

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

Title: Nucleophilic aromatic substitution at benzene with powerful strontium hydride and alkyl complexes

Authors: Sjoerd Harder, Bastian Rösch, Thomas Xaver Gentner, Holger Elsen, Christian A. Fischer, Jens Langer, and Michael Wiesinger

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201901548 Angew. Chem. 10.1002/ange.201901548

Link to VoR: http://dx.doi.org/10.1002/anie.201901548 http://dx.doi.org/10.1002/ange.201901548

WILEY-VCH

Nucleophilic aromatic substitution at benzene with powerful strontium hydride and alkyl complexes

Bastian Rösch, Thomas Xaver Gentner, Holger Elsen, Christian A. Fischer, Jens Langer, Michael

Wiesinger and Sjoerd Harder*

B. Rösch, T. X. Gentner, H. Elsen, C. A. Fischer, Dr. J. Langer, M. Wiesinger, Prof. Dr. S. Harder*
Chair of Inorganic and Organometallic Chemistry, Universität Erlangen-Nürnberg, Egerlandstrasse 1, 91058
Erlangen, Germany
Fax: (+49) 9131-8527387
E-mail: sjoerd.harder@fau.de

Supporting information for this article is available on the WWW under http//:www.angewandte.chemie.org or from the author.

Keywords: Alkaline Earth Metal – Strontium – Alkylmetal – Nucelophilic Aromatic Substitution –DFT calculations

Table of Contents



The first unstabilized alkylstrontium complex could be obtained using a very robust superbulky ßdiketiminate ligand. The very high nucleophilicity of its Sr hydride and Sr ethyl complexes is demonstrated by D-exchange reactions with C_6D_6 and D_2 . Catalytic deuteration of C_6H_6 with D_2 is presented. Metal alkyl complexes are typically extremely reactive and often burn upon contact with air. Despite challenging syntheses and handling, they represent the earliest known examples of organometallic compounds.^[1,2] Schlenk's alkyllithium^[3] and Grignard's alkylmagnesium reagents^[4] are true milestones in organometallic chemistry and essential to modern organic synthesis. Alkyl complexes of the larger, more electropositive, heavier group 1 metals are even more reactive: the superbase *n*BuK deprotonates THF already at -50 °C.^[5,6] These bases and other smart mixtures with heavier alkali metals^[7] are routinely used in large scale specialty applications.^[7] In contrast, heavier group 2 metal reagents remained elusive for at least a century.^[8] Organocalcium chemistry is slowly awakening but its recent developments mainly included syntheses of benzyl-,^[9] aryl-,^[10] allyl,^[11] or silylated methyl^[12] compounds. The much more potent unsubstituted alkyl metal complexes were a long sought after Holy Grail in alkaline earth metal chemistry and this quest has only very recently been realized.^[13-15]

Synthesis of highly reactive alkylcalcium complexes requires robust ligands and use of inert solvents (THF should be avoided). Our endeavors to isolate an alkylcalcium reagent by reaction of a solvent-free calcium hydride complex with the highly polarized C=C bond in a N-heterocyclic olefin gave metallation of the ligand backbone (Scheme 1a).^[16] Attempts to isolate a THF-free version of the earlier reported ß-diketiminate calcium hydride complex [(^{DIPP}BDI)CaH·(THF)]₂ (^{DIPP}BDI = CH[C(Me)N-DIPP]₂, DIPP =2,6-di*iso*propylphenyl)^[17] were frustrated by the Schlenk equilibrium, resulting in (CaH₂)_∞ precipitation (Scheme 1b),^[18,19] but using an excess of the hydride transfer reagent PhSiH₃, Hill and coworkers isolated [(^{DIPP}BDI)CaH]₂ (Scheme 1c).^[13]



Scheme 1. (a) Reaction of an amidinate calcium hydride complex with a N-heterocyclic olefin led to backbone deprotonation. (b) Attempted synthesis of $[(^{DIPP}BDI)CaH]_2$ using stoichiometric quantities of PhSiH₃ led to ligand exchange. (c) Using an excess of PhSiH₃ gave the expected product which reacted with alkenes to give alkylcalcium complexes.

Although this effect of reagent stoichiometry is not fully understood, NMR investigations suggest that equilibria involving hypervalent silicate species prevent destructive Schlenk equilibria (Figure S23-24). Addition of alkenes to [(^{DIPP}BDI)CaH]₂ gave the first "true" alkylcalcium compounds (Scheme 1c).^[13] Simultaneously, the Anwander group prepared Me₂Ca by metal exchange between MeLi and Ca[N(SiMe₃)₂]₂.^[14] The very high reactivity of these unstabilized alkylcalcium complexes was demonstrated by alkyl/H exchange with the benzene solvent at 60 °C.^[13] Without having explored the full scope,^[15,20] their unusual reactivity spurs the isolation of the increasingly more reactive alkyl complexes of Sr and Ba. As alkylbarium complexes have so far only been discussed as fleeting extremely reactive intermediates,^[21] isolation of alkylstrontium complexes is a more realistic goal.

The main hurdle towards the synthesis of alkylstrontium complexes is the challenging isolation of a simple, THF-free, strontium hydride complex LSrH with a robust spectator ligand L. It should be soluble in non-polar solvents, stable towards ligand exchange reactions and decomposition but reactive towards nonconjugated alkenes. Recently reported Sr hydride complexes^[22-25] do not fulfill these requirements. As amidinate ligands with extremely bulky 2,6-Ph₂CH-phenyl substituents failed to stabilize Sr hydride complexes^[23,26] we investigated the Sr chemistry of recently introduced DIPePBDI,^[27] a very robust superbulky β-diketiminate ligand that increases the solubility of polar complexes in apolar solvents (Scheme 2).



Scheme 2. Synthesis and reactivity of strontium hydride and alkyl complexes.

Reaction of ^{DIPeP}BDI-H with SrN"₂ (N" = N(SiMe₃)₂) in hexane at 70 °C reached full conversion to (^{DIPeP}BDI)SrN" after 14 days. Although sluggish, this direct ligand deprotonation is very convenient. In contrast to (^{DIPP}BDI)AeN" complexes (Ae = Sr, Ba),^[28] (^{DIPeP}BDI)SrN" is extremely stable towards ligand

CCEDted ManuScript

exchange: a toluene- d_8 solution at 140 °C did even after 6 days not decompose. Complex (^{DIPeP}BDI)SrN" crystallizes as a monomer (Figure 1a) in which the N(SiMe₃)₂ ligand is asymmetrically bound to Sr (Sr-N-Si1 = 130.5(1)°, Sr-N-Si2 = 106.1(1)°) on account of a strong Sr…Me-Si agostic interaction which is the shortest of its kind: Sr…C = 3.057(2) Å. A somewhat longer agostic interaction with the diisopentyl substituent (3.310(2) Å) complements the Sr coordination sphere, demonstrating that the flexible arms of the ^{DIPeP}BDI ligand are ideally suited to stabilize complexes with larger metals by secondary interactions.

The hydride complex (^{DIPeP}BDI)SrH was obtained in 53% yield by warming a hexane solution of (^{DIPeP}BDI)SrN'' and PhSiH₃ from -80 °C to 20 °C. It crystallized as a dimer with bridging hydride ligands that were freely refined (Figure 1b). The average Sr-(μ^2)H distance of 2.35 Å is, considering a 0.03 Å standard deviation, within the 2.26(5)-2.43(3) Å range for other dimeric Sr hydride complexes.^[23,25] The coordination sphere of Sr2 is supplemented by Sr···C(isopentyl) agostic interactions, making all bonds to Sr2 slightly longer. The ligand bulk in [(^{DIPeP}BDI)SrH]₂ and [(^{DIPP}BDI)CaH]₂^[13] was compared by calculation of buried volume: the ^{DIPeP}BDI ligand ($V_{bur} = 61.5\%$) is substantially bulkier then the ^{DIPP}BDI ligand ($V_{bur} = 51.1\%$); Figure S59.



Figure 1. Crystal structures. (a) Complex (^{DIPeP}BDI)SrN''. (b) Complex [(^{DIPeP}BDI)SrH]₂. (c) Complex [(^{DIPeP}BDI)SrE]₂. Selected distances are given in Å and angles in degrees.

The eight highly flexible isopentyl arms in $[(^{DIPeP}BDI)SrH]_2$ make this complex very soluble in alkanes or aromatic solvents. The ¹H NMR spectrum in C₆D₆ shows for the hydride ligands a sharp singlet at 5.41 ppm fitting the 4.48-6.64 ppm range reported for Sr hydride complexes.^[22-25] This C₆D₆ solution of $[(^{DIPeP}BDI)SrH]_2$ is remarkably stable and gave up to 70 °C no ligand exchange. Interestingly, prolonged heating to 60 °C in C₆D₆ led overnight to complete H-D exchange with the deuterated solvent giving $[(^{DIPeP}BDI)SrD]_2$ and C₆D₅H (Scheme 2; somewhat slower H-D exchange is also observed in toluene-*d*₈). The Sr hydride complex gave fast H-D exchange with D₂ (1.5 bar D₂, C₆D₆, 20 °C: >99% deuteration in 2 hours; Scheme 2). This scrambling reaction was found to be much faster than that for a cationic Sr hydride cluster^[24] and, more important, did not lead to decomposition. Therefore,

4

 $[(^{DIPeP}BDI)SrH]_2$ could be used as a catalyst for the deuteration of C₆H₆ by D₂ (TON = 27 in 5 days, Figure S42-45). Although slow, Sr hydride catalyzed H-D isotope exchange in an unactivated aromatic compound like benzene is unparalleled. H-D Exchange reactions are generally mediated by precious metal catalysts,^[29] following a Shilov-type oxidative addition of the C-H bond, or by strong Lewis acids^[30] in which case electrophilic substitution proceeds through a Wheland cyclohexadienyl cation. We propose a mechanism in which benzene is activated for nucleophilic aromatic substitution by an incipient π -complex with the Sr metal, followed by formation of a cyclohexadienyl anion of the Meisenheimer type (Scheme 2).

The very robust $[(^{DIPeP}BDI)SrH]_2$ is the key to alkylstrontium complexes. In C₆D₆, it fully reacted with ethylene at 20 °C and 1 bar within minutes (Scheme 2). The ¹H NMR spectrum showed a variety of alkylstrontium products characterized by multiplets in the -0.5/-1.5 ppm range. NMR and GC-MS analysis indicated two competitive reactions. The Sr-Et intermediate reacts further with ethylene to give Sr-Bu, Sr-hexyl and higher oligomers, a process reminiscent of Ziegler's Et₃Al/C₂H₄ "Aufbau Reaktion". Oligomerization competes with nucleophilic aromatic substitution at C₆D₆ giving $[(^{DIPeP}BDI)SrD]_2$ and a variety of RC₆D₅ products (R = Et, Bu, hexyl, etc.). The lower molecular weight oligomers could be detected by GC-MS but also insoluble long-chain polyethylene has been isolated (Figure S48). Room temperature ethylene (oligo-)polymerization at low pressure illustrates that strontium hydrides may be promising *s*-block metal initiators for polymerization but featured at 60 °C a similar nucleophilic aromatic substitution.^[13]

The conversion of Sr-alkyl into Sr-D species by nucleophilic aromatic substitution with C_6D_6 was circumvented by performing the synthesis in hexane, a solvent in which the isopentyl-decorated species are highly soluble. Overnight reaction of $[(^{DIPeP}BDI)SrH]_2$ in hexane with 1 bar ethylene between -80 to -20 °C gave after crystallization $[(^{DIPeP}BDI)SrEt]_2$ in 33% yield. Similar to $[(^{DIPeP}BDI)CaEt]_2,^{[13]}$ complex $[(^{DIPeP}BDI)SrEt]_2$ crystallized as a centrosymmetric dimer with slightly asymmetric bridging Et ligands (Figure 1c). It is stabilized by strong agostic Sr…CH₃ interactions of 3.034(2) Å, that are only 8.4% longer than the direct Sr-CH₂ bond of 2.798(1) Å, and a secondary Sr…CH₃(isopentyl) interaction of 3.240(4) Å. The freely refined H positions in the Et ligands show essentially sp^3 -hybridized CH₂ groups (the sum of the valence angles is 320.7°).

The Sr alkyl complex $[(^{DIPeP}BDI)SrEt]_2$ is poorly soluble in alkanes but dissolves moderately in C₆D₆. In agreement with the higher ionicity of the Sr-Et *vs.* Ca-Et bond, the Sr-CH₂ ¹H NMR signal (-0.90 ppm) is shifted highfield in respect to the Ca-CH₂ signal in $[(^{DIPP}BDI)CaEt]_2$ (-0.79 ppm).^[13] As the complex instantaneously deprotonates THF, polar solvents should be avoided (Figure S58). The extreme reactivity of $[(^{DIPeP}BDI)SrEt]_2$ is demonstrated by fast reaction with H₂ to give $[(^{DIPeP}BDI)SrH]_2$ and ethane (C₆D₆, 20 °C, 1.5 bar H₂, < 5 min); *cf.* reaction of $[(^{DIPP}BDI)CaEt]_2$ with H₂ needed at least 48 hours).^[20a] Its high reactivity is further demonstrated by very facile nucleophilic substitution at C₆D₆ which proceeds already at 20 °C giving full conversion to $[(^{DIPeP}BDI)SrD]_2$ and EtC₆D₅ within 12 hours. At 60 °C complete conversion was reached within five minutes (*cf.* conversion of $[(^{DIPP}BDI)CaEt]_2$ with C₆D₆ at 60 °C needed 16 hours).^[13] An intermediate in this unusually fast nucleophilic Et-D substitution at C₆D₆ is the mixed Et-D species: $(^{DIPeP}BDI)_2Sr_2(\mu^2-Et)\mu^2-D$ (Figure S50).

Since the ^{DIPeP}BDI ligand inhibits ligand exchange in Sr complexes, catalytic insertion of ethylene in the benzene C-H seemed feasible. Insertion of ethylene in the C-D bond of C_6D_6 with catalyst [(^{DIPeP}BDI)SrEt]₂, however, gave at room temperature apart from ethylbenzene a mixture of products.

As ethylene oligomerization is competitive with alkyl-D exchange, $Et(C_2H_4)_nC_6D_5$ (n = 0-10) and longer alkanes (C₂H₄)_nH₂ (n = 5-18) were detected by GC-MS (Figure S56). In addition, double Et/D exchange was verified by identification of C₆D₄(Et)₂. A signal for the triple Et/D exchange product C₆D₃(Et)₃ was absent. This may be explained by the fact that the π -electron density becomes higher with increasing alkylation, making nucleophilic aromatic substitution progressively more difficult.

In order to provide further insight in this unusual nucleophilic substitution at benzene, an energy profile following that previously reported for the reaction of $[(^{DIPP}BDI)Ca(n-hexyI)]_2$ with benzene^[13] was calculated (Scheme 3a). The calculated Sr-C distances in $[(^{DIPeP}BDI)SrEI]_2$ are in excellent agreement with those in the crystal structure. NPA Charges of +1.81 on Sr and -0.82 on the bridging CH₂ group confirm the strong polarity of the Sr-C bond. Formation of monomeric (M1) is endothermic by +8.1 kcal/mol, a value considerably lower than the dissociation energy of 23.2 kcal/mol calculated for $[(^{DIPP}BDI)Ca(n-hexyI)]_2$.^[13] The large Sr metal in $(^{DIPP}BDI)SrEt$, which is formally only three-coordinate, shows a strong Sr···CH₃ agostic interaction indicated by a Sr-C-C angle of 89.6° that is considerably more acute than the Ca-C-C angle of 117.2° in $(^{DIPP}BDI)Ca(n-hexyI)$.^[13] This agostic interaction is lost by complexation of benzene (M2). The transition state for rear-side attack of Et at the coordinated (activated) benzene ligand (M3*) is essentially barrier-free. The short C···C and long C···H distance indicate that hydride transfer to Sr is at a very advanced state. Complex M4 releases ethylbenzene to give (^{DIPP}BDI)SrH (M5). The total energy gain of -9.2 kcal/mol reflects the lability of the Sr ethyl educt M1 vs. the Sr hydride product M5. The formation of monomeric species M1 (+8.1 kcal/mol) is the most difficult step along the profile.

The problem with this monomeric model system is that rear-side Et attack can only proceed when the Et group acts as a charge-separated nucleophile. Unfavorable Sr-Et cleavage may be facilitated by solvent-stabilization but absence of polar solvents makes this route questionable. This is a common dilemma in nucleophilic substitution reactions: the simple textbook picture of the S_{N2} transition state $(Nu^{\delta-}...CH_3^{\delta+}...X^{\delta-})$ becomes much more complicated when a tightly bound metal cation is considered.^[32] How does the metal cation migrate from nucleophile to leaving group without paying the high penalty for charge separation? Transition states in which $Nu^{\delta-}$ and $X^{\delta-}$ are bridged by a chain of cations and anions were found to be high in energy and equally unsatisfying.^[32] We do, however, not rule out a mechanism in which the 4-membered Sr_2Et_2 ring in the dimer is opened, after which Sr-benzene coordination and attack from the rear can occur. Using a simplified ß-diketiminate ligand with Ph substituents (^{Ph}BDI), we calculated an energy profile for these much larger dimeric systems (Scheme 3b).



Scheme 3. Calculated energy profiles for benzene alkylation (B3PW91/def2tzvpp). Enthalpy differences (Δ H) are given in kcal/mol and selected distances in Å. The ß-diketiminate ligands are only partially shown. (a) Energy profile for a monomeric model system (M) with a ^{DIPeP}BDI ligand. (b) Energy profile for a dimeric model system.

Simplifying the ligand has serious consequences for the cleavage energy of the dimer into monomers which is strongly dependend on the bulk of the aryl substituent: DIPeP (+8.1 kcal/mol), DIPP (+21.2 kcal/mol) and Ph (+24.2 kcal/mol). Opening of a dimer, however, is much easier: insertion of benzene in one of the four Sr-Et bonds in [(^{Ph}BDI)SrEt]₂ costs only 11.5 kcal/mol and leads to loss of both Sr····CH₃ agostic interactions and partial rupture of a second Sr-Et bond (D1). Intramolecular rear-side attack (D2*) needs an activation energy of +26.4 kcal/mol. Formation of the Et···C bond (2.231 Å) results in transformation of benzene into a cyclohexadienyl anion; loss of aromaticity is indicated by deviation from planarity. Product D3 contains an unstable Meisenheimer anion which transfers a hydride anion to Sr through a low energy transition state D4*. The total reaction of [(^{Ph}BDI)SrEt]₂ with benzene to give ethylbenzene and the mixed ethyl-hydride dimer D6 is exothermic by -11.1 kcal/mol.

Transition state D3* (+26.4 kcal/mol) is the highest point along the route. Although the rather high activation energy is not conform the facile nucleophilic substitution at benzene, which proceeds at room temperature, this dimeric model does not suffer from (^{DIPP}BDI)Sr⁺/Et⁻ charge separation, a step that is currently not included in the monomeric model.

In summary, the group of highly reactive alkaline earth metal reagents has been extended with an unstabilized alkyl complex of the heavy metal Sr. The key to isolation of $[(^{DIPeP}BDI)SrEt]_2$ was the very robust strontium hydride complex $[(^{DIPeP}BDI)SrH]_2$ featuring the superbulky $^{DIPeP}BDI$ ligand. This ligand is tailor-made for larger metals, stabilizing complexes not only by its impressive bulk but also by secondary agostic interactions with the isopentyl substituents. The potent nucleophilicity of $[(^{DIPeP}BDI)SrH]_2$ is demonstrated by an unprecedented H-D exchange with C₆D₆ and very fast H-D exchange with D₂. This reactivity is the basis for Sr hydride catalyzed deuteration of C₆H₆ by D₂. The even higher reactivity of $[(^{DIPeP}BDI)SrEt]_2$ is exemplified by ethylene polymerization and facile Et-D exchange with C₆D₆ proceeding already at room temperature. This first example of an unstabilized alkylstrontium complex is currently the most polar and nucleophilic group 2 metal species. This leaves us with the challenging goal to isolate even more reactive alkylbarium complexes.

References

- L. C. Cadet de Gassicourt, "Suite d'Expériences nouvelles sur l'Encre sympathique de M.
 Hellot qui peuvent servir à l'analyse du Cobolt; et Histoire d'une liqueur fumante, tirée de l'Arsènic" Memoires de Mathématique et de Physique. Presentés à l'Académie Royale des Sciences par diverse Savans et lŭs dans ses Assemblées. Tome Troisième, MDCCLX (**1760**), p. 623.
- [2] E. Frankland, Justus Liebigs Ann. Chem. 1853, 85, 329-373.
- [3] W. Schlenk, J. Holtz, Ber. Dtsch. Chem. Ges. **1917**, 50, 262-274.
- [4] V. Grignard, Compt. rend. Hebd. Séances Acad. Sci. 1900, 130, 1322-1324.
- [5] L. Lochmann, M. Janata, *Cent. Eur. J. Chem.* **2014**, *12*, 537.
- [6] R. E. Mulvey, V. L. Blair, W. Clegg, A. R. Kennedy, J. Klett, L. Russo, *Nature Chemistry* **2010**, *2*, 588–591.
- [7] R. E. Mulvey, F. Mongin, M. Uchiyama, Y. Kondo, *Angew. Chem. Int. Ed.* 2007, 46, 3802-3824.
- [8] Alkaline-Earth Metal Compounds: Oddities and Apllications, *Top. Organomet. Chem.* **2013**, *45*; Ed. S. Harder, Springer, Berlin.
- [9] S. Harder, F. Feil, A. Weeber, *Organometallics* **2001**, *20*, 1044-1046.
- [10] R. Fischer, M. Gärtner, H. Görls, M. Westerhausen, Angew. Chem. Int. Ed. 2006, 45, 609–612.
- [11] P. Jochmann, S. Maslek, T. P. Spaniol, J. Okuda, *Organometallics* **2011**, *30*, 1991–1997.
- [12] F. G. N. Cloke, P. B. Hitchcock, M. F. Lappert, G. A. Lawless, B. Royo, *J. Chem. Soc., Chem. Commun.* **1991**, 724–726.
- [13] A. S. S. Wilson, M. S. Hill, M. F. Mahon, C. Dinoi, L. Maron, *Science* **2017**, *358*, 1168-1171.
- [14] B. M. Wolf, C. Stuhl, C. Maichle-Mössmer, R. Anwander, J. Am. Chem. Soc. 2018, 140, 2373-2383.
- [15] R. E. Mulvey, *Science* **2017**, *358*, 1132.
- [16] A. Causero, H. Elsen, J. Pahl, S. Harder, Angew. Chem. Int. Ed. 2017, 56, 6906-6910.
- [17] S. Harder, J. Brettar, Angew. Chem. Int. Ed. 2006, 45, 3474-3478.
- [18] A. Causero, G. Ballmann, J. Pahl, C. Färber, J. Intemann, S. Harder, *Dalton Trans.* **2017**, *46*, 1822-1831.
- [19] See for reviews on group 2 metal hydride complexes: (a) S. Harder, *Chem. Commun.* 2012, 48, 11165-11177. (b) L. Fohlmeister, A. Stasch, *Aust. J. Chem.* 2015, 68, 1190-1201. (c) D.

Mukherjee, J. Okuda, *Angew. Chem. Int. Ed.* **2018**, *57*, 1458-1473. (d) D. Mukherjee, D. Shuhknecht, J. Okuda, *Angew. Chem. Int. Ed.* **2018**, *57*, 9590-9602.

- [20] (a) A. S. S. Wilson, C. Dinoi, M. S. Hill, M. F. Mahon, L. Maron, *Angew. Chem. Int. Ed.* 2018, *57*, 15500-15504. (b) A. S. S. Wilson, M. S. Hill, M. F. Mahon, *Organometallics* 2019, *38*, 351-360.
- [21] M. Wiesinger, B. Maitland, C. Färber, G. Ballmann, C. Fischer, H. Elsen, S. Harder, *Angew. Chem. Int. Ed.* **2017**, *56*, 16654-16659.
- [22] B. Maitland, M. Wiesinger, J. Langer, G. Ballmann, J. Pahl, H. Elsen, C. Färber, S. Harder, *Angew. Chem. Int. Ed.* **2017**, *56*, 11880-11884.
- [23] C. N. de Bruin-Dickason, T. Sutcliffe, C. A. Lamsfus, G. B. Deacon, L. Maron, C. Jones, *Chem. Commun.* **2018**, *54*, 786-789.
- [24] D. Mukherjee, T. Höllerhage, V. Leich, T. P. Spaniol, U. Englert, L. Maron, J. Okuda, J. Am. Chem. Soc. 2018, 140, 3403-3411.
- [25] X. Shi, G. Qin, Y. Wang, L. Zhao, Z. Liu, J. Cheng, Angew. Chem. Int. Ed. 2019, accepted article.
- [26] B. Freitag, J. Pahl, C. Färber, S. Harder, *Organometallics* **2018**, *37*, 469-475.
- [27] T. X. Gentner, B. Rösch, G. Ballmann, J. Langer, H. Elsen, S. Harder, Angew. Chem. Int. Ed. 2019, 58, accepted. DOI:10.1002/anie.201812051
- [28] A. G. Avent, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, Dalton Trans. 2005, 278-284.
- [29] J. Atzrodt, V. Derdau, W. J. Kerr, M. Reid, Angew. Chem. Int. Ed. 2019, 57, 3022-3047.
- [30] D. Munz, M. Webster-Gardiner, R. Fu, T. Strassner, W. A. Goddard III, T. B. Gunnoe, ACS Catal. 2015, 5, 769-775.
- [31] Waxy polyethylene with *MW* in the 1000-3000 range was obtained by ethylene polymerization using *n*BuLi/TMEDA in alkanes at 120 °C and >3.5 bar pressure: G. G. Eberhardt, US Pat. 3.321.479 (1967) and 3.567.703 (1971).
- [32] S. Harder, A. Streitwieser, J. T. Petty, P. von R. Schleyer, *J. Am. Chem. Soc.* **1995**, *117*, 3253-3259 (1995).

Acknowledgements Steffen Brand is acknowledged for assistance in reactivity studies. S. H. acknowledges the Deutsche Forschungsgemeinschaft for financial support (HA 3218/9-1).

Abstract: The key to isolation of the first alkylstrontium complex is the synthesis of a strontium hydride complex that is stable towards ligand exchange reactions. This was achieved by using the superbulky ß-diketiminate ligand $^{DIPeP}BDI$ (CH[C(Me)N-DIPeP]₂, DIPeP =2,6-di*iso*pentylphenyl). Reaction of $^{DIPeP}BDI-H$ with Sr[N(SiMe₃)₂]₂ gave ($^{DIPeP}BDI$)SrN(SiMe₃)₂ which was converted with PhSiH₃ to [($^{DIPeP}BDI$)SrH]₂. Dissolved in C₆D₆, the Sr hydride complex is stable is up to 70 °C. At 60 °C, H-D isotope exchange gave full conversion to [($^{DIPeP}BDI$)SrD]₂ and C₆D₅H. Since H-D exchange with D₂ is also facile, the strontium hydride complex is a catalyst for the deuteration of C₆H₆ by D₂. Reaction of [($^{DIPeP}BDI$)SrH]₂ with ethylene gave [($^{DIPeP}BDI$)SrE]₂. The high reactivity of this first alkylstrontium complex is demonstrated by facile ethylene polymerization and nucleophilic aromatic substitution with C₆D₆ giving alkylated aromatic products and ($^{DIPeP}BDI$)SrD]₂, both processes which proceed at room temperature. DFT calculations illustrate that the latter Et-D exchange with C₆D₆ likely involves the highly instable Meisenheimer anion C₆D₆Et⁻ as an intermediate.