yellow precipitate appeared. Addition of THF (3–4 mL) resulted in a clear solution and cooling in a −20 °C freezer for 10 h gave the product 2 as orange-red crystals. Yield 0.37 g, 36%; m.p. 140 °C (dec. slow). ^{11}B NMR: $\delta = 74.9$.

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[9] ^{1}H NMR (in [D₁₀]xylene, 27 °C): 1: δ = 1.4 (m, THF), 2.25 (s, p-Me), 2.57 (s, o-Me), 2.73 (s, o-Me), 3.45 (m, THF), 6.77 (s, m-H), 6.9 (m, Ph), 7.42 (m, Ph). 2: δ = 1.86 (s, Me₂N), 1.896 (s, CH₂N), 2.24, 2.25 (s, p-Me), 2.663, 2.868 (s, o-Me), 6.87, 6.93 (m-CH), 7.06 (m, Ph), 7.76 (d, Ph).
[10] It is possible to propose that the inequivalence of the mesityl resonances could be due to a restricted rotation around the B-C bonds. Thus, if the mesityls were locked into a position perpendicular to the boron-C10-C1 plane and if the As-C bond were in the mirror plane (i.e., no B-As π interaction), inequivalent ortho-H and meta-H resonances would also be observed. This scenario is unlikely because (1) related studies [1] with B-P compounds fail to show any locking in of the mesityl orientations until a very low temperature (−80 °C) is reached, (2) the barrier observed, 20.9 kcal mol^{-1}, is extremely high and incompatible with a rotation barrier around a B-C bond, (3) two para peaks are observed for the mesityl groups in the ^{1}H NMR spectrum of 2, and (4) the X-ray structure supports π interaction.
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Synthesis and NMR Spectra of 2,3-Dihydro-1,3-methanoindene Derivatives and 1,2,3,5-Tetrahydro-1,3-methanopentalene**

By Manfred Christl* and Horst Reuchlein

1,3-Bridged cyclobutanes are interesting models for theoretical[1] and spectroscopic[1b, c, 2] studies as well as for comparisons of reactivity.[1c, 3] Nonetheless, little is known about bicyclo[2.1.1]hexene and its derivatives, since they are accessible only with difficulty. The benzo derivative 1 (2,3-

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dihydro-1,3-methanoindene) is formed as minor product in the reaction of bicyclo[1.1.0]butane with dehydrobenzene[4a] and has also been synthesized in seven steps from benzonorbornadiene.[4b] Its ^{13}C NMR data are still unknown; however, they were recently calculated.[5]
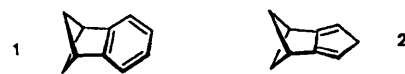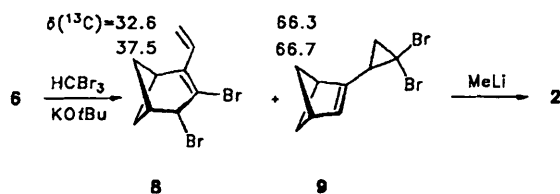

Here we report a route to this system and to 1,2,3,5-tetrahydro-1,3-methanopentalene (2). The relatively readily accessible bicyclo[2.1.1]hexan-2-one (3)[6] can be converted, via 2-vinylbicyclo[2.1.1]hexene (6), into the dimethyl dicarboxylate 1a, as shown in Scheme 1. The key intermediate is 2-lithiobicyclo[2.1.1]hexene (4), formed by reaction of the 2,4,6-triisopropylbenzenesulfonyl hydrazone of 3 with n-butyllithium.[7]
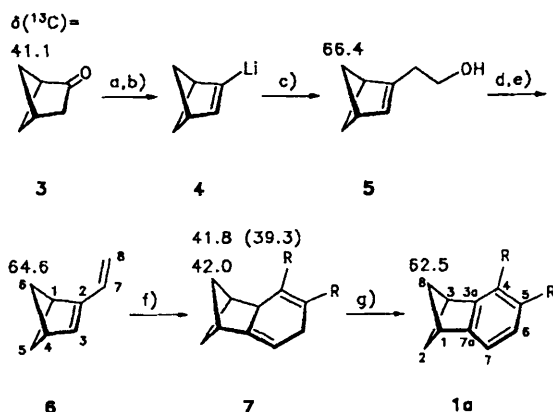
Scheme 1.[8] a) 2,4,6-(iPr)₃C₆H₂SO₂NHNH₂, MeOH, HCl (cat.), 20 °C, 54%. b) 2 equiv. nBuLi, hexane/tetramethylethylenediamine (1:1), −55 to 20 °C. c) 1 equiv. ethylene oxide, 0–20 °C, 49% based on the hydrazone. d) TosCl, pyridine, 90%. e) KOtBu, DMSO, 75 °C, 20 Torr, 82%. f) R-C≡C-R (R = CO₂CH₃), CHCl₃, 20 °C, 75%. g) 1 equiv. 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, C₆H₆, 80 °C, 89%.

To synthesize 2, we first added dibromocarbene to 6 (CHBr₃, KOtBu, pentane, −30 °C, 90%; endocyclic: exocyclic addition 1:3) and obtained the rearranged product 8 together with unrearranged 9.[8] As expected,[9a] reaction of 9 (containing 8) with methyllithium in ether resulted in a Skattebøl rearrangement to give 2[8] (4% yield, isolation by preparative gas chromatography).


If the behavior of isodicyclopentadiene and related compounds[9b] can be extrapolated to 2, then 1,4 additions to the 1,3-cyclopentadiene system of 2 should lead to polycyclic

olefins with a strongly pyramidalized double bond between two bridgehead C atoms. An interplanar angle of 145°, instead of 180° as found for normal olefin geometry, was calculated for the parent hydrocarbon of 10.[10] The hope that, owing to steric hindrance of [2 + 1] cycloaddition by the CH_2 groups of the bicyclohexane system, 2 and dibromocarbene (CBr_4, MeLi, $-78\,°C$) might undergo rare, but known,[11] [4 + 1] cycoladdition to 10 was not fulfilled. Instead, we isolated the bromo derivative 1b[8] in 23 % yield. Compound 1b is presumably formed by [2 + 1] cycloaddition and ring expansion of the resulting dibromocyclopropane derivative followed by elimination of HBr. Compound 2 also undergoes 1,2 addition with 4-methyl-1,2,4-triazole-3,5(4H)-dione (MTAD) (2 → 11)[8] as well as with tetracyanoethylene. However, (E)-1,2-bisphenylsulfonylethylene undergoes slow Diels–Alder reaction with 2 to give 13, which, because of its lability, could not be isolated and was only characterized by an ¹H NMR spectrum.
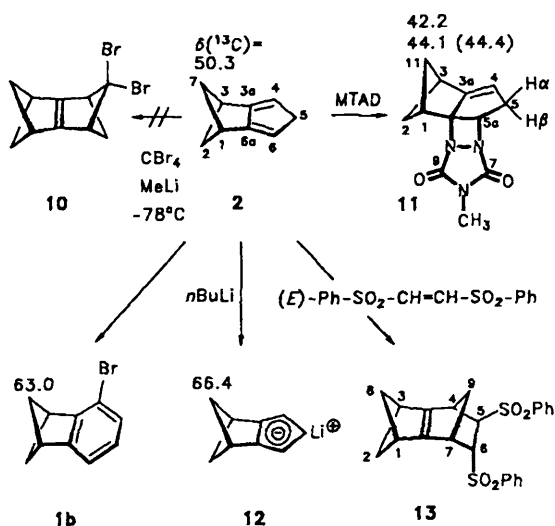
Of particular interest is the ¹³C NMR spectrum of the cycopentadienyl anion 12, which we generated by treatment of 2 with n-butyllithium. C-2,7 ($\delta = 66.4$) absorb at lower field than C-2,7 of 2 ($\Delta\delta = 16.1$) and than C-2, C-11 of 11 ($\Delta\delta = 22.3$ and 24.2). The latter effect resembles that observed for the C-2, C-8 signals when 7 is converted into 1a. Remarkably, the methylene C atoms of the tropylium ion 14 ($\delta = 69.0$[12]) are only slightly more deshielded than those of 12 despite the difference in two units of charge.

The annelation of arenes to bicyclo[2.1.1]hexane (C-5: $\delta = 39.4$[2b]) thus causes the methylene C atoms to be strongly deshielded by an amount similar to the difference between the chemical shifts of C-5 in bicyclo[2.1.1]hexane and -hexene ($\Delta\delta = 28.7$).[2b] This effect is correctly reproduced by calculations using the IGLO method.[13] The result

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of the above-mentioned calculation for the value of C-2 in 1[5] is 30 % too small if 1a, b are accepted as models.

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(3,3-Diphenylallenylidene)trimethylphosphane-titanocene: The First Titanocene Carbene Complex with Three Cumulative Double Bonds

By *Paul Binger,** *Patrik Müller, Regine Wenz,* and *Richard Mynott*

Titanocene carbene complexes are of interest in organic synthesis, especially for carbonyl olefination. Their use is limited, however, by a lack of suitable syntheses for substituted titanocene carbene complexes.[1] We recently reported a novel method for preparing the titanocene vinylcarbene complexes 1a–c from 3,3-disubstituted cyclopropenes and bis(trimethylphosphane)titanocene.[2]

On attempting to carry out a one-pot synthesis of 1a by treating [Cp$_2$TiCl$_2$] with two equivalents of n-butyllithium at −78 °C and then allowing the solution to warm up in the presence of PMe$_3$ and 3,3-diphenylcyclopropene, we found that, in addition to the vinylcarbene complex 1a, (3,3-diphenylallenylidene)trimethylphosphanetitanocene (2) is also formed.[3]
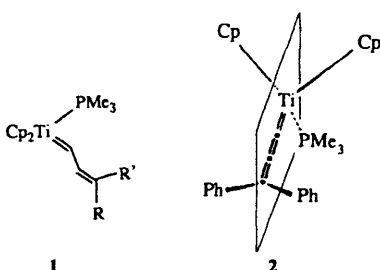

a: R = R'= Ph, b: R = Ph, R'= Me, c: R = R'= CH$_3$

Closer examination of this result showed that n-butyllithium lithiates 3,3-diphenylcyclopropene under the conditions chosen.[4] Reaction of the two starting materials in a molar ratio of 2:1 at 0 °C for 1 h gives a mixture of the two dilithiated compounds 3 and 4 in a ratio of 14:86. At 25 °C, only the immediate formation of 4 (90% purity) is observed; 4 slowly decomposes at room temperature to unidentified products. Apparently, the dilithiocyclopropene derivative 3 rapidly rearranges to the dilithioallene derivative 4. The lith-

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ium derivatives 3 and 4 have not yet been isolated as pure substances; they were trapped by reaction with trimethylchlorosilane to give the corresponding trimethylsilyl derivatives 5 and 6, which were then characterized.
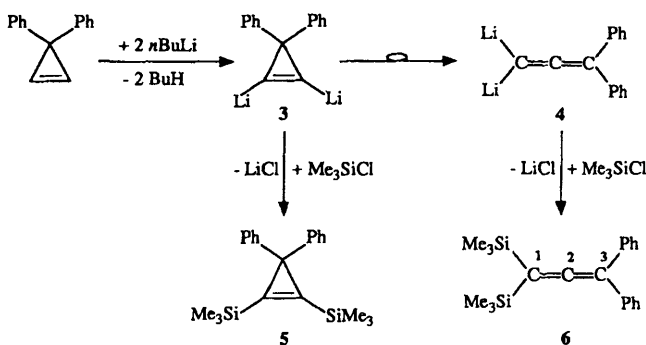
1,1-Dilithio-3,3-diphenylallene (4), prepared at 0 °C, reacts at this temperature with titanocene dichloride and trimethylphosphane to give the (3,3-diphenylallenylidene)-titanocene complex 2 in 71% yield. The route of formation of complex 2 is thereby elucidated. At the same time, these results open up a way of synthesizing as yet unknown allenylidenetitanocene complexes.
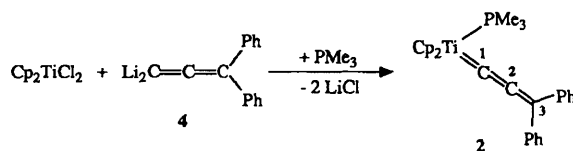
Also new is the selective rearrangement of a 1,2-dilithiocyclopropene to the corresponding 1,1-dilithiopropadiene. Previously, it was known only that both acidic olefinic hydrogen atoms undergo ready lithiation, although almost all preparative applications have used the monometalated cyclopropene.[4, 5] Dilithiated 3,3-dimethylcyclopropene, prepared from 3,3-dimethylcyclopropene and lithium diisopropylamide/tetramethylethylenediamine (LDA/TMEDA) at −60 °C to +20 °C, can be trapped as 3,3-dimethyl-1,2-bis(trimethylsilyl)cyclopropene by reaction with trimethylchlorosilane,[6] even though calculations show that, for the parent compound, structure B is 51.3 kcal mol^{-1} more stable than 1,2-dilithiocyclopropene (A).[7, 8]
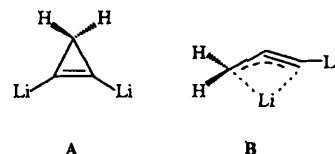
Rearrangements of tetrasubstituted cyclopropenes to allenes occur upon irradiation[9] or upon heating at about 150 °C.[5]

The structures of allenylidene derivatives 2 and 6 were established unambiguously by spectroscopy. The IR spectra show strong bands characteristic of both organic[10]