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Structure of a Super Base in Tetrahydrofuran Solution Studied by ^{6}Li,^{1}H HOESY, ^{133}Cs,^{1}H HOESY, and MNDO. Evidence for Discrete Species Rather Than a Mixed Aggregate

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Abstract: Lithium trityl (Ph_3CLi) and cesium 3-ethyl-3-heptoxide were studied as model components of a "super base" by using ^{6}Li,^{1}H HOESY and ^{133}Cs,^{1}H HOESY (HOESY = heteronuclear Overhauser effect spectroscopy), as well as by ^{1}H,^{1}H ROESY (ROESY = rotating frame nuclear Overhauser effect spectroscopy). At 25 °C in THF-d_8 solution, the individual species are present partly (Ph_3CLi) or quantitatively (cesium alkoxide) as contact ion pairs. In an equimolar mixture of the two species in homogeneous THF-d_8 solution, metal exchange occurs: cesium trityl and lithium 3-ethyl-3-heptoxide are formed in stoichiometric amounts. This is indicated by the NMR detection of close contacts between Cs and the trityl ortho aromatic protons, as well as by close contacts between Li and the alkoxide protons. However, no "mixed aggregate" is present within the NMR detection limits: no correlations are observed between Cs and the alkoxide protons or between Li and the trityl ^{1}H resonance lines. Likewise, no short proton–proton distances are found between the trityl and the alkoxide residues. MNDO calculations on lithium trityl and potassium *tert*-butoxide (with dimethyl ether as a ligand) agree well: the metal exchange reaction is strongly exothermic, whereas the formation of a mixed aggregate is an endothermic process.

Introduction

Organolithium compounds are of fundamental importance in modern synthetic organic chemistry.[1,2] Due to its favorable properties (high pK_a, solubility in hexane), *n*-butyllithium (*n*BuLi, **1**) is widely employed as a deprotonating reagent. More than two decades ago, it was recognized that the reactivity of *n*BuLi and other organolithium compounds may be enormously enhanced upon the addition of a potassium (or sodium) alkoxide.[3,4] These mixtures were termed "super bases", "complex bases", "LICKOR" reagents, etc.[5] For example, toluene in heptane solution is almost completely inert toward *n*BuLi ($t_{1/2}$ for deprotonation > 10 000 h).[6] By contrast, addition of potassium *tert*-pentoxide (KO*t*Pe) results in rapid deprotonation of toluene ($t_{1/2}$ = 0.036 h) to give potassium benzyl.[3,6]


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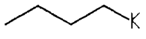
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In order to achieve efficient reactivity enhancement of the organolithium compound, the potassium alkoxide must be added in *stoichiometric* amounts.[7] In addition, an excess of potassium alkoxide (preferably 3-fold) was found to even further enhance the reactivity of the organolithium species in deprotonation or other reactions.[8,9] Likewise, the use of alkoxides branched to a higher extent than potassium *tert*-butoxide (KO*t*Bu) is beneficial.[8,9]

Super bases may be employed either as suspensions in apolar solvents (hexane, heptane)[10] or as homogeneous solutions in THF.[11] However, since THF is readily attacked by super basic reagents, temperatures below ca. −50 °C must be maintained.[12] A further variant consists of a *homogeneous* mixture of *n*BuLi, hexane, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), and a sodium or potassium alkoxide.[13,14] Modified premixed "complex bases" are now commercially available.[15]

Both the structure of super bases in solution as well as the nature of the actual reactive species have been the objects of controversial discussions. Several experiments suggest that the metalating species in LICKOR mixtures is purely a potassium organic compound. Upon mixing *n*BuLi in hexane with KOtBu or potassium (−)-(1*R*)-menthoxide, a precipitate forms which consists of pure *n*-butylpotassium (*n*BuK, **2**).[16a,b] Addition of an *n*BuLi- or (2-ethylhexyl)lithium/KOtBu/hexane mixture to excess benzene produces pure potassium phenyl.[17] When cumene is metalated with an organolithium compound in the presence of various potassium alkoxides in THF, the nature of the alkoxide has no significant influence on the product distribution.[4]

The overall rate of the metalation of toluene by a mixture of *n*BuLi and KO*t*Pe in heptane at room temperature varied only slightly in the presence of LiO*t*Pe: addition of LiO*t*Pe (up to 7 equiv) proved to be essentially without influence. Thus, any significant interaction between the lithium alkoxide and the organopotassium compound was not indicated under these conditions.[6]

Efforts have been made to characterize super bases and their reaction products by spectroscopic methods. Various benzylic type compounds were treated with *n*BuLi/KO*t*Bu in pentane, followed by replacement of the solvent with THF. The ^{1}H and ^{13}C NMR spectra of these species are identical with those of authentic organopotassium compounds and differ from those of the pure lithium organic species.[18] When cycloheptene reacts with nBuLi/KOtPe, the cycloheptatrienyl radical anion is formed in a stepwise reaction. Its ESR spectrum in THF is consistent with a potassium rather than with a lithium compound.[19]

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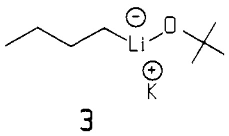
Thus, it might be concluded that quantitative metal exchange occurs upon mixing an organolithium compound and a potassium alkoxide and that the reactive species possibly is a pure organopotassium compound, at least in the donor solvent, THF. However, according to Schlosser, in LICKOR reagents "...the true superbasic reagent is an organometal/alcoholate aggregate which is fairly long-lived in cold tetrahydrofuran...".[20] This seemed to be supported by the observation of kinetic isotope effects in the deprotonation reaction of benzene/benzene-d_6: in THF at -75 °C, k_H/k_D is 16 for *n*BuLi/KO*t*Bu as compared to 40 for pure *n*BuK.[21] Further evidence for different structures of pure *n*BuK and a LICKOR reagent came from the observation that an *n*BuLi/KO*t*Bu mixture is stable in THF up to -50 °C, whereas THF is attacked by pure *n*BuK already at -75 °C.[12] Very recently, Arnett and Moe[22] determined enthalpies of the deprotonation of isopropyl alcohol with lithium or potassium bis(trimethylsilyl)amide (LiHMDS or KHMDS). A 1:1 mixture of both LiHMDS/KO*t*Bu and KHMDS/LiO*t*Bu gave exactly the same value, consistent with the presence of KHMDS and LiO*t*Bu in both cases. In that study, the observed increased enthalpies of these mixtures when compared to KHMDS without additives might possibly be explained by the formation of a mixed LiO*t*-Bu/KO*i*Pr aggregate subsequent to the deprotonation step.

*n*BuLi was found to form mixed aggregates with lithium alkoxides: in THF solution, tetrameric *n*BuLi/LiO*n*Bu aggregates were observed by using ^{1}H and ^{7}Li NMR spectroscopy.[23] Similarly, the formation of a mixed *n*BuLi/LiO*t*Bu species was observed in heptane solution.[24]

Recent X-ray structural analyses confirmed the existence of mixed organolithium/alkali alkoxide aggregates in the solid state. The crystal structure of a mixed *n*BuLi/LiO*t*Bu aggregate was reported.[25a] Williard et al. described the structures of a mixed lithium pinacolonate/KO*t*Bu complex[25b] and mixed metal bis(trimethylsilyl)amide bases.[25c]

Structures 3–6 have been discussed for a hypothetical *n*BuLi/KO*t*Bu super base aggregate in solution.[4] In this paper, we provide evidence that in THF a model super base does *not* consist of a mixed aggregate.



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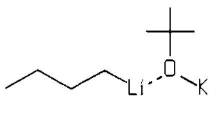

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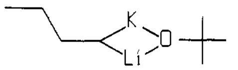

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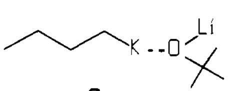

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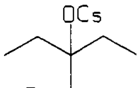
NMR Methods

Of the two stable lithium isotopes, ^{6}Li (7.4% abundance, spin $I = 1$) has more favorable properties as compared to the major isotope ^{7}Li (92.6%, $I = {}^3/_2$). Due to its very small quadrupole moment ($Q = -8 \times 10^{-4}$ b[26]), ^{6}Li behaves almost like a spin $I = {}^1/_2$ nucleus.[27] Structure elucidation of organolithium compounds in solution by NMR analysis is now frequently carried out by using ^{6}Li-enriched material. New results of NMR structural investigations of organolithium compounds have been reviewed.[28]

Of the other alkali metal nuclei pertinent to super bases, neither ^{23}Na nor ^{39,41}K nor ^{85,87}Rb is of particular benefit for NMR investigations due to their large quadrupole moments. These nuclei usually have quite short spin lattice relaxation times, T_1, and exhibit only broad NMR lines.[26] However, ^{133}Cs (100% abundance, $I = {}^7/_2$, $Q = -3 \times 10^{-3}$ b[26]) is a "good" NMR nucleus. Due to its relatively small quadrupole moment, its spin lattice relaxation times, T_1, are moderately large and sharp NMR lines may often be obtained. Hence, we chose ^{133}Cs as a "model nucleus" for sodium and potassium in our NMR studies on super bases.

Similar to the homonuclear NOESY experiment,[29] short distances between spin $I = {}^1/_2$ nuclei (e.g., ^{13}C and ^{1}H) may be detected by using 2D heteronuclear Overhauser effect spectroscopy, HOESY.[30,31] We have successfully applied HOESY for nuclei with spin quantum numbers $I > {}^1/_2$. Since ^{6}Li relaxes from a moderate to high extent according to the dipole–dipole mechanism,[32] ^{6}Li,^{1}H HOESY spectra may be recorded easily.[33] ^{6}Li,^{1}H HOESY has now been extensively employed for the structural analysis of organolithium compounds.[34]

With respect to the detection of heteronuclear Overhauser effects, the properties of ^{133}Cs are less favorable. Despite its comparatively large spin lattice relaxation times, the dipole–dipole mechanism contributes only in negligible amounts to the relaxation of ^{133}Cs. Instead, the quadrupolar mechanism is predominant.[35,36] By using one-dimensional heteronuclear difference NOE spectroscopy, weak fractional enhancements of 0.2% for ^{133}Cs{^{1}H} were observed in cesium 3-methylpentoxide (7).[37] Nonetheless, we have recently shown that two-dimensional ^{133}Cs,^{1}H HOESY experiments may be successfully carried out in favorable cases.[37]



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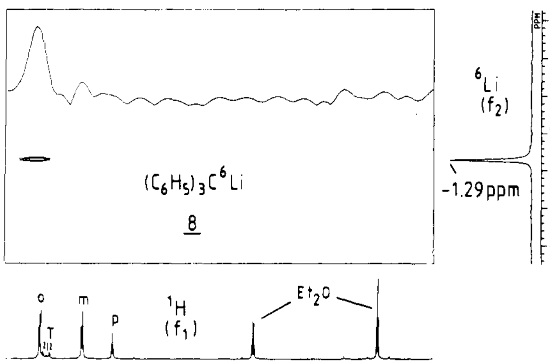


Figure 1. ^{6}Li,^{1}H HOESY contour plot of lithium trityl **8**; crystals of **8** (with 2 equiv of diethyl ether and enriched 96% with ^{6}Li) were dissolved in THF-d_8 (0.35 M, 26 °C, mixing time 2.0 s). Inset: f_1 cross section at $\delta_{^6Li}$ = −1.29 ppm; T = triphenylmethane.

NMR Investigations

In order to study super bases by NMR spectroscopy, the following conditions must be met.

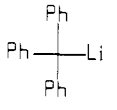
(i) The use of suspensions has to be avoided. Hence, apolar solvents such as hexane are not suitable in most cases. Instead, homogeneous solutions in THF are adequate.

(ii) Since THF is metalated and cleaved by strong bases,[38] either the base properties of the super base must not be too strong or low temperatures must be maintained (less than ca. −50 °C).

(iii) HOESY spectra usually suffer from limited digital resolution in the f_1 (^{1}H) domain. Thus, in order to unequivocally assign HOESY cross peaks, spectral overlap of the ^{1}H signals of the super base components must be avoided.

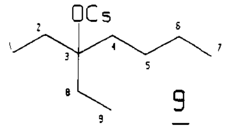
(iv) Empirically, when using ^{133}Cs in HOESY experiments, the spin lattice relaxation time (T_1) of ^{133}Cs should not be lower than ca. 100 ms.[37] The spin lattice relaxation times of ^{133}Cs decrease with temperature due to the more efficient quadrupole relaxation mechanism.[39] Hence, heteronuclear NOE measurements which involve ^{133}Cs should preferably be carried out at room temperature or even elevated temperatures.

A convenient system with respect to these limitations turned out to be trityllithium (**8**) (isotopically enriched with ^{6}Li) and cesium 3-ethyl-3-heptoxide (**9**). An equimolar mixture of **8** and **9** is homogeneous in THF. The base properties of neither the trityl anion (pK_a of Ph$_3$CH = 31.5[40]) nor the alkoxide are sufficiently large to attack THF. Both the separate components **8** and **9** as well as their mixtures may be handled in THF at room temperature without decomposition of the solvent. The ^{1}H resonances of **8** and **9** are well separated. In addition, the ortho, meta, and para proton resonances in **8** are clearly resolved[41] (cf. Figure 1). Likewise, in **9** there are seven different ^{1}H chemical shifts[42] with adequate separation even for moderate digital resolution in HOESY experiments (cf. Figure 2).



$$\mathrm{Ph_3C{-}Li}$$

8



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In order to characterize the *separate* components, individual HOESY experiments were performed on **8** and **9**. From UV spectroscopy results, trityllithium (**8**) is known to exist as a contact ion pair (CIP)/solvent-separated ion pair (SSIP) equilibrium mixture in THF.[43] At 25 °C, the equilibrium is largely on the side of the SSIP ($K_{SSIP/CIP}$ = 39, $c = 3 \times 10^{-4}$ M). Within the ^{13}C NMR detection limit, **8** consists exclusively of a SSIP in MeTHF at 25 °C.[44]

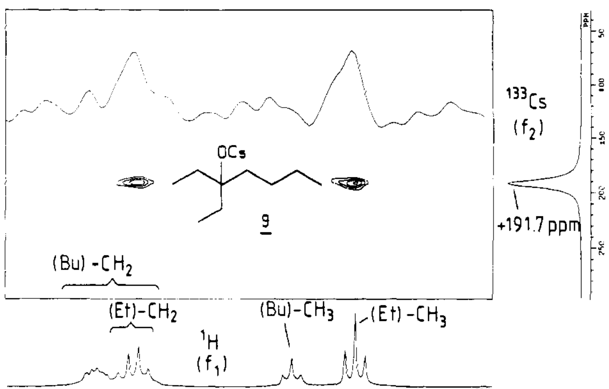

Figure 2. ^{133}Cs,^{1}H HOESY contour plot of cesium 3-ethyl-3-heptoxide **9**: crystals of **9** were dissolved in THF-d_8 (1.2 M, 40 °C, mixing time 0.3 s). Inset: f_1 cross section at $\delta_{^{133}Cs}$ = +191.7 ppm.

Figure 1 shows the ^{6}Li,^{1}H HOESY spectrum of **8**. Crystals of **8** were dissolved in THF-d_8. These contained 2 equiv of diethyl ether. In the contour plot and in the corresponding f_1 cross section, a single, intense cross peak is detected which includes the signal of the ortho protons of **8**. Only a small fraction of **8** is present as a CIP under these conditions. Since only the CIP may lead to cross peaks which involve the hydrocarbon moiety, the signal to noise ratio in Figure 1 is comparatively low. No cross peaks are detected for the Et$_2$O ligand (introduced by the crystals). Thus, Et$_2$O obviously does not coordinate to lithium and is replaced by the bulk donor solvent, THF-d_8.

The chemical shift of ^{6}Li of **8** in THF-d_8 (δ = −1.29 ppm) is in agreement with data obtained earlier by Cox and Terry[45] (δ = −1.11 ppm) in THF. Lithium located above a trityl anion should exhibit a diamagnetic (upfield) chemical shift. However, since only a fraction of **8** is present as a CIP, the time-averaged contribution of the trityl anion to $\delta_{^6Li}$ is small. In the solid state with TMEDA as a ligand, trityllithium is a CIP with the lithium atom in a noncentral location above the anion.[46]

Figure 2 shows the ^{133}Cs,^{1}H HOESY spectrum of cesium alkoxide **9** in THF solution. Clear cross peaks are observed between the alkali metal peak and the resonance lines of spatially close ^{1}H nuclei. These nuclei involve positions 1, 2, 4, 5, 8, and 9[47] (for numbering, see formula **9** in text). No close contacts are detected for the remote positions 6 and 7. Presumably, **9** forms a tetrameric aggregate in THF as was found for KO*t*Bu in the same solvent,[48] as well as for KO*t*Bu and CsO*t*Bu in the solid state.[49]

The chemical shift of the ^{133}Cs signal (δ = +191.7 ppm) is exceptionally large and is near the downfield end of the ^{133}Cs shifts observed so far (ca. +250 to −100 ppm).[50] This may be rationalized by the strong polarizing field of the three nearest alkoxide oxygen atoms in an assumed tetrameric aggregate of **9** in THF. Comparable strong downfield chemical shifts of ^{133}Cs have been observed in cryptand C222 complexes.[51]

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(51) Mei, E.; Popov, A. I.; Dye, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 6532.

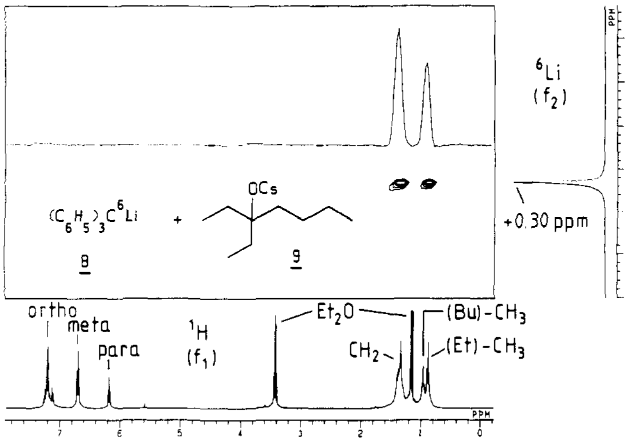
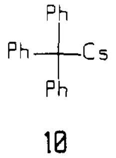
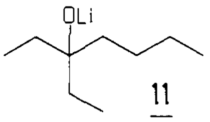


Figure 3. ^{6}Li,^{1}H HOESY contour plot of a mixture of lithium trityl **8** and cesium 3-ethyl-3-heptoxide (**9**) (1:1.5 molar ratio); crystals of **8** (with 2 equiv of diethyl ether and enriched 96% with ^{6}Li) and crystals of **9** were dissolved in THF-d_8 (0.6 M in **8**, 26 °C, mixing time 2.0 s). Inset: f_1 cross section at $\delta_{^6\text{Li}}$ = +0.30 ppm.

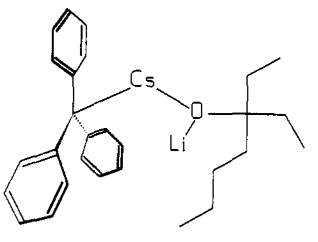
Figure 3 depicts the ^{6}Li,^{1}H HOESY spectrum of a mixture of **8** and **9** in a 1:1.5 molar ratio in THF-d_8. The intense cross peak of Figure 1 that included the ortho aromatic protons is not observed any longer. This indicates that lithium is *not* in close contact with the Ph$_3$C moiety under these conditions. Instead, intense cross peaks involving the aliphatic alkoxide residue are now found.[52] This indicates that *quantitative* metal exchange must have taken place, and compounds **10** and **11** seem to have formed. In addition, the lack of cross peaks in Figure 3 which include the aromatic protons indicates that **10** and **11** must be remote from each other. Evidently, no mixed aggregate **12** is present.[53]



10



11



12

The ^{6}Li signal in Figure 3 is shifted downfield by 1.59 ppm as compared to Figure 1 ($\delta_{^6\text{Li}}$ = +0.30 ppm). This is typical of lithium coordinated by oxygen ligands[50] and confirms the metal exchange reaction in mixtures of **8** and **9**. Note, however, that the NMR chemical shift range of lithium is quite small (ca. −2 to +2 ppm)[55] unless unusual magnetic anisotropies are involved.[45,56] Due to nonstandard methods of referencing, literature Li chemical shifts should be compared with caution.

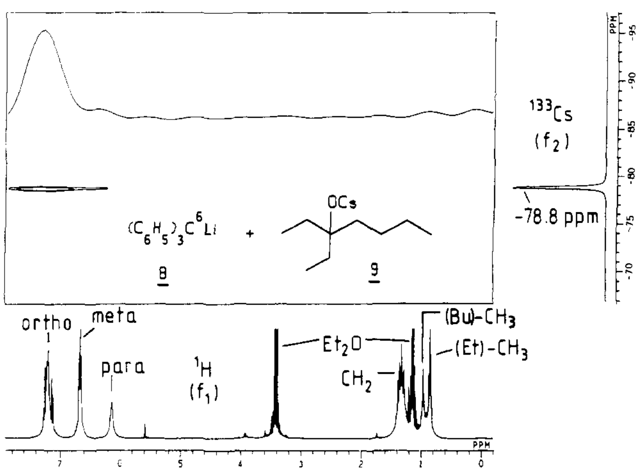
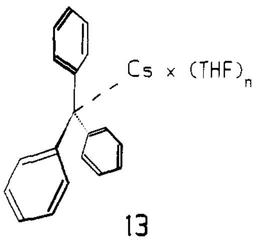


Figure 4. ^{133}Cs,^{1}H HOESY contour plot of a mixture of lithium trityl **8** and cesium 3-ethyl-3-heptoxide (**9**) (1.2:1 molar ratio); crystals of **8** (with 2 equiv of diethyl ether and enriched 96% with ^{6}Li) and crystals of **9** were dissolved in THF-d_8 (0.6 M in **8**, +26 °C, mixing time 0.35 s). Inset: f_1 cross section at $\delta_{^{133}\text{Cs}}$ = −78.8 ppm.

Figure 4 shows a ^{133}Cs,^{1}H HOESY spectrum of a 1.2:1 molar ratio of **8** and **9**.[57] Here, a single intense cross peak is observed that involves the ortho aromatic protons. Similar to the conclusions drawn from Figure 3, this indicates that stoichiometric metal exchange has occurred subsequent to the mixing of **8** and **9** in THF. The cesium nucleus is now tightly attached to the trityl skeleton. The absence of cross peaks in Figure 4 which include the alkoxide ^{1}H resonance lines suggests the *absence* of a mixed aggregate **12**.[58] As was concluded from Figure 3, separate species **10** and **11** are indicated to coexist under these conditions.

As compared to cesium alkoxide **9** (Figure 2), the ^{133}Cs signal in Figure 4 is shifted upfield by 270.5 ppm and resonates at δ = −78.8 ppm. With the exception of the cesium anion, Cs$^-$, to our knowledge this is the largest upfield Cs chemical shift observed so far.[50] This high-field cesium chemical shift is indicative of a strong magnetically anisotropic environment (trityl anion). Hence, we conclude that a contact ion pair **13** is present under these conditions.



13

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[52] A slight excess of **9** instead of an exactly equimolar mixture was employed deliberately for the generation of Figure 3. This was done in order to avoid any artificial residual cross peaks between lithium and the aromatic protons due to scaling tolerances.

[53] It is generally accepted that the detection of a nuclear Overhauser enhancement in *homonuclear* NOE experiments *is* indicative of close spatial relationships between the involved nuclei, provided that spin diffusion phenomena are not involved. By contrast, the lack of a homonuclear NOE does *not* prove that the corresponding nuclei are remote. This is due to the fact that in the homonuclear case the NOE crosses zero for $\omega\tau_c$ = 1.12 (where ω is the Larmor frequency and τ_c is the molecular correlation time).[54a] By contrast, in heteronuclear NOE experiments the NOE may cross zero *only* if γ_I/γ_S < 2.38.[54b] For the ^{6}Li,^{1}H couple this condition is not met. Furthermore, under the conditions chosen to generate Figure 3, the molecular correlation time, τ_c, is assumed to be small ($\tau_c \ll 1/\omega$). Hence, any short internuclear ^{6}Li,^{1}H distances should be manifested in the appearance of cross peaks in a ^{6}Li,^{1}H HOESY experiment. The lack of an appropriate cross peak *is* indicative of large separations (greater than ca. 3.5 Å).

[54] (a) Neuhaus, D.; Williamson, M. P. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH: New York, 1989. (b) See ref 54a, p 57.

[55] Lindman, B.; Forsēn, S. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; p 129 f.

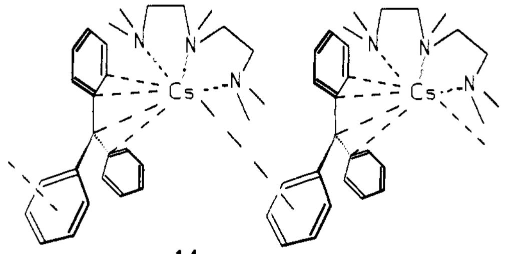
[56] Cox, R. H.; Terry, H. W., Jr.; Harrison, L. W. *J. Am. Chem. Soc.* **1971**, *93*, 3297.

[57] Analogously to ref 52, a slight excess of **8** was employed rather than an exactly equimolar ratio in order to avoid misleading cross peaks due to scaling tolerances. For example, in the sample used to generate Figure 3 (**8**:**9** = 1:1.5), cross peaks appear in a ^{133}Cs,^{1}H HOESY experiment which include both the aromatic *and* the aliphatic region. However, this is not indicative of a mixed aggregate, e.g., **12**. Rather, we observe cesium trityl (from metal exchange) and excess cesium alkoxide. In this system, there is rapid chemical exchange of the cesium cation at 25 °C, and an averaged ^{133}Cs signal appears at $\delta_{^{133}\text{Cs}}$ = −43.7 ppm.

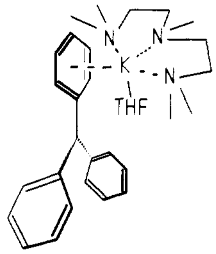
[58] The same arguments outlined in ref 53 hold for the interpretation of the ^{133}Cs,^{1}H HOESY experiment of Figure 4. On a 9.4 T NMR instrument, the involved Larmor frequencies are as follows: γ_0 (^{1}H) = 400 MHz; γ_0 (^{6}Li) = 58.8 MHz, γ_0 (^{133}Cs) = 52.4 MHz.

In contrast to lithium trityl, which is a 39:1 SSIP/CIP mixture at 25 °C in THF,[43] the SSIP/CIP ratio is reduced to 2.0 for potassium trityl under the same conditions (UV spectroscopic determination).[43] On the basis of NMR results, sodium trityl is a 1:10 SSIP/CIP mixture in THF at 25 °C.[44] For cesium trityl, a still lower SSIP/CIP ratio may be assumed and, hence, a larger time-averaged amount of close cesium–trityl–hydrogen contacts. This rationalizes the comparatively good signal to noise ratio in Figure 4, despite the insensitivity of the ^{133}Cs,^{1}H HOESY method.[37]

The X-ray structure of [tritylcesium·PMDTA] **14** (PMDTA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) has been solved recently.[59] In the polymeric aggregate **14**, cesium is bound η^4 to one trityl anion. Further coordination is provided by the triamine ligand. Bridging of cesium to a neighbor trityl anion is achieved by η^6 coordination with one phenyl ring. A related structure [potassium trityl·PMDTA·THF] **15** is monomeric in the solid state.[60]

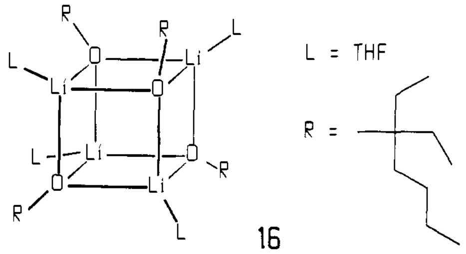


14



15

According to molecular weight determinations by thermoelectric methods, (triphenylmethyl)sodium has been found to be a monomer in THF at 30 °C.[48] We believe that in THF solution cesium trityl (formed upon metal exchange after mixing of **8** and **9**) is monomeric as well. Furthermore, from the NMR spectral results shown in Figures 3 and 4, we conclude that mixing of **8** and **9** in THF affords a contact ion pair, lithium 3-ethyl-3-heptoxide (**11**). This must be remote from cesium trityl **10**. In addition, since LiO*t*Bu is tetrameric in THF,[48] we presumably observe stoichiometric amounts of tetrameric alkoxide **16** (with a nondetermined amount of THF solvation) under the conditions of Figures 3 and 4.



16

An additional homonuclear ^{1}H NMR experiment was employed in order to study the existence of a mixed aggregate **12**. In contrast to homonuclear ^{1}H,^{1}H NOESY,[29,54a] ^{1}H,^{1}H rotating frame nuclear Overhauser effect spectroscopy (ROESY)[29,54a] throughout leads to positive ROEs even for slowly tumbling molecules (i.e., under conditions outside the "extreme narrowing limit").[54a] Figure 5 shows f_1 cross sections of a ^{1}H,^{1}H ROESY experiment applied to a 1:1.5 molar ratio of **8** and **9** in THF-d_8. Only f_1 cross sections cut at the indicated ^{1}H chemical shifts are depicted. Diagonal peaks appear downward, whereas cross peaks due to dipolar interaction appear upward.

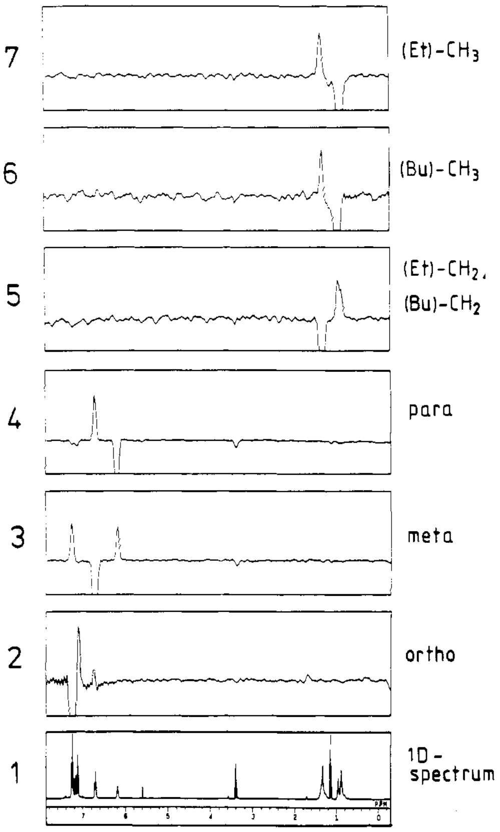


Figure 5. ^{1}H,^{1}H ROESY spectrum of a mixture of lithium trityl **8** and cesium 3-ethyl-3-heptoxide (**9**) (1:1.5 molar ratio); crystals of **8** (with 2 equiv of diethyl ether and enriched 96% with ^{6}Li) and crystals of **9** were dissolved in THF-d_8 (0.6 M in **8**, 20 °C; spin lock time 1.0 s). Only f_1 cross sections cut at the indicated ^{1}H chemical shifts are depicted. Diagonal peaks and cross peaks appear downward and upward, respectively. For assignment of the one-dimensional spectrum (slice 1), see Figures 1–4.

Clearly, within the ^{1}H resonances of the trityl aromatic rings, the expected intense cross peaks indicate the relationships of the ortho, meta, and para protons. However, the relevant cross sections (slices 2, 3, 4) show no cross peaks involving ^{1}H positions of the alkoxide residue. In the f_1 cross sections of the alkoxide ^{1}H resonances (slices 5, 6, 7), expected intense cross peaks indicate close relationships of the individual aliphatic protons. However, in neither of these slices are cross peaks observed which include signals of the trityl anion. From MNDO calculations (see below), sufficiently close interproton contacts in a hypothetical mixed aggregate **12** may be deduced.

These results support the above findings (Figures 3 and 4) that the aromatic and the aliphatic moieties must be *separate* species in THF solution. Hence, the existence of a mixed aggregate **12** in bulk amounts is not indicated under these conditions.

From the ^{13}C chemical shift data of **8**, **9**, and mixtures of these two species (Table I) comes further evidence for stoichiometric metal exchange as was deduced from the spectra shown in Figures 1–4. The carbon atoms close to the assumed location of the cation (the "central" carbon in **8** and C3 in **9**) show significant deviations in a mixture of **8** and **9** as compared to the separate components **8** and **9**. By contrast, other carbon positions show only minor discrepancies.

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(59) Hoffmann, D.; Schleyer, P. v. R. Manuscript in preparation.

(60) Hoffmann, D.; Schleyer, P. v. R.; Stalke, D. Manuscript in preparation.

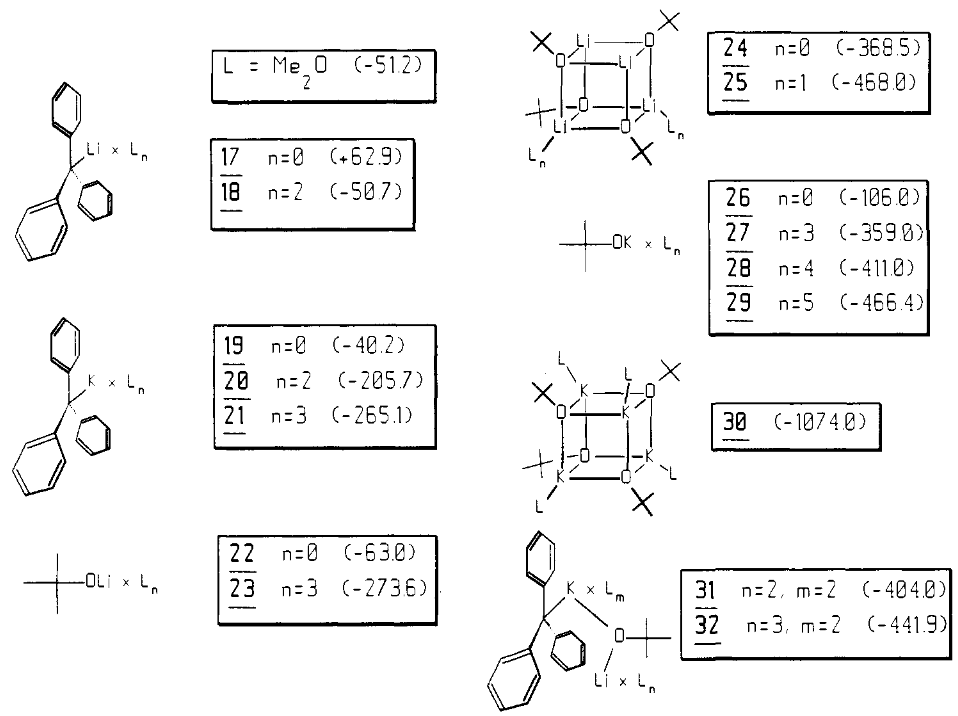

Figure 6. MNDO-calculated heats of formation (in brackets, kilocalories/mole) of lithium trityl, potassium trityl, (LiO*t*Bu)$_x$, (KO*t*Bu)$_x$ (x = 1, 4), and mixed potassium trityl/LiO*t*Bu aggregates with different states of solvation.

Table I. ^{13}C NMR Chemical Shifts (δ, ppm) of **8**, **9**, and a 1:1.5 Molar Ratio Mixture of **8** and **9** in THF-d_8[a]

C	**8** (27 °C)	**9** (40 °C)	**8** + **9** (26 °C)
central	90.43		88.85
ipso	149.84		148.37
ortho	123.93		123.59
meta	127.86		127.54
para	112.88		115.27
1,9		9.96	10.18
2,8		35.78	35.69
3		74.64	72.71
4		43.52	43.17
5		28.30	28.45
6		25.16	24.99
7		14.88	14.94

[a] For numbering in **9**, see formula in text.

MNDO Calculations

Semiempirical MNDO calculations[61] are now established as a useful tool in structural analyses of organolithium compounds.[62] Despite the known deficiencies of the lithium parametrization[63] (overestimation of Li,C and Li,H interactions), remarkably accurate results are often obtained.

All MNDO geometry optimizations described below were carried out without symmetry constraints. The MNDO parameters of potassium were provided recently.[64] Dimethyl ether (Me$_2$O) was employed as a model donor ligand for THF.

Figure 6 shows the MNDO heats of formation (H°_f, in kilocalories/mole) for lithium trityl, potassium trityl, LiO*t*Bu, KO*t*Bu, and mixed aggregates of these species with different states of aggregation and/or solvation. The solvation of lithium trityl by two molecules of Me$_2$O (**17** → **18**) is exothermic (ΔH° = −11.2 kcal/mol). A similar calculation with three Me$_2$O ligands in lithium trityl results in "extrusion" of one Me$_2$O molecule. Thus, disolvated lithium trityl **18** is considered to be the most stable species and is employed in subsequent calculations.

The second component of a super basic reagent, KO*t*Bu, was calculated as a monomer and as a tetramer with different degrees of solvation by Me$_2$O. Of the monomers, pentasolvated KO*t*Bu **29** proved to be the most stable. A cube-shaped tetrameric aggregate of KO*t*Bu was calculated with four ligands (**30**) and with no ligands. Whereas for **30** the calculation converged, negative eigenvalues resulted throughout for the unsolvated species. Hence, unsolvated (KO*t*Bu)$_4$ was excluded from further consideration.

As is shown by eq 1, the formation of a tetrameric KO*t*Bu aggregate from the monomers is exothermic (ΔH° = −27.6 kcal/mol). In addition, the aggregation reaction in eq 1 is favored

$$\begin{array}{lllll} 4\ \mathbf{29} & \longrightarrow & \mathbf{30} & + & 16\mathrm{Me_2O} \qquad (1) \\ 4\times(-466.4) & & -1074.0 & & 16\times(-51.2)\quad \Delta H^\circ = -27.6\ \text{kcal/mol} \end{array}$$

by entropy due to the release of ligands. This confirms the experimentally found tetrameric aggregate of KO*t*Bu in THF solution[48] and in the solid state.[49] Note, however, that the X-ray structure of (KO*t*Bu)$_4$ does not contain peripheral donor ligands.[49]

Of the potassium trityl species formed subsequent to the metal exchange reaction, a solvatomer with three Me$_2$O ligands, **21**, is most stable. Additional Me$_2$O ligands at K do not "stick" and are extruded.

As expected, of the various LiO*t*Bu isomers which may result from metal exchange, a monomer with three Me$_2$O ligands, **23**, is considerably more stable than LiO*t*Bu without ligands, **22**. In agreement with the experimentally found tetramer of LiO*t*Bu in THF,[48] the tetramerization of LiO*t*Bu (eq 2) is exothermic (ΔH° = −29.6 kcal/mol).

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(61) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899 and 4907.

(62) Bauer, W.; O'Doherty, G. A.; Schleyer, P. v. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1991**, *113*, 7093. Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776. Bausch, J. W.; Gregory, P. S.; Olah, G. A.; Prakasch, G. K.; Schleyer, P. v. R.; Segal, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 3633. McKee, M. L. *J. Am. Chem. Soc.* **1987**, *109*, 559. Hacker, R.; Kaufmann, E.; Schleyer, P. v. R.; Mahdi, W.; Dietrich, H. *Chem. Ber.* **1987**, *120*, 1533. Hacker, R.; Schleyer, P. v. R.; Reber, G.; Müller, G.; Brandsma, L. *J. Organomet. Chem.* **1986**, *316*, C4. Wilhelm, D.; Clark, T.; Schleyer, P. v. R.; Dietrich, H.; Mahdi, W. *J. Organomet. Chem.* **1985**, *280*, C6. Schleyer, P. v. R.; Hacker, R.; Dietrich, H.; Mahdi, W. *Chem. Commun.* **1985**, 622. Neugebauer, W.; Geiger, G. A. P.; Kos, A. J.; Stezowski, J. J.; Schleyer, P. v. R. *Chem. Ber.* **1985**, *118*, 1504. Stezowski, J. J.; Hoier, H.; Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *Chem. Commun.* **1985**, 1263. Dietrich, H.; Mahdi, W.; Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *Angew. Chem.* **1984**, *96*, 623; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 621. Boche, G.; Decher, G.; Etzrodt, H.; Dietrich, H.; Mahdi, W.; Kos, A. J.; Schleyer, P. v. R. *Chem. Commun.* **1984**, 1493.

(63) Thiel, W.; Clark, T. Unpublished results.

(64) Z. Havlas, Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia, unpublished results.

$$\begin{array}{lccccr} 4\ \mathbf{23} & \longrightarrow & \mathbf{25} & + & 10Me_2O & (2) \\ 4\times(-237.6) & & -468.0 & & 10\times(-51.2) & \Delta H^\circ = -29.6\ \text{kcal/mol} \end{array}$$

Interestingly, a solvatomer of composition $(LiO\textit{t}Bu{\cdot}Me_2O)_4$ is not stable. Two Me_2O ligands are extruded during the geometry optimization to give a stable solvatomer $[(LiO\textit{t}Bu)_4{\cdot}2Me_2O]$ with structure **25**. An isomer $(LiO\textit{t}Bu)_4$ with no ligands, **24**, is less stable.

As is shown by eq 3, the overall metal exchange reaction is strongly exothermic ($\Delta H^\circ = -149.2$ kcal/mol). This exceeds by far the entropy losses in eq 3 due to fixation of two Me_2O molecules. Thus, the reaction of eq 3 must be strongly exergonic. The agrees nicely with our NMR results described above (with cesium instead of potassium).

$$\begin{array}{lccccccccr} 4\ \mathbf{18} & \longrightarrow & \mathbf{30} & + & 2Me_2O & \longrightarrow & 4\ \mathbf{21} & + & \mathbf{25} & (3) \\ 4\times(-50.7) & & -1074.0 & & 2\times(-51.2) & & 4\times(-265.1) & & -468.0 & \\ & & & & & & & & & \Delta H^\circ = -149.2\ \text{kcal/mol} \end{array}$$

Solvatomers **31** and **32** were calculated as possible structures of a mixed aggregate between potassium trityl and LiO*t*Bu. By analogy with the results described above for Ph_3CK, more than two Me_2O ligands at K proved to be unstable (extrusion of excessive ligands). Interestingly, solvatomer **31** with only two Me_2O ligands at lithium is more stable than the coordinatively saturated species **32**.

The key reaction of this paper, the formation of a mixed aggregate between potassium trityl and LiO*t*Bu, is calculated:

$$\begin{array}{lccccccr} 4\ \mathbf{21} & \longrightarrow & \mathbf{25} & + & 2Me_2O & \longrightarrow & 4\ \mathbf{31} & (4) \\ 4\times(-265.1) & & -468.0 & & 2\times(-51.2) & & 4\times(-404.0) & \\ & & & & & & & \Delta H^\circ = 14.8\ \text{kcal/mol} \end{array}$$

Clearly, the formation of a mixed species **31** is *disfavored*. This nicely corrobrates the experimentally found absence of a mixed cesium trityl/lithium alkoxide species **12**.

Within the MNDO-calculated structure **31**, internuclear contacts are detected which are sufficiently close to allow observation by any of the NMR methods employed in Figures 3–5 (nearest MNDO distances in **31** are the following: $Li{-}H_{trityl}$ 2.28, 2.79, 3.74 Å; $K{-}H_{O\textit{t}Bu}$ 2.47, 2.57, 3.67 Å; $H_{trityl}{-}H_{O\textit{t}Bu}$ 2.19, 2.85, 3.50 Å). Thus, a mixed aggregate should be detectable by the above NMR experiments, if it were present.

A cautionary note should be added. Water is often employed in MNDO calculations of organolithium compounds as a simplified model for ethereal donor ligands such as THF. However, this may produce erroneous and misleading results, as will be outlined briefly.

By using H_2O as a ligand, the formation of a solvated aggregate $(LiOtBu{\cdot}H_2O)_4$ from four monomers ($LiO\textit{t}Bu + 3H_2O$) was calculated to the *endothermic* ($\Delta H^\circ = +10.5$ kcal/mol). This is in contrast to the analogous calculation with Me_2O as a ligand (eq 2) and in contrast with the experimentally found tetrameric aggregate of LiO*t*Bu in THF.[48] Likewise, the formation of a water-solvated mixed aggregate, analogous to **12**, from separate $Ph_3CK + 4H_2O$ and $LiO\textit{t}Bu + 3H_2O$ units proved to be *exothermic* ($\Delta H^\circ = -16.4$ kcal/mol). This is in contrast to eq 4 and in disagreement with our NMR results described above. Hence, we suggest that "real" ligands like Me_2O or THF should be employed in dedicated MNDO calculations despite the higher computational demands.[65]

Conclusions

In this paper we have investigated by NMR and MNDO methods a model super base. Both homonuclear ($^1H,^1H$ ROESY) and heteronuclear ($^6Li,^1H$ and $^{133}Cs,^1H$ HOESY) NMR methods were employed. An approximately equimolar mixture of lithium trityl **8** and cesium 3-ethyl-3-heptoxide (**9**) undergoes quantitative metal exchange in homogeneous THF solution at 25 °C: cesium trityl **10** and lithium 3-ethyl-3-heptoxide (**11**) are formed in stoichiometric amounts. However, neither NMR method provides any evidence for a mixed aggregate **12** between **10** and **11**. Hence, such a species should be present only in non-NMR-detectable amounts, if at all.[66]

MNDO calculations on appropriate compounds (lithium trityl and KO*t*Bu, with dimethyl ether ligands) agree well with the NMR results: according to MNDO, the metal exchange is strongly exothermic whereas the subsequent formation of a mixed potassium trityl/LiO*t*Bu aggregate is endothermic. With very severe precautions, this situation might also hold for other super basic systems in THF. The prevailing species under these conditions might be a potassium organic compound and a separate lithium alkoxide. However, this generalization results from a study of a benzylic type organolithium compound (Ph_3CLi). Possibly, alkyl or aryl type organolithium compounds behave differently in THF.

Furthermore, we emphasize that our results and predictions do not necessarily address the *reactive* species in reactions which involve an *n*BuLi/potassium alkoxide mixture. Some of the literature results described in the introductory section suggest that there *is* a difference between, for example, *n*BuK and a super base consisting of *n*BuK/LiO*t*Bu. Therefore, the participation of mixed super basic aggregates cannot be completely ruled out in reactions of particular substrates under specific conditions. For similar systems in hydrocarbons, such effects might be even more pronounced. Both experimental and calculational studies on this topic are in progress.

We have demonstrated that $^{133}Cs,^1H$ HOESY is a powerful tool in the structural analysis of alkali metal organic compounds. The results presented in this paper indicate that $^{133}Cs,^1H$ HOESY and $^6Li,^1H$ HOESY may be complementary.

Experimental Section

All reactions and measurements were carried out in flame-dried glassware under an atmosphere of purified argon.

Crystals of [^{6}Li]Lithium Trityl 8·2Et$_2$O. Triphenylmethane (2.40 g, 9.8 mmol) is dissolved in 13 mL of dry diethyl ether. Upon gentle shaking, ^{6}Li-enriched *n*-butyllithium[67] (5.3 mL, 9.8 mmol, 1.85 M in hexane) is added. The solution slowly turns red and is kept at room temperature without stirring. After 4 days, the mother liquor is withdrawn and the red needles that formed are dried in vacuo. ^{1}H NMR analysis in THF-d_8 reveals the stoichiometry [^{6}Li]lithium trityl:Et_2O = 1:2. Yield: 1.92 g (4.83 mmol, 49%).

Cesium 3-Ethyl-3-heptoxide (9). A mixture of cesium metal (8.5 g, 64 mmol) and 3-ethyl-3-heptanol (6.2 g, 43 mmol) in pentane (40 mL) is refluxed with stirring for 20 h. The solid particles are removed by filtration, and the almost colorless solution is evaporated to dryness in vacuo for 10 h at 50 °C/1 mbar. Yield of **9**: 9.5 g (80% based on the alcohol). Cs content found (AAS) 47.2, calcd 48.13. Traces of the solvent cannot be removed even by extensive drying.

NMR measurements were carried out on a JEOL GX400 spectrometer (9.4 T; for ^{1}H 400 MHz). For heteronuclear measurements involving alkali metal ions, a 10-mm multinuclear probehead was employed. Carbon-13 measurements were carried out on a 5-mm dual probehead. Homonuclear ^{1}H spectra were recorded on a selective 5-mm probehead. Pulse widths (90°) were as follows: ^{6}Li, 28 μs; ^{133}Cs, 38 μs; ^{13}C, 9 μs; ^{1}H, 28 μs (multinuclear probehead) and 38 μs (selective probehead, attenuated for ROESY).

THF-d_8 was dried over an Na/Pb alloy. ^{6}Li chemical shifts were referenced to 1 M LiBr in THF-d_8.[68] The reference measurements were carried out prior to the sample measurements at the indicated temperatures. ^{133}Cs chemical shifts were referenced to saturated $CsNO_3$ in D_2O at 25 °C. No corrections for different temperatures and bulk magnetic susceptibilities were made. With respect to the large chemical shift range of ^{133}Cs, any errors introduced by this method of referencing are con-

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(65) Kaufmann, E.; Gose, J.; Schleyer, P. v. R. *Organometallics* **1989**, *8*, 2577.

(66) From the signal to noise ratios, we estimate the NMR detection limits (molar fraction) for a mixed aggregate **12** to be ca. 3% (^{6}Li,^{1}H HOESY, Figure 3) and ca. 10% (^{133}Cs,^{1}H HOESY, Figure 4), respectively.

(67) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308.

(68) A new and general method of referencing ^{6}Li/^{7}Li NMR chemical shifts has been described recently by Jackman et al. (*J. Am. Chem. Soc.* **1991**, *113*, 4101). Therein, a ^{13}C solvent signal of a reference sample is converted to an absolute frequency of the standard lithium signal. Likewise, the absolute frequencies of the sample lithium signals are determined from the frequencies of the sample solvent ^{13}C NMR signals. The differences of the absolute lithium standard and sample frequencies are converted to conventional chemical shifts. These numbers are free of errors due to different magnetic susceptibilities.

J. Am. Chem. Soc. **1992**, *114*, 7489-7493

sidered to be negligible. ^{13}C chemical shifts were referenced to the signal of the solvent, THF-d_8, α-C = 67.4 ppm. ^{1}H chemical shifts were referenced to the residual solvent signal, THF-d_7, α-H = 3.58 ppm. Deuterium lock on THF-d_8 was obtained by using the upfield (β-D) signal of the solvent. We found this to be more convenient than using the α-D signal since the β-deuterium resonance line appears to be generally sharper. This is beneficial for the shimming procedure.

All 2D NMR spectra were recorded in the phase-sensitive mode (pure absorption quadrature detection in f_1 by the method described by States et al.[69]). Details of phase-sensitive ^{6}Li,^{1}H HOESY[33] and ^{133}Cs,^{1}H HOESY[37] have been described elsewhere. Selected recording parameters of the individual spectra were as follows.

For the spectrum in Figure 1 (^{6}Li,^{1}H HOESY of **8**): 0.35 M solution in THF-d_8 (dissolved crystals of [^{6}Li]lithium trityl with 2 equiv of Et$_2$O), 26 °C, 5-mm sample tube; spectral widths: 400 (f_2) and 3157 Hz (f_1); 512 data points in t_2, 32 increments in t_1, zero-filled to 128 data points, exponential line broadening in t_2, Gaussian apodization in t_1; 128 scans per t_1 increment, mixing time 2.0 s, interpulse delay 3.0 s, 12.8 h spectrometer time.

For the spectrum in Figure 2 (^{133}Cs,^{1}H HOESY of **9**): 1.2 M solution in THF-d_8 (dissolved crystals of **9**), 40 °C, 5-mm sample tube; spectral widths: 14 006 (f_2) and 364 Hz (f_1); 512 data points in t_2, 32 increments in t_1, zero-filled to 128 data points, Gaussian apodization in t_1 and t_2, 256 scans per t_1 increment; mixing time 300 ms. A crude estimation of the spin lattice relaxation time, T_1, of ^{133}Cs afforded $T_1 \approx 400$ ms (achieved by null point determination in a single inversion recovery experiment, divided by ln 2); interpulse delay 2.1 s, 11.0 h spectrometer time.

For the spectrum in Figure 3 (^{6}Li,^{1}H HOESY of a mixture of **8** and **9**): Crystals of **8** (enriched with ^{6}Li and with 2 equiv of Et$_2$O) and crystals of **9** dissolved in THF-d_8, 1:1.5 molar ratio, 0.6 M in **8**, 26 °C, 10-mm sample tube; spectral widths: 400 (f_2) and 3270 Hz (f_1); 512 data points in t_2, 64 increments in t_1, zero-filled to 256 points; exponential line broadening in t_2, Gaussian apodization in t_1; mixing time 2.0 s, interpulse delay 3.2 s, 13.3 h spectrometer time.

For the spectrum in Figure 4 (^{133}Cs,^{1}H HOESY of a mixture of **8** and **9**): Crystals of **8** (enriched with ^{6}Li and with 2 equiv of Et$_2$O) and crystals of **9** dissolved in THF-d_8, 1.2:1 molar ratio, 0.6 M in 8, 26 °C, 10-mm sample tube; spectral widths: 1600 (f_2) and 3270 Hz (f_1); 512 data points in t_2, 16 increments in t_1, zero-filled to 128 points, Gaussian apodization in t_1 and t_2, 640 scans per t_1 increment; mixing time 350 ms (an estimation afforded $T_1(^{133}\text{Cs}) \approx 370$ ms; see explanation given above for Figure 2); interpulse delay 3.2 s, 21 h spectrometer time.

For the spectrum in Figure 5 (^{1}H,^{1}H ROESY of a mixture of **8** and **9**): Crystals of **8** (enriched with ^{6}Li and with 2 equiv of Et$_2$O) and crystals of **9** dissolved in THF-d_8, 1:1.5 molar ratio, 0.6 M in **8**, 20 °C; spectral width 3270 Hz; pulse sequence $90°-t_1-(12.6\text{-}\mu\text{s pulse}-126\text{-}\mu\text{s delay})_{7200}$–acquisition–delay;[70] 2048 data points in t_2, 128 increments in t_1, zero-filled to 256 data points; 64 scans per t_1 increment, Gaussian apodization in t_1 and t_2; spin lock time 1.0 s, interpulse delay 2.0 s, 4.6 h spectrometer time.

MNDO calculations were carried out on a CONVEX C220 computer using the VAMP4 (vectorized AMPAC) program. All geometry optimizations involved the keywords PRECISE (criteria for convergence to be increased by a factor of 10–100) or EF (eigenvector following). No symmetry constraints were imposed in any case.

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^{87}Rb Dynamic-Angle Spinning NMR Spectroscopy of Inorganic Rubidium Salts

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Abstract: Five inorganic rubidium salts, RbCl, RbClO$_4$, Rb$_2$SO$_4$, Rb$_2$CrO$_4$, and RbNO$_3$, were examined using ^{87}Rb NMR spectroscopy. Significant line narrowing occurs under dynamic-angle spinning (DAS) compared to magic-angle spinning (MAS) or variable-angle spinning (VAS). From DAS spectra acquired at various magnetic field strengths, isotropic chemical shifts and isotropic second-order quadrupolar shifts were obtained. By simulations of single-site line shapes obtained from MAS-detected DAS experiments, complete chemical shift and quadrupolar parameters were determined for each of the three crystallographically distinct rubidium sites in RbNO$_3$.

Introduction

Solid-state nuclear magnetic resonance (NMR) spectroscopy of the central ($-^1/_2 \leftrightarrow +^1/_2$) transition of half-odd-integer quadrupolar nuclei can yield information about the nuclear quadrupole interaction, which in turn can be correlated with the structural properties of a material.[1,2] Typically, though, the spectral line from the central transition is broadened by the second-order anisotropic quadrupolar interaction, which cannot be averaged under magic-angle spinning (MAS) or variable-angle spinning (VAS). Recent work has shown, however, that dynamic-angle spinning (DAS) can average such broadening, producing narrow lines and resolution of crystallographically distinct sites for ^{23}Na, ^{17}O, and ^{27}Al spectra of minerals, zeolites, and other

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