6 Hz], 41.49 (m, apparent *J* 3.5 Hz, C-1′), 42.15 (m, apparent *J* 3.5 Hz, C-4′), 49.09 (unresolved, C-3), 49.19 (unresolved, C-1), 121.11 and 122.25 (2 dm, ^1J 156 Hz, C-7/-4), 124.48 (dm, ^1J 157 Hz, C-8′), 126.06 (dd, ^1J 160 Hz, ^3J 7.5 Hz, C-6′), 126.48 (dm, ^1J 157 Hz, C-5′), [126.68 (C-6 or C-5), 126.69 (C-7′), 126.74 (C-5 or C-6), altogether 3×dm with ^1J 159 Hz], [127.14 (C-*o*), 129.02 (C-*m*), 129.78 (second C-*o*), 132.25 (second C-*m*), altogether 4×broadened d with ^1J 158 Hz], 134.83 (t, ^3J 3.5 Hz, C-α), 136.37 (>qi, ^3J 4.8 Hz to 4′-CH_3, C-3′), 136.86 (tq, ^3J 7.7 Hz, ^2J 5.5 Hz, C-*p*), 140.58 (t, ^3J 7.5 Hz, C-*ipso*), 141.62 (m, C-4a′), 143.05 (m, ^3J 4.5 Hz, C-2′), 144.35 (m, C-8a′), [149.79 (C-3a) and 150.11 (C-7a), 2×tm with ^3J 5.5 and ^3J 3.8 Hz], 156.23 (m, coupled to CH_3 only, C-2) ppm, assigned through the $^1J_{C,H}$ values, off-resonance {^1H} decoupling, and selective {^1H} decoupling experiments as follows: {*p*-CH_3}→C-*p* as a t ^3J 7.7 Hz to *m*-H; {broadened *m*-H}→*p*-CH_3 as a sharp q ^1J 126 Hz, C-*ipso* as a s; {broadened *o*-H at δ_H 7.74 ppm}→C-α as a s; {all aromatic H centered at δ_H 7.25 ppm}→C-5/-6/-6′/-7′/-8′/-α/-*ipso* as seven sharp s, C-2 and C-2′ fully coupled, C-5′/-4/-7 as three shrinked d, C-1′ and C-4′ simplified, C-*p* as a q ^2J 5.5 Hz, *p*-CH_3 as a sharp q, C-4a′ and C-8a′ as two m ^3J 3.6 Hz to 1′-/4′-CH_3, C-3a and C-7a as two m ^3J 3.8 Hz to 1-/3-CH_3, only C-*o* at δ_C 129.8 ppm as a shrinked d with residual $^1J_{C,H}$ to *o*-H at δ_H 7.74 ppm; {1′a-CH_3 at δ_H 0.63 ppm}→1′a-CH_3 disturbed, 1′b-CH_3 as a sharp q with ^1J 126 Hz, C-1′ as a dq coupled to 8′-H and 1′b-CH_3, C-2′ as a q ^3J 4.5 Hz to 1′b-CH_3; {all CH_3 centered at δ_H 1.62 ppm}→C-2/-2′/-3′ as 3s, C-7a as a t ^3J 5.5 Hz to 4-/6-H, C-3a as a t ^3J 5.6 Hz to 5-/7-H, C-8a′ as a broadened t (overlaid by residual ^3J to 1′a-CH_3 at δ_H 0.63 ppm) but C-4a′ as a t ^3J 6 Hz to 6′-/8′-H, C-*p* as a broadened t (overlaid by residual ^2J to *p*-CH_3), C-1/-3 narrowed, C-1′ broadened (residual ^2J to 1′a-CH_3) but C-4′ as a d ^3J 3 Hz to 5′-H. Final assignments were made by two-dimensional COLOCS experiments (window 4 Hz) as follows. (a) $^3J_{C,H}$ correlations: 1′a-CH_3↔C-2′↔1′b-CH_3, 4′a-CH_3↔C-3′↔4′b-CH_3, 1′a-CH_3↔1′b-CH_3, 1′b-CH_3↔1′a-CH_3, 4′a-CH_3↔4′b-CH_3, 4′b-CH_3↔4′a-CH_3, 1a-CH_3↔1b-CH_3, 1b-CH_3↔1a-CH_3, 3a-CH_3↔3b-CH_3, 3b-CH_3↔3a-CH_3, 4-H↔C-6, 7-H↔C-5, C-4↔5-/6-H↔C-7, 5′-H↔C-7′, 6′-H↔C-8′, 7′-H↔C-5′, 8′-H↔C-6′; (b) $^2J_{C,H}$ correlations: *p*-CH_3↔C-*p*, 1a-CH_3↔C-1↔1b-CH_3, 1′a-CH_3↔C-1′↔1′b-CH_3, 3a-CH_3↔C-3↔3b-CH_3, 4′a-CH_3↔C-4′↔4′b-CH_3; IR (KBr) ν 2971, 2927, 1621 (w), 1486, 1459, 1383, 1362, 823, 755 (s), 586 cm^{-1}. Anal. Calcd for $C_{35}H_{39}Cl$ (495.1): C, 84.90; H, 7.94; Cl, 7.16. Found: C, 84.34; H, 7.33; Cl, 6.92.

The transparent, orthorhombic rodlets suitable for X-ray diffraction analysis at 20 °C (Fig. 1) were obtained through slow evaporation of a $CDCl_3$ solution. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as

supplementary publication no. CCDC 259731. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.Uk).

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