Inorg. Chem. **2008**, *47*, 1190–1195

Inorganic Chemistry
Article

Synthesis, Characterization, and Reactivity of [Li(N^6,N^9-Me$_2$Ade$_{-H}$)]: A Structurally Characterized Lithiated Adenine

Thomas Krüger,[†] Tobias Rüffer,[‡] Heinrich Lang,[‡] Christoph Wagner,[†] and Dirk Steinborn*,[†]

Institut für Chemie−Anorganische Chemie, Martin-Luther-Universität Halle-Wittenberg,
D-06120 Halle, Kurt-Mothes-Strasse 2, Germany, and Institut für Chemie, Lehrstuhl für
Anorganische Chemie, Technische Universität Chemnitz, D-09111 Chemnitz,
Strasse der Nationen 62, Germany

Received August 7, 2007

The reaction of N^6,N^9-dimethyladenine (N^6,N^9-Me$_2$Ade, **1**) with methyllithium in aprotic solvents such as tetrahydrofuran and pyridine resulted in the formation of the lithiated adenine [Li(N^6,N^9-Me$_2$Ade$_{-H}$)] (**2**) that was isolated as highly air and moisture sensitive tetrahydrofuran (**2**$\cdot$$^1/_4$THF) and pyridine (**2**$\cdot$py) adducts in excellent yields (>90%). The identities of **2**$\cdot$$^1/_4$THF and **2**$\cdot$py were confirmed by ^{1}H and ^{13}C NMR spectroscopy. In crystals of **2**$\cdot$$^3/_2$py, the dimethyladeninato ligand exhibited a chelating and bridging coordination mode ($\kappa^2N^6,N^7{:}\kappa N^3$) resulting in a 1-D polymeric chain-like structure in which the tetrahedral coordination sphere of the lithium atoms was completed by a pyridine molecule. Reactions of **2**$\cdot$$^1/_4$THF with electrophiles such as MeI, Me$_3$SiCl, and Me$_3$SnCl resulted in high yields (88–98%) of the formation of the adenine derivatives N^6,N^6,N^9-Me$_3$Ade$_{-H}$ (**3**), N^6-(SiMe$_3$)-N^6,N^9-Me$_2$Ade$_{-H}$ (**4**), and N^6-(SnMe$_3$)-N^6,N^9-Me$_2$Ade$_{-H}$ (**5**), respectively. Compounds **3**–**5** were characterized by ^{1}H, ^{13}C, ^{29}Si (**4**), and ^{119}Sn (**5**) NMR spectroscopy and MS investigations, and the stannylated derivative **5** also was characterized by single-crystal diffraction analysis exhibiting a mononuclear structure. The reaction of the stannylated adenine **5** with *n*-BuLi in *n*-hexane proceeded in the sense of a tin-lithium transmetalation reaction yielding the solvent-free lithium adeninate [Li(N^6,N^9-Me$_2$Ade$_{-H}$)] (**2**) in 90% yield.

1. Introduction

Interactions between bioligands such as nucleobases (NB) and metal ions are of great interest because of their important roles in biological processes.[1] A significant amount of work over the last years has dealt with understanding the interactions (in an aqueous/alcoholic environment) between alkaline metal ions and nucleobases without their deprotonation (M^+-NB; M = alkaline metal).[2] Thus, Russo et al. performed quantum chemical calculations to describe the affinity of lithium ions toward DNA and RNA nucleobases.[3] Furthermore, metalation can occur, resulting in deprotonation of the nucleobase ($M-NB_{-H}$). Especially, transition metals are known as yielding complexes with deprotonated nucleobases having, in general, manifold donor sites (N and O), thus giving rise to a rich coordination chemistry.[4] In contrast, the binding modes of alkaline metals to deprotonated nucleobases are much less investigated. For understanding the binding modes in lithiated nucleobases ($Li-NB_{-H}$), a prerequisite is to synthesize them as model compounds. In the case of adenine, for instance, deprotonation can occur at four positions (N^9-H, N^6-H, C^2-H, and C^8-H). The N^9-H proton in adenine (pK_a = 14.2 in DMSO)[5] is much more acidic than the NH$_2$ group. Thus, reactions with bases, such as alkali alcoholates or hydroxides, in protic solvents

---

* To whom correspondence should be addressed. E-mail: dirk.steinborn@chemie.uni-halle.de; tel.: +49-345-5525620; fax: +49-345-5527028.

[†] Martin-Luther-Universität Halle-Wittenberg.

[‡] Technische Universität Chemnitz.

(1) (a) Lippert, B. *Prog. Inorg. Chem.* **2005**, *54*, 385−447. (b) Sivakova, S.; Rowan, S. J. *Chem. Soc. Rev.* **2005**, *34*, 9−21. (c) Terrón, A.; Fiol, J. J.; García-Raso, A.; Barceló-Oliver, M.; Moreno V. *Coord. Chem. Rev.* **2007**, *251*, 1973−1986. (d) Freisinger, E.; Sigel, R. K. O. *Coord. Chem. Rev.* **2007**, *251*, 1834−1851.

(2) (a) Monajjemi, M.; Ketabi, S.; Ghiasi, R.; Zare, K.; Passdar, H.; Karimkhani, M.; Saedi, L. *Internet Electron. J. Mol. Des.* **2004**, *3*, 789−801. (b) Zhu, W.; Luo, X.; Puah, C. M.; Tan, X.; Shen, J.; Gu, J.; Chen, K.; Jiang H. *J. Phys. Chem. A* **2004**, *108*, 4008−4018. (c) Rodgers, M. T.; Armentrout, P. B. *J. Am. Chem. Soc.* **2000**, *122*, 8548−8558. (d) Reddy, B. S.; Saenger, W.; Mühlegger, K.; Weimann, G. *J. Am. Chem. Soc.* **1981**, *103*, 907−914.

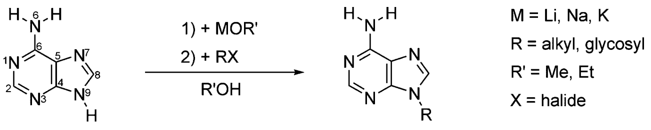
(3) Russo, N.; Toscano, M.; Grand, A. *J. Phys. Chem. B* **2001**, *105*, 4735−4741.

(4) (a) Navarro, J. A. R.; Lippert, B. *Coord. Chem. Rev.* **1999**, *185−186*, 653−667. (b) Lippert, B. *Coord. Chem. Rev.* **2000**, *200−202*, 487−516. (c) Houlton, A. *Adv. Inorg. Chem.* **2002**, *53*, 87−158.

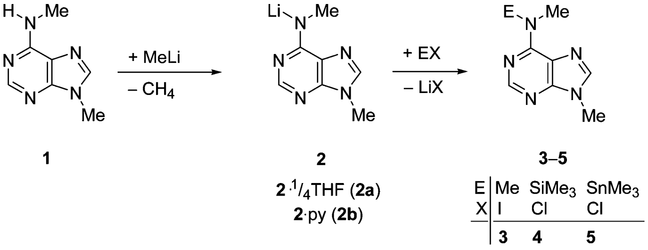
(5) (a) Li, J.-N.; Liu, L.; Fu, Y.; Guo, Q.-X. *Tetrahedron* **2006**, *62*, 4453−4462. (b) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463. (c) Chen, E. C. M.; Herder, C.; Chen, E. S. *J. Mol. Struct.* **2006**, *798*, 126−133.

10.1021/ic701569j CCC: $40.75

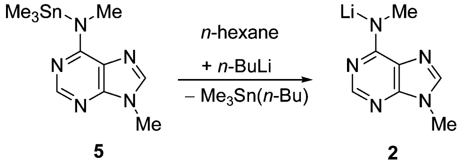
Scheme 1



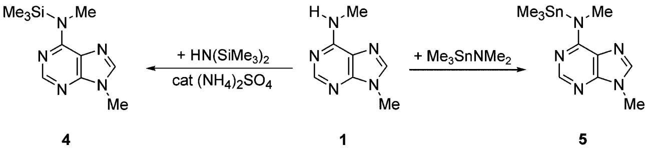
Scheme 2



Scheme 3



Scheme 4



(preferably alcohols) followed by the addition of RX resulted in the formation of N^9 substituted adenine derivatives (Scheme 1). This reaction route is frequently used in (bio)-organic and synthetic chemistry.[6] Usually, the alkaline salts of adenine were prepared in situ and were neither isolated nor characterized. Furthermore, due to a lower acidity of the N^6–H proton (N^9-methyladenine: pK_a = 17 in DMSO),[7] its deprotonation requires stronger reaction conditions (liquid ammonia or KNH$_2$).[8] This may give rise to C–H activation and isomerization side reactions preventing direct access to N^6 substituted adenines in this way. This may be overcome when transition metals are coordinated at N^1 or N^7 of the adenine derivatives that can result in a severe increase of the acidity of the N^6–H protons[4b] that may give rise to a smooth deprotonation or tautomerization of N^6–H bonds under mild conditions.[9]

N–H deprotonation reactions of adenines in aprotic solvents yielding alkaline metal adeninates in a pure isolated state and subsequent investigation of the reactivity has not yet been described. Here, we report the synthesis of a lithium adeninate complex, [Li(N^6,N^9-Me$_2$Ade$_{-H}$)] **2**, the structure of its pyridine adduct, and its reactivity toward electrophiles yielding novel N^6 functionalized adenine derivatives.

2. Results and Discussion

2.1. Syntheses. N^6,N^9-Me$_2$Ade (**1**) was found to react with MeLi through deprotonation of N^6, yielding [Li(N^6,N^9-Me$_2$-Ade$_{-H}$)] (**2**), which precipitated from THF as **2**·$^1/_4$THF and from pyridine as **2**·py (Scheme 2). The compounds were obtained in excellent yields (92 and 98%, respectively) as white highly air and moisture sensitive powders. They were characterized by ^{1}H and ^{13}C NMR spectroscopy and in the case of the pyridine derivative also by X-ray crystallographic investigations. The lithiated dimethyladenine (**2**·$^1/_4$THF) proved to be highly reactive against electrophiles of group 14 (Scheme 2). Thus, it reacted with methyl iodide, yielding the three-fold methylated adenine N^6,N^6,N^9-Me$_3$Ade$_{-H}$ (**3**) (yield 88%) with a concomitant formation of lithium iodide. The corresponding silylated N^6-(SiMe$_3$)-N^6,N^9-Me$_2$Ade$_{-H}$ (**4**) and stannylated N^6-(SnMe$_3$)-N^6,N^9-Me$_2$Ade$_{-H}$ (**5**) compounds were obtained by the reaction of **2**·$^1/_4$THF with trimethylsilyl chloride and trimethyltin chloride, respectively. Both compounds were isolated in nearly quantitative yields (90 and 98%, respectively) as white air and moisture sensitive powders. Compounds **3**–**5** were fully characterized by NMR spectroscopy as well as by MS investigations and single-crystal X-ray crystallography (**5**). Furthermore, it was found that the stannylated adenine N^6-(SnMe$_3$)-N^6,N^9-Me$_2$Ade$_{-H}$ (**5**) reacted with *n*-BuLi in *n*-hexane, undergoing a tin-lithium transmetalation reaction,[10] to yield the lithiated adenine **2** and the requisite tetraalkyltin Me$_3$Sn(*n*-Bu) (Scheme 3). Thus, the synthesis of the solvent-free lithiated adenine [Li-(N^6,N^9-Me$_2$Ade$_{-H}$)] (**2**) was achieved as a highly air and moisture sensitive powder in 90% yield.

For comparison, the silylated and stannylated adenines **4** and **5** were prepared directly from N^6,N^9-Me$_2$Ade (**1**) via an alternative procedure (Scheme 4): The silylation of **1** with hexamethyldisilazane in the presence of catalytic amounts of (NH$_4$)$_2$SO$_4$ resulted in the formation of N^6-(SiMe$_3$)-N^6,N^9-Me$_2$Ade$_{-H}$ (**4**) but—contrary to the lithium route (Scheme 2)—only in a low yield (12%). The stannylated adenine derivative **5** was formed in a good yield (89%) from the reaction of N^6,N^9-Me$_2$Ade (**1**) with Me$_3$SnNMe$_2$ via a transamination reaction at room temperature. Proton NMR spectroscopic investigations revealed that both reaction products were identical to those obtained according to Scheme 2.

2.2. Spectroscopic Characterization. All compounds were fully characterized by means of ^{1}H and ^{13}C NMR spectroscopy. The spectra showed the expected singlet resonances (with couplings to ^{29}Si and $^{117/119}$Sn for **4**/**5**) having the correct intensities in proton NMR spectra. The ^{1}H NMR spectra of **2**·$^1/_4$THF (Me$_2$Ade$_{-H}$/THF = 4:1) and **2**·py (Me$_2$Ade$_{-H}$/py = 1/:1) in DMSO-d_6 are consistent with the composition of the compounds. The chemical shifts of the starting material N^6,N^9-Me$_2$Ade (**1**) differ only slightly from those of the lithiated adenine **2**·$^1/_4$THF. Thus, lithiation at N^6 gave rise to only a slight upfield shift of the protons

---

(6) Rasmussen, M.; Hope, J. M. *Aust. J. Chem.* **1982**, *35*, 535–542.

(7) Stewart, R.; Harris, M. G. *Can. J. Chem.* **1977**, *55*, 3807–3814.

(8) Kos, N. J.; Van der Plas, H. C.; Blees, W. J. F. *J. Org. Chem.* **1983**, *48*, 850–855.

(9) (a) Arpalahti, J.; Klika, K. D. *Eur. J. Inorg. Chem.* **1999**, 1199–1201. (b) Clarke, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 5068–5075. (c) Zamora, F.; Kunsman, M.; Sabat, M.; Lippert, B. *Inorg. Chem.* **1997**, *36*, 1583–1587. (d) Zhu, X.; Rusanov, E.; Kluge, R.; Schmidt, H.; Steinborn, D. *Inorg. Chem.* **2002**, *41*, 2667–2671.

(10) (a) Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 3583–3586. (b) Orita, A.; Otera, J. In *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley VCH: Weinheim, Germany, 2004; pp 621–720.

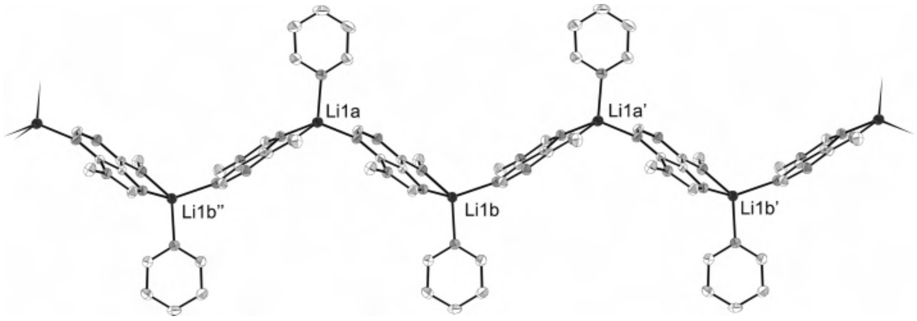


Figure 1. 1-D chain of [Li(N^6,N^9-Me$_2$Ade$_{-H}$)(py)] (**2**·py) in crystals of **2**·$^3/_2$py. H atoms and the packing pyridine molecule are omitted for clarity.

(3.07−2.98 ppm; THF-d_8) and a downfield shift of the C atom (27.3−31.2 ppm; DMSO-d_6) of the N^6−CH$_3$ group. On the other hand, in the three-fold methylated system, the silylated and stannylated derivatives (**3**−**5**) were observed both for the N^6−CH$_3$ proton (3.38−3.55 in THF-d_8) and for the N^6−CH$_3$ carbon atom (32.8−36.1 in THF-d_8) downfield shifts. The chemical shifts of the silylated nucleobase **4** correspond well with values of analogous substances given in the literature (chemical shifts for the TMS group: **4** (in THF-d_8) vs N^6,N^9-bis(trimethylsilyl)adenine (in CDCl$_3$): δ_H 0.36 vs 0.38; δ_C 1.0 vs −0.1; and δ_{Si} 7.2 vs 6.9).[11]

The substitution of the Cl in Me$_3$SiCl and Me$_3$SnCl by the N^6-deprotonated adenine N^6,N^9-Me$_2$Ade$_{-H}$ gives rise to strong highfield shifts of the silicium (δ_{Si} 29.8 in Me$_3$SiCl[12] vs 7.2 in **4**; THF-d_8) and tin resonances (δ_{Sn} 84.3 in Me$_3$SnCl vs 31.7 in **5**; THF-d_8). In compounds Me$_3$EX (E = Si, Sn and X = any ligand), the magnitudes of the $^1J_{E,C}$ (E = ^{29}Si, ^{119}Sn) coupling constants reflect the electronic influence of the substituents X.[13,14] Thus, the relative large values in **4** ($^1J_{Si,C}$ = 59 Hz) and **5** ($^1J_{Sn,C}$ = 417 Hz) (as compared to those in other Me$_3$EX derivatives; cf. $^1J_{Si,C}/^1J_{Sn,C}$ with X = Me, 51/338 Hz and X = Cl, 58/380 Hz)[13,15] indicate a relatively low electronic influence of the N^6-deprotonated adenine group. Even within the N-bound ligands, the electronic influence of the N^6-deprotonated adenine proved to be the lowest one:[16] -NR$_2$ (R = Me/Et, 381/379 Hz) > -NH(py-H) (2-aminopyridine; 394 Hz) > N^6,N^9−Me$_2$−Ade$_{-H}$ (417 Hz).

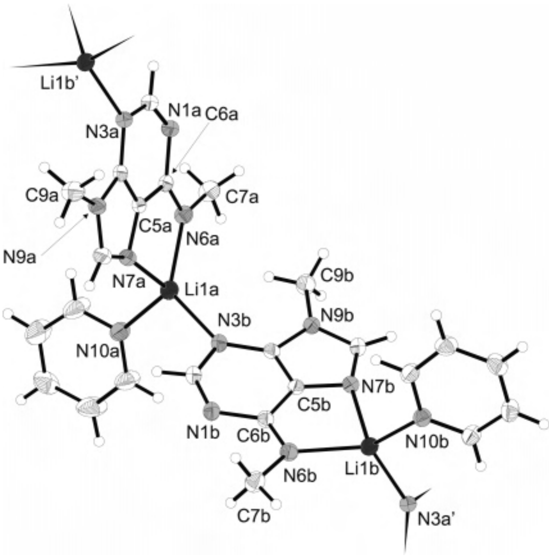


Figure 2. Asymmetric unit of [Li(N^6,N^9-Me$_2$Ade$_{-H}$)(py)]·$^1/_2$py (**2**·$^3/_2$py). Displacement ellipsoids are drawn at the 30% probability level. The noncoordinated pyridine molecule is omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of **2**·$^3/_2$py

Li1a−N3b	2.038(4)	N6a−Li1a−N7a	88.6(1)
Li1a−N6a	2.058(4)	N6a−Li1a−N10a	113.6(2)
Li1a−N7a	2.127(4)	N6a−Li1a−N3b	129.9(2)
Li1a−N10a	2.040(4)	N7a−Li1a−N10a	111.0(2)
Li1b−N6b	2.102(4)	N7a−Li1a−N3b	104.2(2)
Li1b−N7b	2.118(4)	N10a−Li1a−N3b	106.4(2)
Li1b−N10b	2.049(4)	N6b−Li1b−N7b	88.8(1)
Li1b−N3a	2.074(4)	N6b−Li1b−N10b	120.2(2)
		N6b−Li1b−N3a	122.3(2)
		N7b−Li1b−N10b	107.4(2)
		N7b−Li1b−N3a	107.1(2)
		N10b−Li1b−N3a	107.4(2)

2.3. Structural Characterization. Slow crystallization from reaction solutions of **2** in pyridine at room temperature resulted in the formation of well-shaped crystals having the composition **2**·$^3/_2$py that proved to be suitable for single-crystal X-ray diffraction measurements. These crystals **2**·$^3/_2$py were found to contain in the asymmetric unit two structurally very similar moieties [Li(N^6,N^9-Me$_2$Ade$_{-H}$)(py)] (**2**·py) (in the following labeled as a and b) and, additionally, a pyridine molecule. The lithiated adenine **2**·py forms 1-D polymeric chains that are oriented along the crystallographic b-axis. There are no unusual interactions either between neighboring polymeric chains (shortest distance between non-hydrogen atoms is 3.303(3) Å, C8a···N1b′) or to the additional pyridine molecule (shortest distance between non-hydrogen atoms is 3.47(1) Å, N···C9b). The conformation of the 1-D chain is shown in Figure 1, and a detailed view is shown in Figure 2. Selected bond lengths and angles are given in Table 1. The two crystallographically independent N^6,N^9-Me$_2$Ade$_{-H}$ units are essentially planar; the largest deviations from the mean planes are 0.035(2) Å for C9a and 0.065(2) for C7b. The Li atoms (Li1a/Li1b) are tetrahedrally coordinated through N6 and N7 of a dimethyladeninato ligand and through N3 of another dimethyladeninato ligand resulting in a chelating and bridging coordination mode ($\kappa^2N^6,N^7{:}\kappa N^3$). The fourth coordination site of Li is occupied by a pyridine molecule. The chelate coordination of the

---

(11) Schraml, J.; Kvicalova, M.; Blechta, V.; Rericha, R.; Rozenski, J.; Herdewijn, P. *Magn. Reson. Chem.* **1998**, *36*, 55−63.

(12) Olah, G. A.; Hunadi, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 6989−6992.

(13) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73−186.

(14) Steinborn, D. *Angew. Chem.* **1992**, *104*, 392−412.

(15) Harris, R. K.; Kimber, B. J. *J. Magn. Reson.* **1975**, *17*, 174−188.

(16) The $^1J_{Sn,C}$ coupling constants are given in parentheses. (a) Bishop, M. E.; Schaeffer, C. D., Jr.; Zuckerman, J. J. *J. Organomet. Chem.* **1975**, *101*, C16−C23. (b) Wrackmeyer, B.; Kehr, G.; Zhou, H.; Ali, S. *Magn. Reson. Chem.* **1996**, *34*, 921−928.

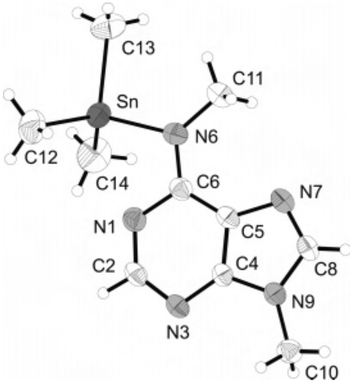


Figure 3. Molecular structure of N^6-($SnMe_3$)-N^6,N^9-Me_2Ade_{-H} in crystals of **5**. Displacement ellipsoids are drawn at the 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **5**

Sn−N6	2.090(4)	N6−Sn−C12	108.9(2)
Sn−C12	2.129(6)	N6−Sn−C13	100.2(2)
Sn−C13	2.159(6)	N6−Sn−C14	111.0(2)
Sn−C14	2.124(6)	C12−Sn−C13	108.9(3)
N1−C6	1.368(6)	C12−Sn−C14	118.7(3)
N6−C6	1.357(6)	C13−Sn−C14	107.5(3)
N6−C11	1.453(6)		

lithium atoms is such that the five-membered rings (Li1−N7−C5−C6−N6) are essentially planar (largest deviation from the mean plane: 0.046(2) Å for N7a and 0.043(2) Å for N6b) with N6−Li1−N7 angles of 88.6(1) and 88.8(1)° for units a and b, respectively. These are the smallest angles at the strongly tetrahedrally distorted lithium atoms, whereas the largest are 129.9(2)° (N6a−Li1a−N3b) and 122.3(2)° (N6b−Li1b−N3a′). The Li−N distances are between 2.038(4) and 2.127(4) Å and comparable to values given in the literature (Li−N in lithium pyridine compounds; median: 2.071 Å; lower/upper quartile: 2.036/2.104 Å; and number of observations: $n = 601$).[17]

The N^6-trimethyltin substituted dimethyladenine derivative **5** was found to crystallize in discrete molecules without any unusual intermolecular interactions; the shortest distance between non-hydrogen atoms is 3.150(6) Å (C8···C8′). The molecular structure of **5** is shown in Figure 3. Selected bond lengths and angles are given in Table 2. The tin atom has a typical (distorted) tetrahedral coordination. Inspection of C−Sn−C (107.5(3), 108.9(3), and 118.7(3)°) and N−Sn−C angles (100.2(2), 108.9(2), and 111.0(2)°) revealed that one of the three C−Sn−C and N−Sn−C angles each is unusually large and small, respectively. The ligand plane bisects this large C−Sn−C angle (C12−Sn−C14: 118.7(3)°) with the lone electron pair on N1 directed along the bisector of this angle. As a consequence, the C12···N1 (3.313(7) Å) and C14···N1 (3.349(6) Å) distances are small, indicating a steric hindrance that may be the cause of the widening of the C12−Sn−C14 angle by about 10° (as compared to the other two C−Sn−C angles). In accordance with that, a concomitant reduction of the angle N6−Sn−C13 (the $C13H_3$ ligand lies in the plane of the nucleobase ligand) by about 10° (as compared to the other two N−Sn−C angles) is observed.

The N^6,N^9-dimethyladeninato ligand is bound through the N6 atom to tin. The Sn−N6 bond length (2.090(4) Å) is in the typical range of tin-nitrogen bonds (Sn−N bond length in fragments R_3Sn−N: median 2.103 Å; lower/upper quartile 2.068/2.156 Å; and $n = 140$).[17] The nucleobase ligand is essentially planar; the greatest deviation from the mean plane is 0.043(4) Å for C5.

3. Conclusion

It has been shown that reactions of N^6,N^9-dimethyladenine with methyllithium in aprotic solvents (tetrahydrofuran and pyridine) proceeded with deprotonation, yielding well-defined lithiated adenines that could be isolated as THF (**2**·$^1/_4$THF) and pyridine adducts (**2**·py and **2**·$^3/_2$py) as well as solvent-free (**2**). These are the first representatives for isolated in a pure state and fully characterized alkaline metal nucleobase complexes, and **2**·$^3/_2$py is the first structurally characterized derivative. The lithiated adenine **2** exhibited a high reactivity toward electrophiles such as RX (X = I, Cl) resulting in N^6 substituted adenine derivatives N^6-R-N^6,N^9-Me_2Ade_{-H} (R = Me, **3**; Me_3Si, **4**; and Me_3Sn, **5**) that were isolated and fully characterized. To the best of our knowledge, the solid state structure of **5** is the first example of a tin compound with an amide bound nucleobase.

The lithiated adenine **2** represents a new synthon in (bio)-organic and coordination chemistry that could give easy access to N^6 substituted adenine derivatives starting from commericially available (less expensive) compounds. Because of the high yields in the formation of **3**−**5** (88−98%), this route could be an attractive alternative to syntheses starting from (highly expensive) 6-chlorpurine derivates.[18]

4. Experimental Procedures

4.1. Materials and Measurements. Syntheses of all compounds were carried out under argon using standard Schlenk techniques. All solvents were dried (pyridine and pyridine-d_5 over CaH_2; THF, THF-d_8, and benzene-d_6 over Na-benzophenone; *n*-hexane over $LiAlH_4$; and DMSO-d_6 over molecular sieve) and distilled prior to use. Starting materials were commercially available from Aldrich (Me_3SnCl, Me_3SiCl, and Me_3SnNMe_2), Acros (adenine, $HN(SiMe_3)_2$, MeI, and MeLi in Et_2O), and Merck (*n*-BuLi in *n*-hexane). N^6,N^9-Me_2Ade (**1**) was synthesized according to the literature.[19] NMR spectra were recorded at room temperature on Varian Unity 500 and VXR 400 spectrometers operating at 500 and 400 MHz for ^1H, respectively. Solvent signals (^1H and ^{13}C) were used as internal references. $\delta(^{119}Sn)$ and $\delta(^{29}Si)$ are relative to external $SnMe_4$ in benzene-d_6 and $SiMe_4$ in $CDCl_3$, respectively. Microanalyses (C and H) were performed by the microanalytical laboratory of the University of Halle using a CHNS-932 (LECO) elemental analyzer. GC−MS investigations were carried out on an HP 5890II/5972 instrument (Hewlett-Packard). Mass spectra were obtained on an AMD 402 instrument (AMD Intectra GmbH; 70 eV, EI-MS).

4.2. Synthesis of [Li(N^6,N^9-Me_2Ade_{-H})]·$^1/_4$THF (2·$^1/_4$THF). At −40 °C to a solution of N^6,N^9-Me_2Ade (**1**) (100 mg, 0.61 mmol) in tetrahydrofuran (8 mL), MeLi (0.4 M solution in Et_2O, 0.64 mmol) was added dropwise with stirring. A precipitate immediately formed, and the resulting suspension was stirred for another 2 h and then slowly warmed to room temperature. The highly air and

---

(17) *Cambrigde Structural Database (CSD)*, version 1.9; Cambridge Crystallographic Data Centre, University Chemical Laboratory: Cambridge, U.K., 2006.

(18) Robins, R. K.; Lin, H. H. *J. Am. Chem. Soc.* **1957**, *79*, 490−494.

(19) Talman, E. G.; Brüning, W.; Reedijk, J.; Spek, A. L.; Veldman, N. *Inorg. Chem.* **1997**, *36*, 854−861.

moisture sensitive product was filtered off, washed with *n*-hexane (2 × 5 mL), and dried in vacuo. Yield: 105 mg (92%).

^{1}H NMR (THF-d_8, 400 MHz): δ 2.98 (s, br, 3H, N^6−C*H*$_3$); 3.58 (s, 3H, N^9−C*H*$_3$); 7.32 (s, 1H, *H*^{8}); 7.82 (s, 1H, *H*^{2}). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.88 (s, br, 3H, N^6−C*H*$_3$); 3.59 (s, br, 3H, N^9−C*H*$_3$); 7.69 (s, 1H, *H*^{8}); 7.84 (s, 1H, *H*^{2}); 1.79/3.59 (m/m, br, 1H/1H, $^1/_4$THF). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 28.9 (s, N^9−*C*H$_3$); 31.2 (s, N^6−*C*H$_3$); 128.1 (s, *C*^{5}); 136.7 (s, *C*^{8}); 146.2 (s, *C*^{4}); 153.5 (s, *C*^{2}); 158.0 (s, *C*^{6}); 25.0/66.9 (s/s, THF).

4.3. Synthesis of [Li(N^6,N^9-Me$_2$Ade$_{-H}$)]·py (2·py). To a stirred solution of N^6,N^9-Me$_2$Ade (**1**) (57 mg, 0.35 mmol) in pyridine (5 mL), MeLi (0.4 M solution in Et$_2$O, 0.36 mmol) was added dropwise at room temperature. The color of the solution changed to light yellow, and methane was evolved. Stirring was stopped after 2 h, and the product crystallized within a few hours. After 12 h, **2**·py, which proved to be highly air and moisture sensitive, was filtered off, washed with *n*-hexane (2 × 3 mL), and dried in vacuo. Yield: 85 mg (98%).

^{1}H NMR (pyridine-d_5, 400 MHz): δ 3.61 (s, br, 6H, N^6−C*H*$_3$ + N^9−C*H*$_3$); 7.70 (s, 1H, *H*^{8}); 8.82 (s, 1H, *H*^{2}). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.90 (s, br, 3H, N^6−C*H*$_3$); 3.63 (s, 3H, N^9−C*H*$_3$); 7.81 (s, 1H, *H*^{8}); 7.97 (s, 1H, *H*^{2}); 7.37/7.76/8.56 (m/m/m, 2 H/2H/1H, py). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 29.0 (s, N^9−*C*H$_3$); 29.6 (s, N^6−*C*H$_3$); 128.2 (s, *C*^{5}); 138.2 (s, *C*^{8}); 147.5 (s, *C*^{4}); 152.9 (s, *C*^{2}); 156.4 (s, *C*^{6}), 123.7/135.9/149.4 (s/s/s, py).

4.4. Synthesis of N^6,N^6,N^9-Me$_3$Ade$_{-H}$ (3). At −40 °C to a solution of N^6,N^9-Me$_2$Ade (**1**) (105 mg, 0.64 mmol) in tetrahydrofuran (10 mL), MeLi (1.6 M solution in Et$_2$O, 0.65 mmol) was added dropwise whereupon a precipitate was gradually formed. After 1 h, methyl iodide (92 mg, 0.65 mmol) was slowly added. The reaction mixture was stirred for 2 h and warmed to room temperature, and the solvent was then removed in vacuo. The white residue was extracted with benzene (2 × 10 mL). From the combined organic phases, the solvent was removed under reduced pressure, and the residual white powder was dried in vacuo. Yield: 100 mg (88%).

Anal. calcd for $C_8H_{11}N_5$: C, 54.22; H, 6.26; N, 39.52. Found: C, 54.11; H, 6.20; N, 39.39. ^{1}H NMR (THF-d_8, 400 MHz): δ 3.48 (s, br, 6H, N^6(C*H*$_3$)$_2$); 3.74 (s, 3H, N^9−C*H*$_3$); 7.82 (1H, *H*^{8}); 8.17 (1H, *H*^{2}). ^{13}C NMR (THF-d_8, 100 MHz): δ 29.0 (s, N^9−*C*H$_3$); 36.1 (s, N^6(*C*H$_3$)$_2$); 120.0 (s, *C*^{5}); 138.2 (s, *C*^{8}); 151.0 (s, *C*^{4}); 151.9 (s, *C*^{2}); 156.7 (s, *C*^{6}). GC−MS: *m*/*z* (%) 177(100) $[M]^{+\bullet}$ (obsd intensities agree with isotopic pattern calcd for $C_8H_{11}N_5$); 176(30) $[M-H]^+$; 162(8) $[M-CH_3]^+$; 149(84); 148(44); 147(51) $[M-2CH_3]^+$; 133(9) $[M-C_2H_6N]^+$; 121(77) $[M-C_2H_4N_2]^+$; 106(9); 93(7); 80(47); 67(18).

4.5. Synthesis of N^6-(SiMe$_3$)-N^6,N^9-Me$_2$Ade$_{-H}$ (4) and N^6-(SnMe$_3$)-N^6,N^9-Me$_2$Ade$_{-H}$ (5). At −40 °C to a solution of N^6,N^9-Me$_2$Ade (**1**) (150 mg, 0.92 mmol) in tetrahydrofuran (8 mL), MeLi (1.6 M solution in Et$_2$O, 0.95 mmol) was added dropwise, resulting in the formation of a precipitate. After 4 h of stirring, either Me$_3$SiCl (109 mg, 1.00 mmol) or Me$_3$SnCl (200 mg in 2 mL of THF, 1.00 mmol), respectively, was added dropwise, resulting in a clear solution within a few minutes. The reaction mixture was stirred for a further 2 h. After warming to room temperature, the solvent was removed in vacuo, the residue was extracted with *n*-hexane (12 mL), and the resulting suspension was filtered. In the case of **4**, the solvent was removed under reduced pressure, and the residual solid was dried in vacuo. In the case of **5**, the hexane solution was concentrated to a volume of ca. 5 mL. Within 1 day at −40 °C **5** crystallized as colorless, well-shaped crystals that were filtered off and dried in vacuo. Both these compounds proved to be very air and moisture sensitive.

Compound **4**. Yield: 195 mg (90%). ^{1}H NMR (benzene-d_6, 400 MHz): δ 0.41 (s, 9 H, Si(C*H*$_3$)$_3$); 2.89 (s, 3H, N^6−C*H*$_3$); 3.67 (s, 3H, N^9−C*H*$_3$); 6.95 (1H, *H*^{8}); 8.55 (1H, *H*^{2}). ^{29}Si NMR (benzene-d_6, 100 MHz): δ 7.0 (s, *Si*(CH$_3$)$_3$). ^{1}H NMR (THF-d_8, 500 MHz): δ 0.36 (s, br, 9H, Si(C*H*$_3$)$_3$); 3.38 (s, 3H, N^6−C*H*$_3$); 3.77 (s, 3H, N^9−C*H*$_3$); 7.90 (s, 1H, *H*^{8}); 8.13 (s, 1H, *H*^{2}). ^{13}C NMR (THF-d_8, 125 MHz): δ 1.0 (s + d, Si(*C*H$_3$)$_3$ $^1J_{C,Si} = 59.4$ Hz); 29.3 (s, N^9−*C*H$_3$); 32.8 (s, N^6−*C*H$_3$); 125.8 (s, *C*^{5}); 141.0 (s, *C*^{8}); 151.7 (s, *C*^{4}); 153.1 (s, *C*^{2}); 155.7 (s, *C*^{6}). ^{29}Si NMR (THF-d_8, 100 MHz): δ 7.2 (s, *Si*(CH$_3$)$_3$). MS: *m*/*z* (%) 235(15) $[M]^{+\bullet}$ (obsd intensities agree with isotopic pattern calcd for $C_{10}H_{17}N_5Si$); 220 (100) $[M-CH_3]^+$; 205(3) $[M-2CH_3]^+$; 190(4) $[M-3CH_3]^+$; 177(5); 162(10) $[M-Si(C_3H_9)]^+$; 152(8); 135(7); 107(7), 73 (10) $[M-Si(CH_3)_3]^+$.

Compound **5**. Yield: 295 mg (98%). ^{1}H NMR (THF-d_8, 400 MHz): δ 0.41 (s+d, $^2J_{Sn,H} = 59.1$ Hz, 9H, Sn(C*H*$_3$)$_3$); 3.55 (s, 3H, N^6−C*H*$_3$); 3.72 (s, 3H, N^9−C*H*$_3$); 7.78 (s, 1H, *H*^{8}); 7.95 (s, 1H, *H*^{2}). ^{13}C NMR (THF-d_8, 100 MHz): δ −3.9 (s + d, Sn(*C*H$_3$)$_3$, $^1J_{Sn,C} = 416.9$ Hz); 29.5 (s, N^9−*C*H$_3$); 34.4 (s, N^6−*C*H$_3$); 121.2 (s, *C*^{5}); 140.1 (s, *C*^{8}); 151.8 (s, *C*^{4}); 152.7 (s, *C*^{2}); 160.1 (s, *C*^{6}). ^{119}Sn NMR (THF-d_8, 186 MHz): δ 31.74 (s, *Sn*(CH$_3$)$_3$). MS: *m*/*z*(%) 327(<1) $[M]^{\bullet+}$ (obsd intensities agree with isotopic pattern calcd for $C_{10}H_{17}N_5Sn$); 312(4) $[M-CH_3]^+$; 282(4) $[M-3CH_3]^+$; 163(100) $[M-Sn(C_3H_8)]^+$; 135(63); 107(51).

4.6. Tin-Lithium Transmetalation Reaction. At −40 °C to a solution of N^6-(SnMe$_3$)-N^6,N^9-Me$_2$Ade$_{-H}$ (**5**) (103 mg, 0.32 mmol) in *n*-hexane (6 mL), BuLi (1.6 M in *n*-hexane, 0.35 mmol) was slowly added. The reaction mixture became cloudy, and after 2 h, the suspension was warmed to room temperature. The solid product **2** was then filtered off, washed with *n*-hexane (2 × 5 mL), and dried in vacuo. Yield: 50 mg (90%). Compound **2** was identified by ^{1}H NMR spectroscopy.

4.7. Synthesis of 4 by Reaction of N^6,N^9-Me$_2$Ade (1) with HN(SiMe$_3$)$_2$. N^6,N^9-Me$_2$Ade (**1**) (120 mg, 0.74 mmol) and a catalytic amount of $(NH_4)_2SO_4$ (5 mg) were suspended in HN(SiMe$_3$)$_2$ (10 mL) and refluxed for 10 h until the reaction mixture became clear. At room temperature, the excess HN(SiMe$_3$)$_2$ was removed under reduced pressure. The resulting white solid was extracted with *n*-hexane (2 × 5 mL). From the combined organic phases, the solvent was removed in vacuo, and the residual product was dried in vacuo. Yield: 20 mg (12%). Compound **4** was identified by ^{1}H NMR spectroscopy.

4.8. Synthesis of 5 by Reaction of N^6,N^9-Me$_2$Ade (1) with Me$_3$SnNMe$_2$. N^6,N^9-Me$_2$Ade (**1**) (50 mg, 0.31 mmol) and Me$_3$SnNMe$_2$ (644 mg, 3.1 mmol) were stirred together at room temperature for 2 h. During the reaction, HNMe$_2$ was evolved. Then, the excess of Me$_3$SnNMe$_2$ was removed under reduced pressure, and the resulting residue was mixed with *n*-hexane (5 mL). The suspension was filtered, and the solvent was removed under reduced pressure. The white residue was dried in vacuo. Yield: 90 mg (89%). The product was identified as **5** by ^{1}H NMR spectroscopy.

4.9. X-ray Crystal Structure Determinations. Single crystals suitable for X-ray diffraction measurements were obtained from a reaction mixture at room temperature (**2**·$^3/_2$py) and from a *n*-hexane solution at −40 °C (**5**), respectively. Data were collected on a Oxford Gemini diffractometer at 100(2) K (**2**·$^3/_2$py) and on a STOE IPDS diffractometer at 220(2) K (**5**), respectively, using Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were carried out semiempirically (T_{min}/T_{max} 0.94/1.00; **2**·$^3/_2$py) and numerically (T_{min}/T_{max} 0.23/0.85; **5**), respectively. A summary of crystallographic data, data collection parameters, and refinement parameters is given in Table 3. The structures were solved by direct methods using SHELXS-97[20] refined by full-matrix least-square procedures on F^2

Table 3. Crystal Data and Details on Structure Determinations of **2**·$^3/_2$py and **5**

	2·$^3/_2$py	**5**
chemical formula	$C_{29}H_{31}Li_2N_{13}$	$C_{10}H_{17}N_5Sn$
fw	575.55	325.98
cryst syst/space group	monoclinic/$P2_1/n$	monoclinic/$P2_1/a$
a (Å)	15.027(1)	6.879(2)
b (Å)	12.148(1)	11.818(2)
c (Å)	17.616(1)	17.033(4)
β (deg)	108.79(1)	100.86(3)
V (Å^3)	3044.4(4)	1359.8(5)
Z	4	4
ρ (g cm^{-3})	1.256	1.592
μ(Mo Kα) (mm^{-1})	0.080	1.863
index ranges	$-17 \leq h \leq 18$, $-14 \leq k \leq 14$, $-21 \leq l \leq 21$	$-8 \leq h \leq 8$ $-13 \leq k \leq 13$, $-20 \leq l \leq 20$
reflns collected	23635	10422
reflns independent	5945 ($R_{int} = 0.0216$)	2566 ($R_{int} = 0.1099$)
data/restraints/params	5945/0/397	2566/0/151
GOF on F^2	1.126	0.986
$R[I > 2\sigma(I)]$	R1 = 0.0543, wr2 = 0.1566	R1 = 0.0394, wR2 = 0.0839
R (all data)	R1 = 0.0770, wR2 = 0.1683	R1 = 0.0599, wR2 = 0.0903
largest diff. peak and hole (e Å^{-3})	0.519 and −0.539	0.516 and −0.757

using SHELXL-97.[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined with isotropic displacement parameters according to the riding model. Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as Supplementary Publications CCDC-664701 (**2**·$^3/_2$py) and CCDC-664702 (**5**).

Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft and gifts of chemicals from Merck (Darmstadt) are gratefully acknowledged. We thank Dr. H. Schmidt (University of Halle) for GC−MS and MS investigations.

Supporting Information Available: Crystallographic information files of structures of **2**·$^3/_2$py and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC701569J

---

(20) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1990.

(21) Sheldrick, G. M. *SHELXL-97, Program for Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.