Tetracyclopropylmethane: A Unique Hydrocarbon with S_4 Symmetry**

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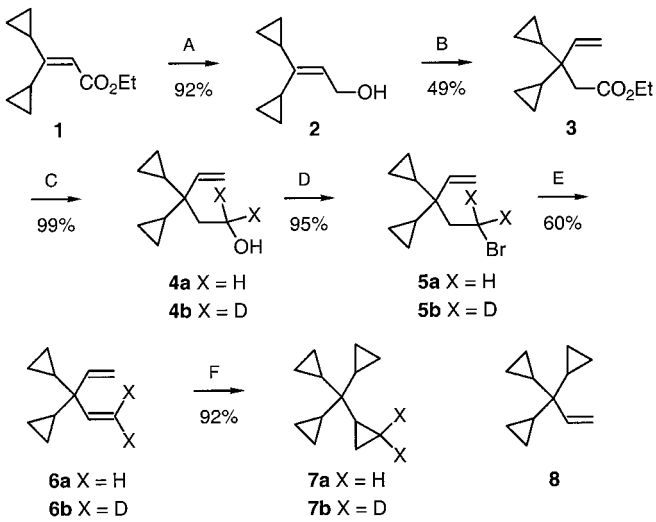
Dedicated to Professor Marit Trætteberg on the occasion of her 70th birthday

The static and dynamic stereochemistry of organoelement compounds containing the respective maximum number of geminal cyclopropyl groups, Cpr_nX (Cpr = cyclopropyl), has attracted considerable attention.[1–4] Nevertheless, the corresponding carbon compound, tetracyclopropylmethane (**7a**), has remained elusive. Neither the two commonly used approaches to percyclopropylated element derivatives,[5] nor the methods for the preparation of tricyclopropylamine[4] can be used to form **7a**. An attempted direct geminal biscyclopropylation of dicyclopropyl ketone with in situ generated $[Cpr_2TiCl_2]$[6] analogous to the reported geminal bismethylation of ketones with $[Me_2TiCl_2]$[7] only led to tricyclopropylmethane in a moderate yield (34%). Therefore, we considered the possibility of preparing **7a** by a twofold cyclopropanation of dicyclopropyldiethenylmethane (**6a**),[8] and to use ethyl 3,3-dicyclopropylacrylate (**1**)[9] as the starting material (Scheme 1).[10] The allyl alcohol **2**, obtained by the reduction of **1**, was transformed into **6a** by the following pathway: an orthoester Claisen rearrangement,[11] subsequent reduction of the ester **3** with $LiAlH_4$ to the alcohol **4**, transformation to the bromide **5**, and its eventual dehydrobromination with potassium *tert*-butoxide in DMSO (Scheme 1).



Scheme 1. Synthesis of **7**. A) AlH_3, THF, 0 °C, 3 h; B) $MeC(OEt)_3$, PhOH, 150 °C, 7 h; C) $LiAlH_4$ or $LiAlD_4$, Et_2O, 34 °C, 1 h; D) $Ph_3P \cdot Br_2$, CH_2Cl_2, −15 → 20 °C, 6 h; E) *t*BuOK, DMSO, 20 °C, 6 h; F) CH_2N_2 (10 equiv), inverse addition of $Pd(OAc)_2$,[14] −20 → 25 °C, repeated six times.

The crucial step in this sequence was the cyclopropanation of **6a**. In contrast to the successful cyclopropanations of other tricyclopropylethenylelement compounds Cpr_3VinX (X = Si, Ge, Sn; Vin = CH=CH_2),[5h] no reaction occurred with **6a** under classical Simmons–Smith conditions,[12a] and with Me_3Al/CH_2I_2 (6 equiv) or $ZnEt_2/CH_2I_2$ (12 equiv)[12b] tricyclopropylethenylmethane (**8**) was obtained at best in 9 and 30% yield, respectively. The $Pd(OAc)_2$-catalyzed cyclopropanation of **6a** with diazomethane[13] gave **8** in only 13% yield. The reactivity of the double bonds in **6a** is apparently retarded by the steric congestion around the quaternary carbon atom. However, the yield could be improved by the addition of the catalyst $Pd(OAc)_2$, in one portion, to a solution of **6a** in ~1.9 M ethereal diazomethane.[14] By repeating this procedure six times, tetracyclopropylmethane (**7a**) was obtained from **6a** in 92% yield. After only three repetitions, tricyclopropylethenylmethane (**8**) was isolated in 80% yield along with **6a** and **7a** (10% each). Tricyclopropyl(2,2-dideuteriocyclopropyl)methane **7b** was obtained in the same way from **6b** (which was prepared from **3** by reduction with $LiAlD_4$ and further transformations of the resulting **4b** as elaborated for **4a** in Scheme 1).[15]

By looking at molecular models, it can be predicted that three of the four cyclopropyl groups in **7a** cannot have the same orientation as the corresponding three groups in tricyclopropylmethane,[16] which in the crystal structure adopts the same C_{3v}-symmetrical conformation (Figure 1)[17] as tricyclopropylamine.[4a,b] According to B3LYP/6-31 + G** computations,[18] the fourth cyclopropyl group in **7a** affects the orientation of the three others in such a way that the overall symmetry becomes S_4 (Table 1). The result of the X-ray structure analysis[17] displays nearly S_4 symmetry for the molecules of **7a** (Figure 1). In contrast, tetracyclopropylsilane Cpr_4Si, Cpr_4Ge, and Cpr_4Sn all have D_{2d} symmetry.[3]

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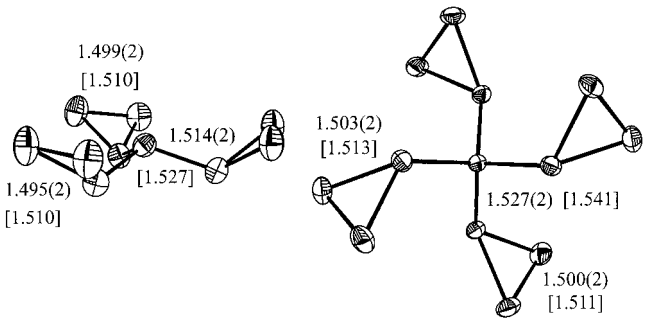


Figure 1. Molecular structures of tricyclopropylmethane and tetracyclopropylmethane (**7a**).[17] The bond lengths [Å] are mean values based on assumed C_{3v} symmetry for tricyclopropylmethane and S_4 symmetry for **7a**; computed values at B3LYP/6-31 + G** in parentheses.

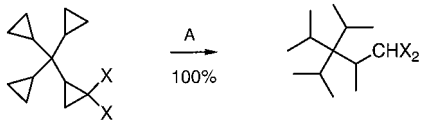
Table 1. Computed energies [kcal mol^{-1}] for tetracyclopropylmethane and tetraisopropylmethane conformations and their rotational transition structures (TS). The energies are given relative to the lowest lying geometry of the molecules **7a** and **9a**. N_{Imag} = number of imaginary frequencies; ZVPE = zero-point vibrational energy.

Molecule	Symmetry	N_{Imag}	E	ZPVE	H_0	G_{298K}
7a	S_4	0	0.0	186.8	0.0	0.0
7a	D_{2d}	3	29.5	186.8	20.7	32.2
7a (TS)	C_1	1	7.6	186.7	7.0	8.2
9a	D_{2d}	0	0.0	243.4	0.0	0.0
9a	S_4	0	0.5	242.8	0.8	1.2
9a (TS)	C_1	1	4.1	243.5	3.6	4.9

For comparison, tetravinylmethane has no symmetry (C_1) in the gas phase[19a] or the crystalline state,[19b] tetravinyl derivatives of Si and Ge are also nonsymmetric, as are the respective Sn and Pb derivatives which differ only in their conformations.[19b] The closest cousin to **7a**, hexacyclopropylethane, displays S_6 symmetry in the crystalline state[20a] as well as, according to MM2[20a] and MM3[20b] calculations, in the gas phase. As a result of the repulsion of the cyclopropyl groups in hexacyclopropylethane, the central C–C bond length (1.636 Å) is significantly longer than an ordinary C–C σ bond.[20a]

In accord with the computational result that the attachment of a fourth cyclopropyl group onto the central carbon in tricyclopropylmethane does not significantly enhance the overall strain, the C–CH bond length in **7a** (1.527(2) Å) is only slightly longer than that in tricyclopropylmethane (1.514(2) Å), and the CH–CH_2 and CH_2–CH_2 bond lengths in the three-membered rings are virtually the same, namely 1.503(2) and 1.500(2) Å, respectively, that is, practically identical to that in unsubstituted cyclopropane (1.499(1) Å).[21] Yet, the computed (B3LYP/6-31 + G**) rotational barrier of the cyclopropyl groups in **7a** of 8.2 kcal mol^{-1} (298 K) is higher than that for rotation around the central bond in hexacyclopropylethane (6.4 kcal mol^{-1}),[20a] but comparable to the barrier for the rotation of the cyclopropyl groups in the tricyclopropylmethyl cation (~8–10 kcal mol^{-1}).[22] However, in their ^{1}H, ^{2}H, and ^{13}C NMR spectra neither tetracyclopropylmethane (**7a**) nor its dideutero analogue **7b** showed any sign of nonequivalence of the sites, even at −130 °C in a CD_2Cl_2/$CHCl_2F$ mixture. A small change in the ^{13}C NMR spectra was observed upon lowering the temperature, but this is because the deuterated carbon with a signal at $\delta = 0.91$ in **7b** loses its coupling to deuterium, and the signal becomes more intense because of the more efficient quadrupolar relaxation of deuterium nuclei at lower temperatures.

Since cyclopropane derivatives are prone to ring opening upon catalytic hydrogenation under appropriate conditions,[23] and the opening of donor-substituted rings usually occurs selectively at the least substituted bond, tetracyclopropylmethane (**7a**) offered itself as a precursor to the previously unknown tetraisopropylmethane (**9**). In fact, hydrogenolysis of hydrocarbons **7a**, **b** over PtO_2 in acetic acid proceeded smoothly with fourfold selective opening of only the distal bonds to give the considerably congested[24] tetraisopropylmethanes (**9a**, **b**) in quantitative yields (Scheme 2).



7a X = H **9a** X = H
7b X = D **9b** X = D

Scheme 2. Catalytic hydrogenation of **7a**, **b** to give the tetraisopropylmethanes **9a**, **b**. A) H_2, AcOH, PtO_2, 20 °C, 4.5 h.

The X-ray analysis of tetraisopropylmethane (**9a**) (Figure 2) shows that it has D_{2d} symmetry with the methyl groups pairwise in an eclipsed orientation with respect to an imaginary line connecting the CH fragments of the corresponding isopropyl groups. This arrangement corresponds to the energetically most favorable conformation of each subunit in the molecule, and it is in excellent agreement with the results of B3LYP/6-31 + G** computations. Yet, the corresponding structure in S_4 symmetry differs only slightly from the D_{2d} structure, both energetically as well as geometrically (Table 1). The single bonds around the central carbon in **9a** (1.599(4) Å; computed: 1.595 Å, Figure 2) are significantly lengthened as a result of the steric interactions between the isopropyl groups. As the shortest nonbonded H ··· H distances in **9a** (2.008 Å; computed 1.995 Å) are between the tertiary

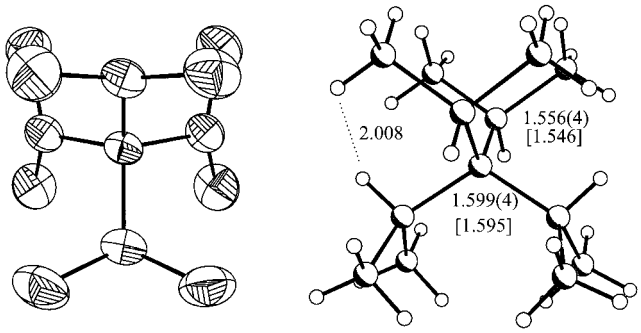


Figure 2. Molecular structure of tetraisopropylmethane (**9a**) according to X-ray structure analysis (left),[17] and in the gas phase (right), according to B3LYP/6-31 + G** calculations (calculated bond lengths in parentheses). The experimental bond lengths [Å] are mean values based on assumed D_{2d} symmetry for **9a**.

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methyne and one hydrogen of the γ-positioned methyl group, the interaction is clearly repulsive. Thus, the arrangement of the four isopropyl groups in **9a** is a compromise between repulsive H···H interactions and favorable local conformations. The shortest H···H distances in tetracyclopropylmethane **7a** are 2.135 Å (computed 2.193 Å), and the interaction is not as repulsive as in **9a**. This is in line with the generally accepted notion that an isopropyl is considerably more sterically demanding than a cyclopropyl substituent.[27]

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[14] **Caution**: This cyclopropanation proceeds very violently. In a typical experiment, a solution of $Pd(OAc)_2$ (200 mg) in CH_2Cl_2 (1 mL) was added in one portion to a precooled (−20 °C) solution of **6** (2.5 g) in ~1.9 M ethereal diazomethane (100 mL) in an 1 L flask. Scaling-up is not recommended.

[15] All new compounds were fully characterized by spectroscopic methods (^{1}H NMR, ^{13}C NMR, MS), elemental analyses and, in part, crystal structure analyses. **7a**: Colorless liquid, m.p. ca. −15 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.15-0.23$ (m, 8H, ½ from $8CH_2$), 0.36–0.46 (m, 12H, ½ from $8CH_2+4CH$); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): $\delta = -0.72$ ($8CH_2$), 15.61 (4CH), 32.65 (C). **7b**: Colorless liquid, m.p. ca. −20 °C; ^{1}H NMR: $\delta = 0.12-0.22$ (m, 7H, ½ from $7CH_2$), 0.33–0.50 (m, 11H, ½ from $7CH_2+4CH$); ^{2}H NMR ($CD_2Cl_2/CHCl_2F$): $\delta = 0.09$ (s), 0.35 (s); ^{13}C NMR: $\delta = -1.35$ (p, J = 24.3 Hz, CD_2), −0.94 (CH_2), −0.72 ($6CH_2$), 15.41 (CH), 15.64 (3CH), 32.65 (C). **6a**: Colorless liquid, b.p. 58–60 °C (12 mbar); ^{1}H NMR: $\delta = 0.27-0.37$ (m, 8H, $4CH_2$), 0.78–0.87 (m, 2H, 2CH), 5.09 (dd, J = 10.8, 1.9 Hz, 2H, $=CH_2$), 5.18 (dd, J = 17.8, 1.9 Hz, 2H, $=CH_2$), 5.59 (dd, J = 17.8, 10.8 Hz, 2H, =CH); ^{13}C NMR: $\delta = -0.22$ ($4CH_2$), 17.17 (2CH), 44.65 (C), 114.81 ($2CH_2$), 141.36 (2CH). **6b**: Colorless liquid, b.p. 65–67 °C (15 mbar); ^{1}H NMR: $\delta = 0.27-0.37$ (m, 8H, $4CH_2$), 0.78–0.85 (m, 2H, 2CH), 5.09 (dd, J = 10.5, 2.0 Hz, 1H, $=CH_2$), 5.18 (dd, J = 17.5, 2.0 Hz, 1H, $=CH_2$), 5.57 (brs, 1H, =CH), 5.59 (dd, J = 17.5, 10.5 Hz, 1H, =CH); ^{13}C NMR: $\delta = -0.22$ ($4CH_2$), 17.19 (2CH), 44.59 (C), 114.27 (quint, J = 23.9 Hz, CD_2), 114.78 (CH_2), 141.10 (CH), 141.33 (CH). **8**: Colorless liquid; ^{1}H NMR: $\delta = 0.25-0.36$ (m, 12H, $6CH_2$), 0.54–0.60 (m, 3H, 3CH), 5.04 (dd, J = 10.5, 2.5 Hz, 1H, $=CH_2$), 5.29 (dd, J = 17.5, 2.5 Hz, 1H, $=CH_2$), 5.47 (dd, J = 17.5, 10.5 Hz, 1H, =CH); ^{13}C NMR: $\delta = -0.41$ ($6CH_2$), 16.32 (3CH), 38.89 (C), 114.66 (CH_2), 141.50 (CH). **9a**: Colorless solid, m.p. 74–76 °C; ^{1}H NMR: $\delta = 1.04$ (d, J = 7.2 Hz, 24H, $8CH_3$), 2.23 (sept, J = 7.2 Hz, 4H, 4CH); ^{13}C NMR: $\delta = 20.87$ ($8CH_3$), 31.94 (4CH), 45.58 (C). **9b**: Colorless solid, m.p. 58–60 °C; ^{1}H NMR: $\delta = 1.05$ (d, J = 7.2 Hz, 21H, $7CH_3$), 1.08 (m, 1H, CD_2H), 2.18–2.30 (m, 1H, CH), 2.24 (sept, J = 7.2 Hz, 3H, 3CH); ^{2}H NMR ($CD_2Cl_2/CHCl_2F$): $\delta = 1.04$ (dd, J = 1.2, 2.0 Hz); ^{13}C NMR: $\delta = 20.31$ (quint, J = 19.0 Hz, CD_2H), 20.89 ($7CH_3$), 31.81 (CH), 31.96 (3CH), 45.59 (C).

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[24] Using the homodesmotic reaction **9a** + neopentane = 2 × 2,3,3,4-tetramethylpentane and the standard enthalpies of formation for neopentane (-40.1 kcal mol^{-1})[25a] and 2,3,3,4-tetramethylpentane (-56.35 kcal mol^{-1}),[25b] the values of $\Delta H_f^0(g) = -72.4$ kcal mol^{-1} and strain energy (SE) = 16.9 kcal mol^{-1} can be estimated for **9a** using the strain-free model proposed by Schleyer et al.[26] The latter is considerably bigger than the strain energy of triisopropylmethane (7.7 kcal mol^{-1}) and dimethyldiisopropylmethane (8.7 kcal mol^{-1}).

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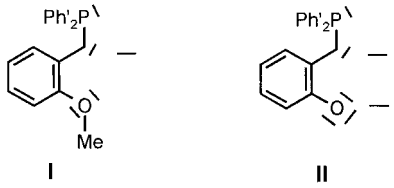
Cyclopentadienyl-Free Calcium Alkyls with Heteroelement-Substituted Anionic Phosphane Ligands: Synthesis and Structure of a Trialkyl Calcate(II) and of an Organocalcium Heterocubane**

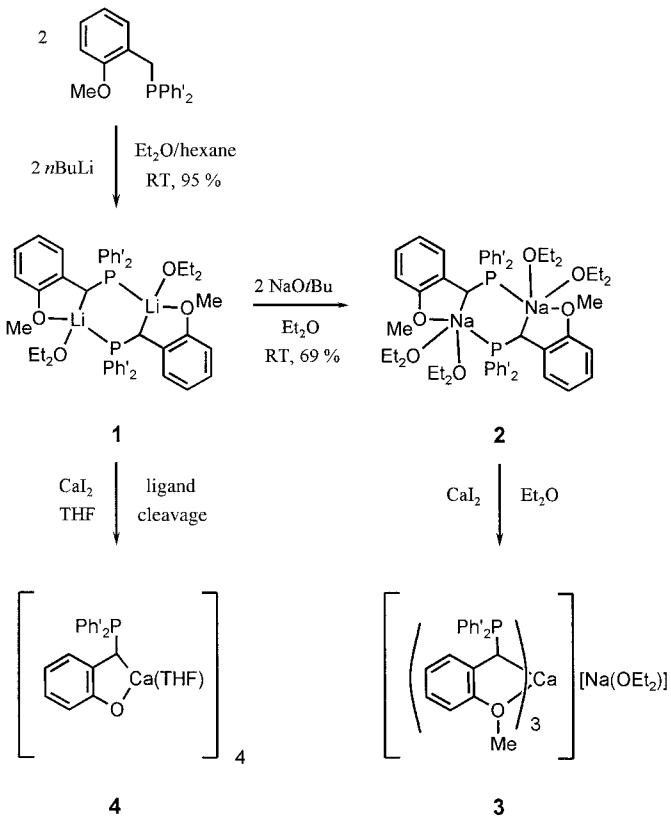
Volker Knapp and Gerhard Müller*

Characteristic for organocalcium chemistry is the predominant use of cyclopentadienyl[1] and related ligands.[2] Their bulk and electronic properties serve in an ideal way to solubilize the highly polar calcium organyls in organic solvents, to control their degree of association, and to kinetically stabilize otherwise highly reactive calcium species. In contrast, the number of cyclopentadienyl-free organocalcium complexes is very limited,[3] particularly noteworthy being $[Ca\{C(SiMe_3)_3\}_2]$.[4] Because of the extreme steric bulk and electron-donating properties of the tris(trimethylsilyl)-methyl ligand, this compound is monomeric with a bent coordination geometry at the two-coordinate calcium center.[4]

By employing the moderately bulky, multidentate, oxygen-substituted anionic phosphanes **I** and **II**, we were able to synthesize and structurally characterize a sodium trialkyl calcate(II) (with the monoanionic ligand **I**) and a calcium organyl with a heterocubane structure (with the dianionic ligand **II**). Soft ligands (such as phosphanes) have been shown to be best suited for complex formation with the hard alkali and alkaline earth metals when they are anionic.[5]



As starting materials for the novel calcium alkyls the lithium and sodium complexes of **I** were used. They are prepared in good yields by lithiation of 2-MeO-$C_6H_4CH_2PPh'_2$ (Ph′ = *p*-tolyl) with *n*BuLi to give **1** (Scheme 1) which reacts by metathesis with NaO*t*Bu to give the sodium complex **2** (see Experimental Section). The constitution and structural details of **1** and **2** are based on crystal structure determinations.[6] The reaction of isolated **2** with CaI_2 (Scheme 1) is not the only way to prepare the trialkyl calcate(II) **3**, it may also be prepared in a one-pot synthesis starting from 2-$MeOC_6H_4CH_2PPh'_2$; the overall product yield is still 40 %.



Scheme 1. Synthesis of complexes **1** – **4**. Ph′ = *p*-tolyl.

Although the good solubility of **3** in aromatic solvents permits the recording of NMR spectra, (see Experimental Section), details of its composition and structure could only be obtained from a crystal structure determination.[7, 12] As Figure 1 shows, calcium is coordinated by the carbanionoid

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