

# Sodium-mediated Magnesiation of Thiophene and Tetrahydrothiophene: Structural Contrasts with Furan and Tetrahydrofuran

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Sulfur-containing heterocycles are currently attracting a great deal of interest in several diverse fields. For instance, substituted tetrahydrothiophenes,<sup>[1]</sup> have received considerable attention due to their extremely wide-ranging chemical and biological applications.<sup>[2]</sup> These include their use as potent  $\alpha$ -glucosidase inhibitors,<sup>[3]</sup> as an inhibitor of copper amine oxidases<sup>[4]</sup> and as selective A<sub>3</sub> agonists and antagonists.<sup>[5]</sup> In addition, they have been utilized in chemical transformations, such as catalytic asymmetric epoxidation, catalytic intramolecular cyclopropanation, and asymmetric metal catalysis hydrogenation.<sup>[6]</sup> From a nanochemical perspective, the adsorption chemistries and physical properties of various thiophenes and tetrahydrothiophenes on gold surfaces have recently come to the fore.<sup>[7]</sup> Polythiophenes are also key compounds in modern materials research, currently utilised in for example the fabrication of semi-conducting, fluorescent, and electronic and optoelectronic materials.<sup>[8]</sup> In this work, metallation (exchange of a hydrogen atom with a metal atom) of the parent heterocycles, tetrahydrothiophene (THT) and thiophene is considered. Metallation is one of the most fundamental reactions in modern day synthesis and is a key tool in the preparation of functionalised aromatic and heterocyclic compounds. It is usually achieved by the utilization of commercially accessible organolithiums (or lithium amides); however, these reactions do have their drawbacks including the intolerance of certain functional groups, the need for cryoscopic temperatures and the inadvertent reactivity with polar reaction solvents. For example, thiophene is generally lithiated at  $-30^{\circ}\text{C}$  using  $n\text{BuLi}$  in pentane/THF solvent to avoid undesired dilithiation.<sup>[9]</sup> Recent work has shown that these drawbacks can generally be overcome by using alkali metal ate complexes as deprotonative agents.<sup>[10]</sup> With reference to O based analogues of sulfur containing heterocycles, it has recently been shown that the sodium zincate (tmeda)Na( $\mu$ -tmp)( $\mu$ -CH<sub>2</sub>SiMe<sub>3</sub>)Zn(CH<sub>2</sub>SiMe<sub>3</sub>) (where TMEDA is *N,N,N',N'*-tetramethylethylenediamine and TMP is 2,2,6,6-tetramethylpiperidide) can directly metallate (zincate) THF at ambient temperature.<sup>[11]</sup> In addition, a related sodium magnesiate base (tmeda)Na( $\mu$ -tmp)( $\mu$ -CH<sub>2</sub>SiMe<sub>3</sub>)Mg(tmp) **1** undergoes a remarkable reaction with furan to produce a spectacular octadecametalllic complex

$[(\text{tmeda})_6\text{Na}_{12}\text{Mg}_6(\text{CH}_2\text{SiMe}_3)_2(\text{C}_4\text{H}_3\text{O})^{-10}(\text{C}_4\text{H}_4\text{O})^{2-}_6]$  **2** which contains ten  $\alpha$ -monometallated and six congeneric  $\alpha$ ,  $\alpha'$ -dideprotonated furan molecules (Figure 1).<sup>[12]</sup> To emphasise the structural complexity of these magnesiation reactions and their alkyl dependency,<sup>[13]</sup> reaction of the *n*-butyl-containing sodium magnesiate  $(\text{tmeda})\text{Na}(\mu\text{-tmp})(\mu\text{-}^n\text{Bu})\text{Mg}(\text{tmp})$  with furan ultimately produces an inverse crown<sup>[14]</sup> complex  $[\{ \{ (\text{thf})_3\text{Na}_2 \} \{ (\text{tmeda})\text{Mg}_2 \} (\text{C}_4\text{H}_3\text{O})_6 \}_\infty]$  (which possesses solely monometallated furanyl anions) via a disproportionation mechanism.<sup>[15]</sup> Turning to the sulfur heterocycles, monodeprotonation at ambient temperature of thiophene<sup>[16]</sup> is possible using  $(^i\text{Pr}_2\text{N})\text{MgCl}$ ,<sup>[16a]</sup>  $(\text{tmeda})\text{LiMgBu}_3$ <sup>[16b]</sup> or  $[(\text{tmp})\text{MgCl}] \cdot \text{LiCl}$ <sup>[16c]</sup> although these earlier reports do not furnish any structural information (solution or solid state) of the metallated thiophene intermediates. Recently, Mongin has shown that thiophene can be  $\alpha, \alpha'$ -dimetallated using the lithium cadmate  $\text{LiCd}(\text{tmp})_3$ .<sup>[17]</sup> Herein we report the smooth, and regiospecific monometallation of thiophene and THT using the sodium magnesiate **1**,<sup>[12]</sup> and detail their respective solid and solution state behaviours and activities towards interception by selected electrophiles.

<FIGURE 1 HERE>

Base **1** was prepared in accord with a previous report<sup>[12]</sup> and was not isolated prior to reaction with thiophene or THT. In order to probe whether sodium-mediated magnesiation of thiophene followed a similar course to that of furan in producing a supramolecular product akin to **2** or the aforementioned inverse crown product,<sup>[15]</sup> **1** was reacted with an equimolar quantity of thiophene in a hydrocarbon medium. Surprisingly this reaction afforded the *tris*-( $\alpha$ -magnesiated) thiophene product  $(\text{tmeda})\text{Na}(\mu\text{-C}_4\text{H}_3\text{S})_3\text{Mg}(\text{tmeda})$  **3** (Scheme 1). This complex has subsequently been prepared rationally in a good isolated yield by reacting  $^n\text{BuNa}$ ,  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ , TMEDA, and thiophene in a 1:1:2:3 ratio in hexane. The original synthesis is likely to occur via a disproportionation reaction similar to that which has been previously observed.<sup>[15]</sup> The unexpected feature of the molecular structure of **3** (Figure 2) is its three (and not one)  $\alpha$ -deprotonated thiophene molecules that engage Mg in a  $\sigma$ -fashion (mean Mg- $\alpha\text{C}$  bond distance, 2.239 Å) and Na more in a  $\pi$ -fashion (mean distance out of the three ring planes for Mg is 0.236 Å and for Na 2.482 Å). These latter Na- $\alpha\text{C}$  bonds vary significantly from each other: one is short, [Na1-C21, 2.628(2) Å]; one is intermediate [Na1-C13, 2.778(2) Å]; and, one is long [Na1-C17, 2.907(2) Å]. Extremely rare in alkali metal magnesiate chemistry, TMEDA ligands complete the coordination spheres of both sodium and magnesium. The former is common but magnesium is usually TMEDA-free (due to its stronger Lewis acidity and its commandeering of anions) except in one lithium and one sodium alkynyl magnesiate.<sup>[18]</sup> This dual TMEDA chelation is largely sterically driven. Overall both sodium and magnesium display penta-coordinate  $\text{C}_3\text{N}_2$  geometries with a wide range of bond angles subtending the metal [bond angles, 73.43(7)–165.74(7)° for Na; and 75.22(7)–151.34(7)° for Mg]. To the best of our knowledge, there is no precedent for an  $\alpha$ -magnesiated thiophene structure in ate chemistry, and only two examples in homometallic systems  $[\{ (\text{C}_4\text{H}_3\text{S})\text{MgBr}(\text{dme})_2 \}]$ <sup>[19]</sup> and  $\{ \textit{trans}\text{-Mg}(\text{C}_4\text{H}_3\text{S})_2(\text{thf})_4 \}$ <sup>[19]</sup> where DME is 1,2-dimethoxyethane]. The Mg-C distances in these complexes are 2.290(6) and 2.171(7) Å; the respective distance in **3** is midway between these distances despite the lower formal coordination number of Mg in **3**. The structures of **2**<sup>[12]</sup> and the related inverse crown<sup>[15]</sup> are

remarkably different from that of **3** despite the apparently minor change of penta-atomic heterocycle (*i.e.*, furan to thiophene) in the respective syntheses. One factor is likely due to the maximisation of desired electrostatic, hard Na $\cdots$ O interactions in these structures contrasting with the absence of significant Na $\cdots$ S interactions in **3** (note that each thiophene ring is disordered by a 180° rotation about the Mg-C axis, emphasising the lack of directionality imparted by S interactions). A further structural difference is that for **2** the dianion of thiophene is captured in the molecule. For **3**, the hard-soft mismatch between Na and S means that the alkali metal must be satisfied with only Na-C  $\pi$ -contacts and the dative bonding with the TMEDA N atoms resulting in a simpler bimetallic arrangement. Since **3** is highly soluble in arene and donor solvents, a NMR spectroscopic study was conducted to probe its solution chemistry. In C<sub>6</sub>D<sub>6</sub> solution, the data suggest that the solid state structure appears to stay intact in solution, as evidenced by the two distinct sets of TMEDA resonances and the complex set of overlapping thiophenyl resonances. Using HSQC and COSY techniques, three distinct sets of thiophenyl resonances can be assigned. In D<sub>8</sub>-THF solution, only one set of TMEDA (corresponding to uncoordinated diamine) and thiophenyl resonances are observed most likely indicating that THF has displaced the bidentate diamine donor, to form a solvent separated arrangement [*e.g.*, {Na(thf)<sub>x</sub>}<sup>+</sup>{(thf)<sub>y</sub>Mg(C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>}<sup>-</sup>].<sup>[20]</sup>

<SCHEME 1 HERE>

Turning to the fully saturated heterocycle THT, when it is treated with an equimolar quantity of **1** in hexane, new magnesiate (tmeda)Na( $\mu$ -tmp)( $\mu$ -C<sub>4</sub>H<sub>7</sub>S)Mg(tmp) **4** was crystallised in moderate yield (Figure 3).<sup>[21]</sup> Thermodynamically, **1** has reacted as an alkyl base (*i.e.*, one equivalent of SiMe<sub>4</sub> is lost), resulting in the THT molecule being selectively mono-magnesiated at an  $\alpha$ -position. It is essentially isostructural to its THF analogue.<sup>[11]</sup> Interestingly, if the solution used to prepare **4** is allowed to stir at ambient temperature for *circa* three weeks, it appears that the THT ring eventually cleaves and a heterometallic complex which contains a dimetallated butadiene fragment [{(tmeda)Na( $\mu$ -tmp)}<sub>2</sub>{1,4-[Mg(TMP)]<sub>2</sub>-C<sub>4</sub>H<sub>4</sub>}] is captured. This complex has previously been observed when **1** is reacted with THF;<sup>[22]</sup> however, this new cleavage reaction occurs more rapidly (as judged by a competition reaction with THT, see supporting information) thus an ‘intermediate’ akin to **4** cannot be isolated. Returning to **4**, this magnesiation generates a chiral centre at the  $\alpha$ C [C1] that induces disorder in the molecular packing; however, overall the crystals are racemic.

<FIGURE 2 HERE>

Unlike in **3**, appreciable Na-S bonding [bond distance, 2.8718(9) Å] is observed. The Na atom’s distorted tetrahedral coordination sphere is completed by bonding to a bidentate TMEDA molecule and the anionic N of TMP. A salient feature of **4** is that its framework contains a five-atom, five element Na–N–Mg–C–S ring. The Mg centre adopts a distorted trigonal planar environment, bonding to the  $\alpha$ -C of the deprotonated THT, a bridging and a terminal TMP N atom. Complex **4** appears to represent the first example of a magnesiated THT molecule; indeed, metallated molecules which contain metallated THT in general are rare. The only other example known thus far is the osmium carbonyl species [Os<sub>3</sub>(CO)<sub>10</sub>(C<sub>4</sub>H<sub>7</sub>S)(H)].<sup>[23]</sup> This was prepared by treating Os<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub> with THT to

give the di-THT solvate, and then subsequent heating (to 97°C) to induce C-H activation and cleavage. It appears that akin to other sodium magnesiates which adopt a similar bimetallic structural motif,<sup>[10, 24]</sup> the solid state structure of **4** stays intact in C<sub>6</sub>D<sub>6</sub> solution as all seven H atoms which remain on the metallated THT ring are spectroscopically and chemically distinct.

<FIGURE 3 HERE>

Some preliminary reactivity studies of **3** and **4** have been performed with common electrophiles such as iodine and benzoyl chloride. Using standard electrophilic quenching procedures, the reaction of a hexane solution of **3** with an excess of iodine in THF solution gave the desired product 2-iodothiophene in an isolated yield of 86%. This result is in stark contrast to that obtained for the reaction of **2** with iodine which resulted in no iodated furans being isolated, presumably due to the complex retaining high nuclearity in THF solution.<sup>[12]</sup> Attempts to produce substituted THT molecules utilising **4** (and iodine or benzoyl chloride) have thus far afforded only trace quantities of the expected products. The reactivities of **3** and **4** will be explored with a greater range of electrophiles under alternative reaction conditions, and indeed with different types of C-C bond-formations in future work.

In summary we have shown that when common sulfur-containing heterocycles (thiophene and THT) are subjected to sodium-mediated magnesiation, selective mono- $\alpha$ -deprotonation occurs. The structural chemistries of the isolated metallo-compounds are remarkably different from those observed previously with their closely related furan and THF analogues.

## Experimental Section

All reactions and manipulations were carried out in an atmosphere of dry, pure argon gas, using standard Schlenk protocols. Hexane was freshly distilled over Na/benzophenone. NMR samples were prepared under a protective atmosphere inside a glovebox using C<sub>6</sub>D<sub>6</sub> or D<sub>8</sub>-THF as solvent (which was degassed using freeze-pump-thaw cycles, and pre-dried over 4 Å molecular sieve). TMEDA was distilled over CaH<sub>2</sub> and stored over 4 Å molecular sieve. <sup>n</sup>BuLi in the form of a 1.6 M solution in hexane was purchased from Aldrich Chemicals and used as received. *n*-Butylsodium,<sup>[25]</sup> and Mg(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub><sup>[13]</sup> were prepared using literature methods. All NMR spectra were measured on a Bruker DPX500 spectrometer. For the X-ray structural determinations, all data were collected with monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 123 K and were measured on an Oxford Diffraction Xcalibur S instrument. CCDC 772560 (**3**) and 772561 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Synthesis of (tmeda)Na( $\mu$ -C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Mg(tmeda) 3:** <sup>n</sup>BuNa (0.08 g, 1 mmol) was suspended in 20 mL of dry *n*-hexane in a dried Schlenk tube, and placed in an ultrasonic bath for 10 minutes. To this white suspension, Mg(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (0.20 g, 1 mmol), was added along with TMEDA (0.31 mL, 2 mmol) to give a colourless, homogeneous solution. Thiophene (0.24 mL, 3 mmol) was subsequently added and the resultant pale yellow solution was allowed to stir at ambient temperature for 3 h. The yellow solution was filtered and the solvent volume

reduced by a quarter *in vacuo*. The solution was placed in a refrigerator operating at 5°C. After two weeks a crop of colourless plate crystals was deposited (yield, 0.28g, 53%). <sup>1</sup>H NMR (500MHz, C<sub>6</sub>D<sub>6</sub>, 300K): δ 8.02 (br s, 1H, H<sub>α</sub>), 7.94 (br s, 1H, H<sub>α</sub>), 7.88 (br s, 2H, 2×H<sub>γ</sub>), 7.78 (br s, 1H, H<sub>γ</sub>), 7.77 (br s, 1H, H<sub>α</sub>), 7.62 (s br, 1H, H<sub>β</sub>), 7.53 (br s, 1H, H<sub>β</sub>), 7.43 (br s, 1H, H<sub>β</sub>), 2.01 (br s, 12H, CH<sub>3</sub>-TMEDA), 1.88 (br s, 4H, CH<sub>2</sub>-TMEDA), 1.59 (br s, 12H, CH<sub>3</sub>-TMEDA), 1.53 (br s, 4H, CH<sub>2</sub>-TMEDA). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 300K): δ 169.12 (q, C-Mg thiophene), 167.38 (q, C-Mg thiophene), 136.61 (3 × C-H<sub>α</sub>), 130.94 (C-H<sub>γ</sub>), 167.38 (C-H<sub>γ</sub>), 128.54 (C-H<sub>β</sub>), 128.04 (C-H<sub>β</sub>), 127.88 (C-H<sub>β</sub>), 56.63 (CH<sub>2</sub>-TMEDA), 46.48 (CH<sub>3</sub>-TMEDA), 45.09 (CH<sub>3</sub>-TMEDA).

**Synthesis of [(TMEDA)Na(TMP)(α-C<sub>4</sub>H<sub>7</sub>S)Mg(TMP)] 4:** TMPH (0.34 mL, 2 mmol) was added to a suspension of BuNa (0.08 g, 1 mmol) in dry n-hexane (20 mL) and the resultant mixture was stirred at room temperature for 1 h. Mg(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (0.20 g, 1 mmol) and TMEDA (0.15 mL, 1 mmol) were then introduced to give a pale yellow solution. Tetrahydrothiophene, (0.08 mL, 1 mmol) was added and the solution was allowed to stir at room temperature for 1 hour. The pale yellow solution was filtered and placed directly in a refrigerator operating at 5°C. After one week colourless block crystals were obtained (0.18 g, 34%). <sup>1</sup>H NMR (500MHz, d<sub>8</sub>-THF, 300K): δ 2.93 (m, 1H, H<sub>β</sub>-THT), 2.62 (m, 1H, H<sub>α</sub>-THT), 2.49 (m, 1H, H<sub>α</sub>-THT), 2.18 (m, 1H, H<sub>β</sub>-THT) 1.93 (br s, 4H, γ-TMP), 1.77 (s, 13H, CH<sub>3</sub>-TMEDA + H<sub>β</sub>-THT), 1.71 (s, 4H, CH<sub>2</sub>-TMEDA), 1.58 (br s, 24H, CH<sub>3</sub>-TMP), 1.41 (m, 8H, β-TMP), 1.91 (m, 1H, H<sub>β</sub>-THT), 0.93 (dd, 1H, H<sub>α</sub>-THT). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 300K): δ 57.19 (CH<sub>2</sub>-TMEDA), 52.18 (q-TMP), 46.20 (CH<sub>3</sub>-TMEDA), 42.47 (C-H<sub>β</sub>-THT), 42.37 (β-CH<sub>2</sub>-TMP), 35.65 (CH<sub>3</sub>-TMP), 31.90 (C-H<sub>β</sub>-THT), 31.78 (C-H<sub>α</sub> + H<sub>α</sub>-THT), 20.34 (γ-CH<sub>2</sub>-TMP).

**Reaction of 3 with iodine:** To a solution of 3 (0.22g, 0.4 mmol) in hexane (10 mL), I<sub>2</sub> (2 mL of 1M solution in THF) was added and the solution allowed to stir at ambient temperature for 18 h. 5 mL of NH<sub>4</sub>Cl were added along with the addition of saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> until bleaching (6 mL) and 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated from the aqueous layer and dried over magnesium sulphate. The solvent was removed under vacuum to give a yellow oil which was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluent to afford 1-iodothiophene 0.2155 g, 86% yield. <sup>1</sup>H NMR (500MHz, C<sub>6</sub>D<sub>6</sub>, 300K): δ 6.90 (dd, 1H, thiophene), 6.67 (dd, 1H, thiophene), 6.27 (m, 1H, thiophene).

**Crystal data for 3:** C<sub>24</sub>H<sub>41</sub>MgN<sub>4</sub>NaS<sub>3</sub>, *M<sub>r</sub>* = 529.09, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 10.1527(8), *b* = 27.855(2), *c* = 11.1678(8) Å, β = 113.372(9)° *V* = 2899.2(4) Å<sup>3</sup>, *Z* = 4, μ = 0.311 mm<sup>-1</sup>; 19264 reflections, 6494 unique, *R*<sub>int</sub> 0.0757; final refinement to convergence on *F*<sup>2</sup> gave *R* = 0.0451 (*F*, 3146 obs. data only) and *R*<sub>w</sub> = 0.0809 (*F*<sup>2</sup>, all data), GOF = 0.794.

**Crystal data for 4:** C<sub>28</sub>H<sub>59</sub>MgN<sub>4</sub>NaS, *M<sub>r</sub>* = 531.15, triclinic, space group *P*  $\bar{1}$ , *a* = 10.3631(7), *b* = 11.1764(8), *c* = 15.5624(10) Å, α = 102.133(6)° β = 107.474(6)° γ = 98.968(6)°, *V* = 1633.88(19) Å<sup>3</sup>, *Z* = 2, μ = 0.153 mm<sup>-1</sup>; 27027 reflections, 7702 unique, *R*<sub>int</sub> 0.0286; final refinement to convergence on *F*<sup>2</sup> gave *R* = 0.0519 (*F*, 5437 obs. data only) and *R*<sub>w</sub> = 0.1530 (*F*<sup>2</sup>, all data), GOF = 1.083.

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**Keywords:** magnesium • metallation • sodium • tetrahydrothiophene • thiophene

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## FIGURE/SCHEME LEGENDS

Figure 1. Structural representation of **2**.<sup>[12]</sup>

Scheme 1. Synthesis of complexes **3** and **4**

Figure 2. Molecular structure of **3**. Hydrogen atoms and minor disorder components are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Na1-C13, 2.778(2); Na1-C17, 2.907(2); Na1-C21, 2.628(2); Na1-N1, 2.495(2); Na1-N2, 2.473(2); Mg1-C13, 2.263(2); Mg1-C17, 2.217(2); Mg1-C21, 2.236(2); Mg1-N3, 2.4583(19); Mg1-N4, 2.2589(19); N2-Na1-N1, 73.43(7); N2-Na1-C21, 165.03(8); N1-Na1-C21, 103.08(8); N2-Na1-C13, 119.49(8); N1-Na1-C13, 118.15(7); C21-Na1-C13, 75.20(7); N2-Na1-C17, 102.14(7); N1-Na1-C17, 165.74(7); C21-Na1-C17, 77.62(7); C13-Na1-C17, 75.96(7); C17-Mg1-C21, 102.62(9); C17-Mg1-N4, 104.69(8); C21-Mg1-N4, 150.13(8); C17-Mg1-C13, 102.74(9); C21-Mg1-C13, 94.36(9); N4-Mg1-C13, 91.24(8); C17-Mg1-N3, 105.08(7); C21-Mg1-N3, 86.24(8); N4-Mg1-N3, 75.22(7); C13-Mg1-N3, 151.34(7).

Figure 3. Molecular structure of **4**. Disorder in the THT and TMEDA units, and hydrogen atoms except those belonging to the THT ring have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Mg1-N1, 1.9890(16); Mg1-N2, 2.0811(15); Mg1-C1, 2.192(2); Na1-N3, 2.481(3); Na1-N2, 2.4926(16); Na1-N4, 2.5832(18); Na1-C1, 2.826(2); Na1-S1, 2.8718(9); N1-Mg1-N2, 134.47(7); N1-Mg1-C1, 117.78(8); N2-Mg1-C1, 107.61(7); N2-Na1-S1, 96.19(4); N2-Na1-N4, 135.88(6); N2-Na1-N3, 136.16(9); S1-Na1-N4, 107.44(5); S1-Na1-N3, 105.28(7); N4-Na1-N3, 72.73(8).

## TOC TEXT

### Headline: Metallation of Sulfur Heterocycles

*Alkali metal-mediated magnesiation* has been employed to regioselectively metallate the *S*-heterocycles thiophene and tetrahydrothiophene at ambient temperature. The structural chemistry of the metallo-compounds is remarkably different from that previously observed for the corresponding *O*-heterocycles.