Cationic Lanthanide Alkyl Complexes. Evidence for an Unprecedented Tetraphenylborate Coordination Mode in $La(C_5Me_5)\{CH(SiMe_3)_2\}BPh_4$

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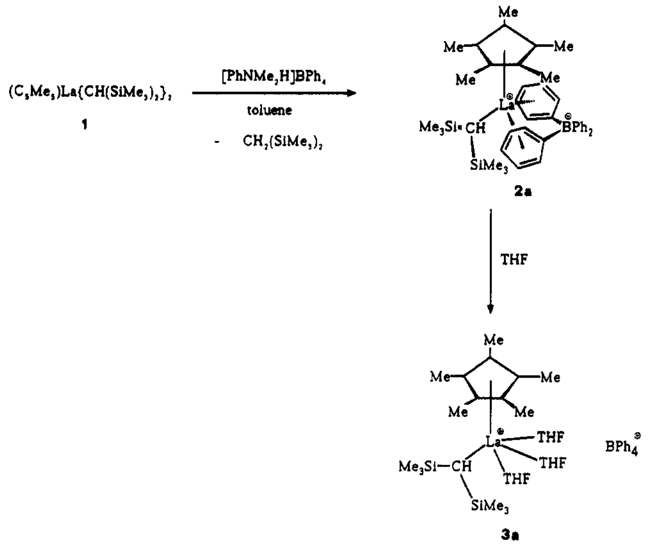
Summary: Reaction of $La(C_5Me_5)\{CH(SiMe_3)_2\}_2$ (1) with $[PhNMe_2H]BPh_4$ affords zwitterionic $La(C_5Me_5)\{CH(SiMe_3)_2\}BPh_4$ (2a), which reacts irreversibly with THF to displace the coordinated tetraphenylborate and afford the first cationic lanthanide alkyl complex $[La(C_5Me_5)\{CH(SiMe_3)_2\}(THF)_3]BPh_4$ (3a).

A combination of the highly unsaturated Lewis acidic metal center, the vacant coordination site, and the reactivity of the M–R′ bond in the cationic complexes $[M(C_5R_5)_2R']^+$ (M = Zr, R = H;[1] M = Zr, R = Me;[1d,2] M = Th, R = Me[3]) are believed to be prerequisites for their olefin polymerization activity. This increasing interest in cationic Ti,[4] Zr,[1,2,5] and Th[3] chemistry is, in part, associated with the realization that an important prerequisite is also a "noncoordinating" anion. Evidence suggests, however, that tetraphenylborates are not necessarily innocuous. For example, η^n-coordination[6] of *one* phenyl ring has been proposed in $Zr(CH_2Ph)_3(\eta^n\text{-}C_6H_5)BPh_3$[5a] and $Cp'_2ZrMe(BPh_4)$,[7] cyclometalation occurs to afford $(C_5Me_5)_2Zr^+(m\text{-}C_6H_4)B^-Ph_3$,[2a] and weak σ-Me coordination has been observed in $(C_5Me_5)_2Zr^+Me(\mu\text{-}Me)B^-Ph_3$.[1d] We report here the first examples of cationic *lanthanide alkyl* species, as well as an unprecedented coordination mode of the tetraphenylborate anion.

Results and Discussion

In order to access the chemistry of analogous cationic lanthanide alkyl complexes, a synthetic requirement is a monocyclopentadienyl precursor. We have previously developed a synthetic methodology to such a species.[8a] Protonation of $La(C_5Me_5)\{CH(SiMe_3)_2\}_2$ (1)[8a] with $[PhNMe_2H]BPh_4$ (1 equiv) in toluene (−30 to +20 °C) cleanly affords a new complex 2a in 93% isolated yield with concomitant formation of 1 equiv of (uncoordinated)

Scheme I



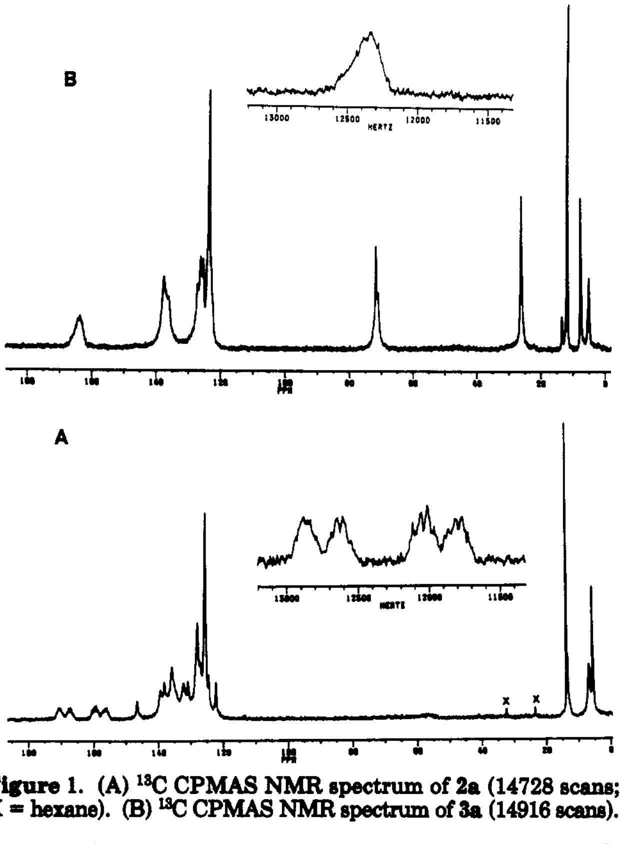


Figure 1. (A) ^{13}C CPMAS NMR spectrum of **2a** (14728 scans; X = hexane). (B) ^{13}C CPMAS NMR spectrum of **3a** (14916 scans).

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(6) The evidence presented for $Zr(CH_2Ph)_3(\eta^n\text{-}C_6H_5)BPh_3$[5a] suggests, but does not unambiguously establish, η^6-phenyl group coordination. In $Cp'_2ZrMe(BPh_4)$,[7] the NMR evidence is consistent with η^3-phenyl coordination or with the rapid equilibration of two diastereomers with η^2-coordinated phenyl rings. η^6-coordination of one phenyl ring of BPh_4^- is not common in electron-rich Ru(II) and Rh(I) chemistry. Kruger, G. J.; DuPreez, A. L.; Haines, R. J. *J. Chem. Soc., Dalton. Trans.* 1974, 1302 and references therein. Uson, R.; Lahuerta, P.; Reyes, J.; Oro, L. A.; Foces-Foces, C.; Cano, F. H.; Garcia-Blanco, S. *Inorg. Chim. Acta* 1980, *42*, 75.

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$PhNMe_2$ and $CH_2(SiMe_3)_2$ (by ^{1}H NMR). Characterization of **2a** by ^{1}H NMR, variable-temperature ^{13}C and ^{29}Si NMR spectroscopy, and elemental analysis indicated the absence of coordinating solvents and the stoichiometry $La(C_5Me_5)\{CH(SiMe_3)_2\}BPh_4$. (See Scheme I). Compound **2a** is insoluble in hexane and C_6H_{12} but dissolves readily in benzene and toluene. It is soluble (and surprisingly stable) in CD_2Cl_2 and $C_2D_2Cl_4$, there being no evidence of decomposition and/or Cl^- abstraction after several hours at 25 °C.

The NMR data for the sterically unsaturated, formally 8-electron $[La(C_5Me_5)\{CH(SiMe_3)_2\}]^+$ fragment in **2a** are unexceptional, the chemical shifts (^{1}H, ^{13}C, and ^{29}Si) being only slightly perturbed from those in **1**.[8a,b] The tetraphenylborate phenyl groups are chemically equivalent, and all ^{13}C NMR resonances remain sharp, down to −85 °C in solution (CD_2Cl_2). The ^{13}C NMR chemical shift of the ipso carbons is very slightly solvent and temperature dependent (see Experimental Section). These C_{ipso} chemical shifts are perturbed upfield (albeit slightly) from those in the uncoordinated tetraphenylborate anion (ca. δ 164.0 ppm).[1b,4c,7] The C_{ipso} peak shapes are also perturbed from that expected for the BPh_4 anion. We attribute this dependence to weak π-coordination of the anion and rapid inter- or intramolecular exchange in these weakly donor solvents (benzene, toluene,[9] CH_2Cl_2[4b,10]). This explanation is also consistent with the solid-state NMR analysis. The ^{13}C CPMAS NMR spectrum of **2a** (Figure 1A) displays two $CH(SiMe_3)_2$ methyl resonances in a 1:1 ratio due to rotation around each C_α–Si_β, exchanging methyl groups in the same (coordinated and uncoordinated) $SiMe_3$ group.[8b] Single C_5Me_5 and $C_5\mathit{Me}_5$ peaks suggest that there are no magnetically inequivalent molecules present in the crystalline asymmetric unit cell giving rise to the multiple C_{ipso} resonances observed. *Four* ipso carbon resonances of equal intensity and similar line shape (multiplets, all with ^{10,11}B coupling[11]) are observed at δ 170.4, 167.3, 159.5, and 156.3 ppm (average = 163.4 ppm). We attribute this to a $(\eta^n\text{-}C_6H_5)_2BPh_2$ tetraphenylborate (in **2a**, $2n$ is necessarily ≤ 10), giving a pseudotetrahedral lanthanum environment. This would give rise to just such a 1:1:1:1 ratio of BPh_4 C_{ipso} resonances, given the asymmetric[8a] coordination of the $CH(SiMe_3)_2$ group.[8b] Alternative structures for **2a**, such as $La(C_5Me_5)\{CH(SiMe_3)_2\}(\eta^n\text{-}C_6H_5)BPh_3$ or dinuclear $[La(C_5Me_5)\{\mu\text{-}CH(SiMe_3)_2\}]_2(BPh_4)_2$, are inconsistent with the (solution and solid-state) NMR evidence. Coordination of just *one* phenyl group would give rise to a 3:1 ratio of C_{ipso} resonances. In $Zr(CH_2Ph)_3(\eta^n\text{-}C_6H_5)BPh_3$[5a] and $Cp'_2ZrMe(\eta^n\text{-}C_6H_5)BPh_3$,[7] π-coordination results in the ipso carbon of the η^n-phenyl group resonating at significantly lower field (δ 178.5–181.0 ppm) and gives a 3:1 ratio of C_{ipso} resonances, as was also observed in the solid-state ^{13}C NMR of cyclometalated $(C_5Me_5)_2Zr^+(m\text{-}C_6H_4)B^-Ph_3$.[2a]

Despite the electronic saturation in **2a**, no evidence for a Si_β—C—La interaction was obtained, there being no significant upfield ^{29}Si NMR chemical shift (as was observed between $[(C_5H_5)_2ZrC(SiMe_3){=}CMe_2][B(p\text{-}C_6H_4F)_4]$ and its MeCN adduct[5d]), compared with THF adduct **3a** (**1** δ −14.62 ppm, C_7D_8, −40 °C;[8b] **2a** δ −10.54 ppm, CD_2Cl_2, temperature invariant +25 to −80 °C; **3a** δ −10.79 ppm, CD_2Cl_2, 25 °C).

Reaction of **2a** with THF (3 equiv) in toluene leads to irreversible displacement of coordinated tetraphenylborate and formation of cationic $[La(C_5Me_5)\{CH(SiMe_3)_2\}(THF)_3]BPh_4$ (**3a**) in high (>85%) isolated yield. (See Scheme I.) The ^{1}H and ^{13}C NMR spectra of both cation and anion are similar to those for **2a**, there being little significant perturbation of the chemical shift of diagnostic resonances. C_{ipso} resonates at δ 164.0 ppm (−30 °C, $C_2D_2Cl_4$) and displays the expected 1:1:1:1 quartet[11] (J_{BC} = 49 Hz) indicative of a noncoordinated, tetrahedral BPh_4 anion.[1b,4c,7] The phenyl region of the ^{13}C CPMAS NMR spectrum of **3a** is much simpler than that for **2a** (Figure 1B). In particular, just one broad resonance at δ 164.0 ppm is observed for all tetraphenylborate C_{ipso} carbons. The $\mathit{C}H(SiMe_3)_2$ resonance was not observed. THF resonances in a 2:1 ratio are observed, consistent with a pseudooctahedral geometry with *fac*[12] THF ligands, C_5Me_5, the La–C σ-bond, and the $SiMe_3$–La secondary interaction of the $CH(SiMe_3)_2$ group occupying the other three sites (see crystal structures of **1**[8a] and **1**·THF[8a]).

To determine the influence of the coordinated anion,[13] $La(C_5Me_5)\{CH(SiMe_3)_2\}B(p\text{-tolyl})_4$ (**2b**) and $[La(C_5Me_5)\{CH(SiMe_3)_2\}(THF)_3]B(p\text{-tolyl})_4$ (**3b**) were prepared using $[NH(^nBu)_3]B(p\text{-tolyl})_4$. In addition, and corroborating the formulation of **2a**/**b** as containing coordinated tetraphenylborate, incorporation of the poorer π-donor C_6H_4F group results in $La(C_5Me_5)\{CH(SiMe_3)_2\}B(p\text{-}C_6H_4F)_4$ (**2c**) {prepared from **1** and $[PhNMe_2H]B(p\text{-}C_6H_4F)_4$; δ 1.67 ppm, C_5Me_5; δ −0.12 ppm, $CH(Si\mathit{Me}_3)_2$} being much less thermally stable than **2a**/**b**. In the solid state, **2c** decomposes after 1 h at 25 °C. The relative instability of cationic zirconocene complexes with $B(p\text{-}C_6H_4F)_4$ as the counteranion has been reported.[5d]

Consistent with the proposed stoichiometry, **2a** reacts with $LiCH(SiMe_3)_2$ (1 equiv) in benzene rapidly and quantitatively to give **1**. **2a** is also a potentially useful precursor for the formation of the mixed species $La(C_5Me_5)\{CH(SiMe_3)_2\}X$, which are inaccessible by other synthetic methodologies. Thus, reaction with $LiOC_6H_3{}^tBu_2{\cdot}OEt_2$ (1 equiv) gives $La(C_5Me_5)\{CH(SiMe_3)_2\}(OC_6H_3{}^tBu_2)$.[14]

Formation of such η^n-phenyl ring stabilized complexes is very dependent on the nature of the attendant ligands.[2,5a] For example, in contrast to $Zr(CH_2Ph)_4$[5a] and **1**, $Lu\{CH(SiMe_3)_2\}_3$ does not react with $[PhNMe_2H]BPh_4$.

In conclusion, the extreme electronic and steric unsaturation created by protonation of **1** allows η^n-coordination of two phenyl rings in **2a**, rather than alternative pathways such as phenyl transfer[1,7] to the metal, metalation,[2a] or η^n-coordination[5a,7] of just one phenyl group. Although, in the absence of X-ray diffraction data, the coordination mode of tetraphenylborate in **2** cannot be unequivocably established, the available NMR evidence strongly indicates $(\eta^n\text{-}C_6H_5)_2BPh_2$ coordination.

Experimental Section

All experiments were performed in an argon atmosphere using Schlenk type glassware or in a Braun single-station drybox equipped with a −40 °C refrigerator under a nitrogen atmosphere. Elemental analyses were performed at Analytische Laboratorien, Elbach, West Germany. ^{1}H NMR spectra were recorded on a

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[11] The dipolar coupling of these resonances to quadrupolar ^{10,11}B confirms their assignment as C_{ipso}.

[12] Although a *mer* THF geometry is possible, this can be excluded by assuming that a $CH(SiMe_3)_2$ group having a secondary Si–C–La interaction occupies two adjacent coordination sites, given the electronically unsaturated nature of **3a**.

[13] Despite many efforts and mounting several crystals on the diffractometer, crystallization of **2a**,**b** and **3a** did not provide crystals suitable for X-ray diffraction purposes. A. G. Orpen, personal communication.

[14] Due to nonselective monosubstitution, $La(C_5Me_5)\{CH(SiMe_3)_2\}(OC_6H_3{}^tBu_2)$ cannot be prepared, either by reaction of **1** with $HOC_6H_3{}^tBu_2$ (1 equiv) or by reaction of $La(C_5Me_5)(OC_6H_3{}^tBu_2)_2$ with $LiCH(SiMe_3)_2$ (1 equiv).

Varian XL-200 or Varian VXR-300 spectrometer. ^{13}C NMR spectra were at 75.4 or 125.76 MHz on the Varian VXR-300 or a Bruker 500 spectrometer, respectively. Chemical shifts are reported in parts per million and referenced to the residual protons in deuterated solvents. Coupling constants are reported in hertz. Coupling constants (J_{C-H}) were obtained from gated (^{1}H NOE enhanced) spectra. Solvents were PA grade. Ether, hexane, and toluene were dried initially over sodium wire, and THF was dried over solid KOH; then they were distilled from the appropriate drying reagent (sodium benzophenone ketyl for ether and THF, sodium for hexane and toluene) under argon prior to use. Deuterated solvents were dried over 4-Å molecular sieves. High-resolution ^{13}C CPMAS NMR spectra of **2a** and **3a** were measured using conditions previously described.[5b] Cross-polarization contact times were 10 ms and the 90° proton pulse was 3.3 μs with a recycle delay of 4 s between pulses. Line broadening was 2 Hz.

Preparation of La(C_5Me_5){CH($SiMe_3$)$_2$}(η^6-C_6H_5)$_2$BPh$_2$ (2a). To a stirred solution of 0.471 g (0.79 mmol) of La(C_5Me_5){CH($SiMe_3$)$_2$}$_2$ (1) in 20 mL toluene at −40 °C was added 0.348 g (1 equiv) of [$PhNMe_2H$]BPh_4 as a solid. The resulting suspension was allowed to warm to room temperature. The initially colorless suspension became a light yellow solution concomitant with dissolution and reaction of [$PhNMe_2H$]BPh_4. After 30 min at 20 °C, the toluene was removed in vacuo and the lemon-yellow powder washed with 2 × 5 mL of hexane to remove residual $PhNMe_2$ and $CH_2(SiMe_3)_2$. Crystallization from 5 mL of toluene/10 mL of hexane at −40 °C afforded 0.555 g of **2a**. Yield: 93%. ^{1}H NMR ($C_2D_2Cl_4$, 25 °C): δ 7.37 (m, Ph), 7.2 (m, Ph), 2.02 (s, 15 H, $C_5\mathit{Me}_5$), −0.18 (s, 18 H, SiMe_3). The methyne resonance could not be unequivocably assigned. ^{13}C NMR (C_6D_6, 25 °C): δ 161.5 (m, C_{ipso}), 136.7 (C_o), 129.3 (C_m), 125.2 (C_p), 124.7 (C_5Me_5), 54.5 (J_{CH} = 97 Hz, *C*H), 12.1 ($C_5\mathit{Me}_5$), 5.0 (SiMe_3). ^{13}C NMR ($C_2D_2Cl_4$, 25 °C): δ 162.7 ("d", J_{BC} = 63 Hz), 136.4, 129.3, 125.2, 124.9 (C_5Me_5), 55.8 (*C*H), 12.55 ($C_5\mathit{Me}_5$), 5.1 (SiMe_3). ^{13}C NMR (CD_2Cl_2, −60 °C): δ 161.1 ("d", J_{BC} = 54 Hz), 134.8, 128.1, 124.0, 123.35 (C_5Me_5), 11.2 ($C_5\mathit{Me}_5$), 3.3 (SiMe_3). ^{13}C NMR (CD_2Cl_2, −85 °C): δ 160.73 (br, C_{ipso}), 134.84 (d, 155 Hz), 128.24 (d, 156 Hz), 124.22 (d, 161 Hz), 123.3 (s, C_5Me_5), 51.78 (d, 96 Hz, *C*H), 11.4 (q, $C_5\mathit{Me}_5$), 2.3 (q, SiMe_3). ^{13}C CPMAS NMR: δ 170.4, 167.3, 159.5, 156.3 (each m, C_{ipso}s), 146.5, 139.3–122.2 (phenyls), 125.3 (C_5Me_5), 57.0 (v br, *C*H), 13.2 ($C_5\mathit{Me}_5$), 6.5 and 5.2 (SiMe_3). ^{13}C CPMAS spectra were also measured with CP times of 0.5, 5.0, and 20 ms. Anal. Calcd for $C_{41}H_{54}LaSi_2B$: C, 65.42; H, 7.23. Found: C, 65.15; H, 7.12.

Preparation of [La(C_5Me_5){CH($SiMe_3$)$_2$}(THF)$_3$]BPh_4 (3a). In the drybox, 0.04 g of La(C_5Me_5){CH($SiMe_3$)$_2$}BPh_4 (**2a**) was dissolved in C_6D_6 and 40 μL of THF added. After standing in the box for ca. 1 h, yellow crystals began to precipitate. After 5 h the supernatant liquor was removed by pipet to yield [La(C_5Me_5)CH($SiMe_3$)$_2$(THF)$_3$]BPh_4 (**3a**). ^{1}H NMR (C_6D_6, 25 °C): δ 3.64 (m, 12 H, THF), 1.94 (s, 15 H, $C_5\mathit{Me}_5$), 1.77 m, 12 H, THF), −0.134 (s, 18 H, SiMe_3). The methyne C*H* resonance could not be unequivocably assigned. ^{13}C NMR ($C_2D_2Cl_4$, −30 °C): δ 164.0 (1:1:1:1 q, J_{BC} = 49 Hz), 136.4 (d, 152 Hz), 126.2 (d, 159 Hz), 123.2 (C_5Me_5), 122.1 (d, 162 Hz), 70.2 (t, 153 Hz, THF), 51.3 (J_{CH} = 94 Hz, *C*H), 25.9 (t, 134 Hz, THF), 12.3 ($C_5\mathit{Me}_5$), 5.0 (SiMe_3). ^{13}C CPMAS NMR: δ 164.0 (br, C_{ipso}s), 137.5, 135.8, 127.0, 126.0, 125.2 (phenyls), 123.4 (C_5Me_5), 122.8 (sh, Ph), 122.4 (sh, Ph), 71.5 and 70.9 (THF), 26.0 and 25.7 (sh) (THF), 11.6 ($C_5\mathit{Me}_5$), 7.5 and 4.9 (SiMe_3). *C*H was not observed. Anal. Calcd for $C_{53}H_{78}LaBO_3Si_2$: C, 65.69; H, 8.11. Found: C, 65.52; H, 7.94.

La(C_5Me_5){CH($SiMe_3$)$_2$}($OC_6H_3{}^tBu_2$). ^{1}H NMR (C_6D_6, 25 °C): δ 7.27 (d, 2 H, H_m), 6.82 (t, 1 H, H_p), 1.96 (s, 15 H, $C_5\mathit{Me}_5$), 1.44 (s, 18 H, CMe_3), 0.24 (s, 18 H, SiMe_3), 0.00 (s, 1 H, C*H*($SiMe_3$)$_2$). ^{13}C NMR (C_6D_6, 25 °C): δ 162.3 (s), 136.5 (s), 128.3 (d, 159 Hz), 122.9 (C_5Me_5), 125.1 (d, 158 Hz), 117.4 (d, 155 Hz), 55.86 (d, 97 Hz, *C*H), 34.68 (s, *C*Me$_3$), 31.80 (q, CMe_3), 11.33 (q, $C_5\mathit{Me}_5$), 4.47 (q, SiMe_3).

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Oxygenation under UV Light of Allylsilanes Catalyzed by Palladium(II) and of (η^3-Allyl)palladium Complexes: A Mechanistic Approach

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Summary: The use of 1-phenyl-3-(trimethylsilyl)-1-propene, 1-phenyl-1-(trimethylsilyl)-2-propene, and bis(μ-chloro)bis((1,2,3-η^3)-1-phenylpropenyl)dipalladium as substrates led us to reject a free-radical mechanism for the title reactions and to retain an incorporation of oxygen at the level of a common organopalladium intermediate.

A few years ago, we showed that the irradiation by UV light of oxygenated solutions of either allylsilanes in the presence of palladium(II) (path a)[1] or (η^3-allyl)palladium complexes (path b)[2] leads to the oxygenation of the allyl groups (Scheme I). In the absence of oxygen, the irradiation of (η^3-allyl)palladium complexes induces the coupling of the allyl ligands (Scheme I, path c).[3] The in situ formation of (η^3-allyl)palladium complexes during the palladium-catalyzed oxidation of allylsilanes was suspected[1] from literature data.[4] EPR[5] and CIDNP[6] studies

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