

# Cocondensation reactions of nitrogen-containing heterocycles with lithium atoms at 77 K

Oscar Mendoza, Helge Müller-Bunz, Matthias Tacke \*

Chemistry Department, Centre for Synthesis and Chemical Biology (CSCB) Conway Institute of Biomolecular and Biomedical Research  
University College Dublin, Belfield, Dublin 4, Ireland

Received 18 March 2005; accepted 7 April 2005  
Available online 31 May 2005

## Abstract

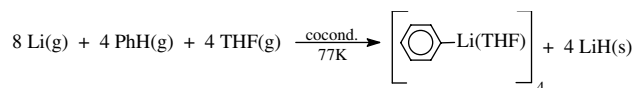
Lithium atoms were cocondensed with aromatic nitrogen-containing heterocycles in the presence of THF at 77 K. The reaction products in the case of the heterocyclic five-membered rings (imidazole) resulted in a C–H bond activation and led to the corresponding aryl lithium compound. Other heterocycles such as pyridine and pyrimidine led to the formation of a non-lithiated aromatic product, in which the parent compound was dimerised with hydrogen being lost. A special case was found, when substituted pyridines carrying methyl and methoxy groups were reacted under these cocondensation conditions. Here a dimeric species is found again, but the product is dilithiated at the two nitrogen atoms and two hexadienes rings were found instead of an aromatic system. DFT calculations at the B3LYP/6-31G\*\* level of theory were carried out in order to interpret the pathways of the cocondensation reactions and identify the possible intermediates involved. In all reactions  $\sigma$ -complexes between lithium molecules and the heterocycles were found as stable intermediates.

© 2005 Elsevier B.V. All rights reserved.

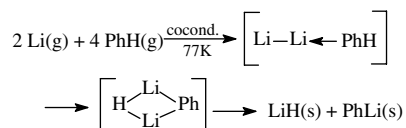
**Keywords:** Lithium atoms; Metal vapour synthesis; CH activation; DFT calculations; Birch reduction

## 1. Introduction

The activation of carbon–hydrogen bonds has been a major topic of research for the last thirty years [1–3]. Earlier reports involving lithium atoms [4–6] showed that they are able to activate aromatic hydrocarbons in the presence of THF selectively under cocondensation conditions at 77 K. This resulted in the direct synthesis of aryl lithium compounds on a synthetic scale.



One of the key intermediates in this reaction is a  $\text{Li}_2$ –benzene  $\pi$ -complex. This complex is capable of undergoing a two-electron transfer from the  $\text{Li}_2$  to the LUMO of the aromatic ring, resulting in the activation of the aromatic C–H bond.



The work has been expanded to +I substituted ( $\text{CMe}_3$ ,  $\text{SiMe}_3$ , *o*- and *m*-xylene) and donor substituted (OMe,  $\text{NMe}_2$ , SMe) benzene derivatives [7] as well as five-membered heterocycles [8]. In the case of anisole a selective C–H bond activation was found to occur in the absence of THF as well; its reaction mechanism

\* Corresponding author. Tel.: +35 317 168 428; fax: +35 317 162 127.  
E-mail address: [matthias.tacke@ucd.ie](mailto:matthias.tacke@ucd.ie) (M. Tacke).

was calculated in detail in a recent DFT study [9]. The aim of this paper is to show the synthetic variety of reactions of lithium atoms and nitrogen-containing heterocycles as well as to demonstrate understanding of their reaction mechanisms.

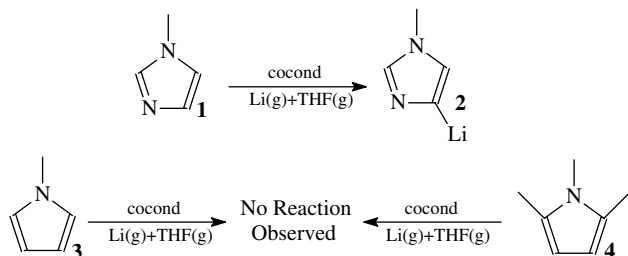
## 2. Results

### 2.1. Experimental studies

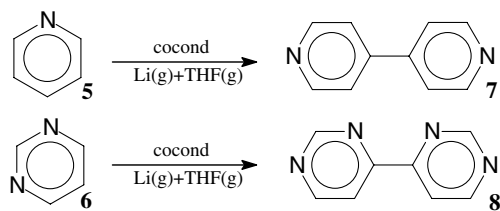
Previous reports showed the reaction of methyl pyrrole (**3**) and 1,2,4-trimethyl pyrrole (**4**) with lithium [8] and in both cases the reaction failed. However, a mono-lithiated product was found for the cocondensation of 1-methyl imidazole (**1**) where the heterocyclic ring showed a C–H activation in the *ortho* position with respect to the methylated nitrogen (Scheme 1). The lithiated compound was identified as the TMS substituted derivative [10].

The reaction of pyridine (**5**) and pyrimidine (**6**) with lithium atoms was carried out as well. The product obtained showed a non-lithiated compound and was identified as dimerised reactant compound. The pyridine reaction product was a white coloured non-lithiated product collected in 63% yield and identified as 4,4'-bipyridine (**7**) [11]. The reaction of pyrimidine gave a dark orange coloured non-lithiated product collected in 32% yield and identified as 4,4'-bipyrimidine (**8**) [12] (Scheme 2).

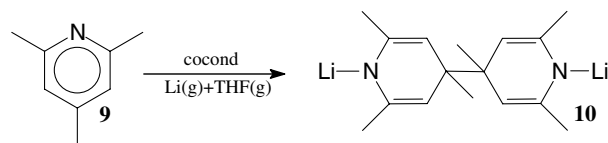
When 2,4,6-collidine (**9**) was cocondensed with lithium atoms, the reaction led to a different and lithium-



Scheme 1. Cocondensation reaction of lithium atoms with heterocycles at 77 K.



Scheme 2. Cocondensation reaction of lithium atoms with pyridine or pyrimidine at 77 K.



Scheme 3. Cocondensation reaction of lithium atoms with 2,4,6-collidine at 77 K.

containing compound **10**, while no C–H activation was found. The lithium is bonded towards the nitrogen and the ring appears dimerised at the *para* position. Also, the aromaticity has disappeared and a hexadiene is found instead (see Scheme 3).

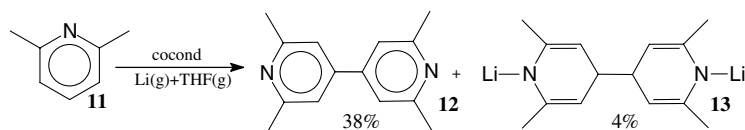
The cocondensation reaction of lithium and 2,6-lutidine (**11**) is a special case since it is leading to two products. The main one (38% yield) was characterised as 4,4'-bilutidine (**14**) [13], therefore lithium atoms do not appear bonded (Scheme 4). The second product (**13**) was obtained in lower yield (4%) and was identified as a lithium-containing compound. The lithium is found bonded through the nitrogen and two rings are connected in the *para* position, which leads to a dimeric hexadiene.

The reaction of 2,4,6-collidine (**9**) with lithium atoms led to the lithiated product **10** that was stored in a Schlenk tube at  $-20\text{ }^{\circ}\text{C}$ . A single crystal of dimerised product suitable for X-ray diffraction experiments was grown. The crystal was exposed to the air and the lithiated compound **10** was hydrolysed (**10b**). The molecular structure determined by X-ray shows two main planes formed by two rings that are connected by a C–C bond (Fig. 1).

The rings are clearly non-aromatic and two C–C double bonds of 132.7 pm are found in the 2 and 5 positions. The other two C–C distances in the 3 and 4 positions are single bonds appearing at 151.3 and 154.7 pm. The remaining two C–N single bonds are found at 136.9 and 138.6 pm. The N–H bond of 71.0 pm is bent out of the ring plane caused by the lone pair situated at the nitrogen atom. A C–C single bond of 154.6 pm connects the two monomers (C3–C3'). A centre of symmetry is situated in the middle of this bond and the second hexadiene can be generated by equivalent atoms using the symmetry operation  $1 -x + 1, -y + 1, -z$ .

The most important distances of the crystal and calculated DFT structure are presented in Table 1. Both data sets show considerable variations in bond length and angles, since the crystal was not of highest quality. Differences are always smaller than 8 pm, except for the N–H bond where a 30 pm longer distance is found in the DFT calculated structure, which gives a more reliable value.

Lithium atoms are able to activate aromatic hydrocarbons selectively under these cocondensation conditions. When a methoxy group is added to the aromatic hydrocarbons, this activation was always found in an



Scheme 4. Cocondensation reaction of lithium atoms with 2,6-lutidine at 77 K.

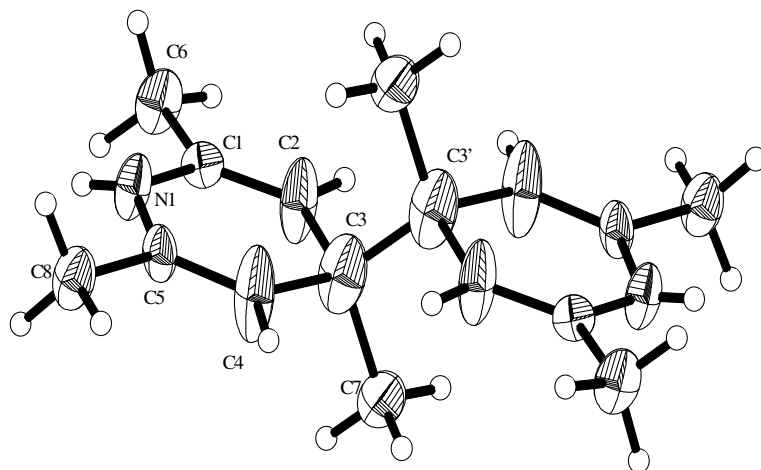
Fig. 1. Molecular structure of **10b** showing the thermal ellipsoids drawn on the 50% probability level. CCDC 258100.

Table 1

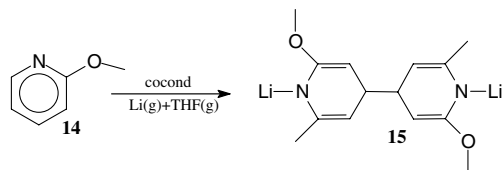
Selected bond distances for **10b** from the crystal and the DFT calculated structure

	Crystal structure	DFT calculation
<i>Bond length (pm)</i>		
N(1)–H(1)	71.0	101.0
N(1)–C(1)	136.9	140.2
N(1)–C(5)	138.6	140.2
C(1)–C(2)	132.7	134.4
C(2)–C(3)	151.3	151.9
C(3)–C(4)	154.7	151.9
C(4)–C(5)	132.8	134.4
C(1)–C(6)	151.0	150.3
C(3)–C(7)	160.4	154.7
C(5)–C(8)	149.5	150.3
C(3)–C(3')	154.6	162.0
<i>Bond angles</i>		
C(3')–C(3)–C(7)	108.4	109.0
C(2)–C(1)–C(6)	124.6	124.3

*ortho* position with respect to the methoxy group [7,8]. Thus methoxy groups can be considered as a useful tool to activate the *ortho* position on hydrocarbon aromatic rings.

The cocondensation reaction of 2-methoxy pyridine (**14**) was carried out and the product was identified as a dimerised hexadiene (**15**). As before, the two lithium atoms were found to be bonded to the nitrogen atoms, while a C–H activation was not observed (Scheme 5).

In order to facilitate an overview all cocondensation reactions are summarised in Scheme 6.



Scheme 5. Cocondensation reaction of lithium atoms with 2-methoxy pyridine at 77 K.

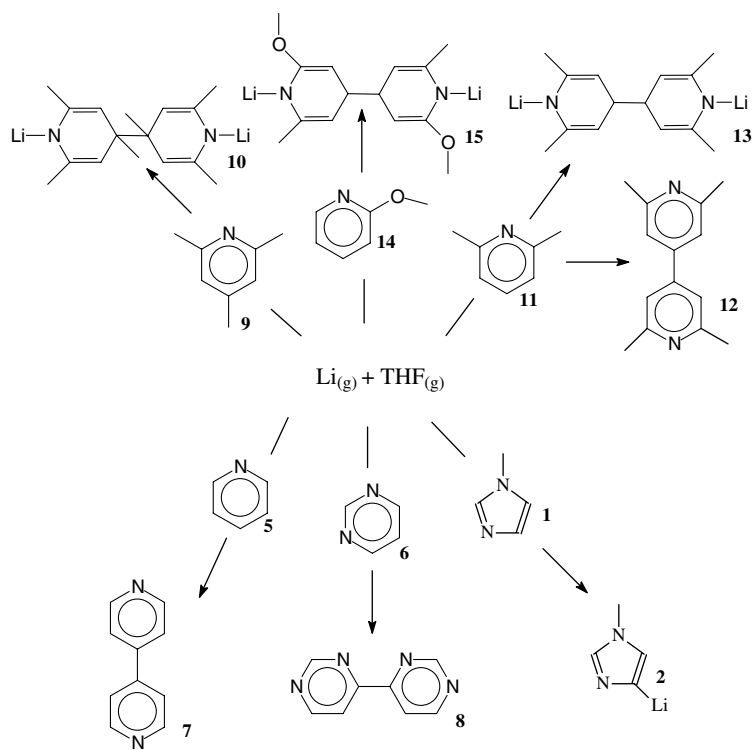
## 2.2. Theoretical studies

The aim of this work was to calculate plausible intermediate species for all cocondensation reactions observed, and thereby identifying the reaction mechanism. Calculations were performed using GAUSSIAN 98 [14] and the B3LYP DFT functional with the 6-31G\*\* basis set.

### 2.2.1. C–H activation of 1-methyl imidazole

The C–H activation of heterocyclic compounds involves at least two steps. After the formation of a Li–Li bond from two lithium atoms, this species is coordinated with the aromatic compound. The second step involves the insertion of the Li<sub>2</sub> molecule into the C–H bond by a double electron transfer via the aromatic system [8].

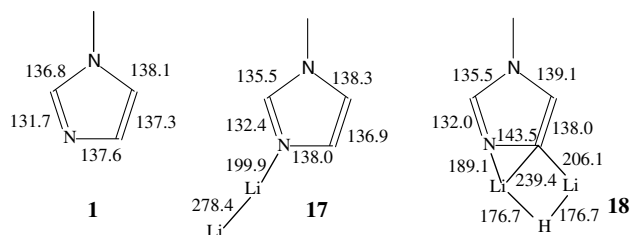
Previous reports [4–6] showed two different possibilities for the coordination of the dilithium molecule. The first possibility is the coordination of the Li<sub>2</sub> to the aromatic ring to form a π-complex, and the second



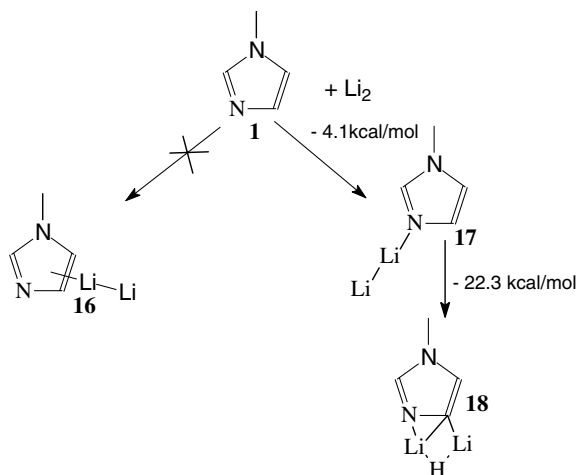
Scheme 6. Summary of the reactions of lithium atoms with nitrogen-containing heterocycles in the presence of THF at 77 K.

possibility is  $\eta^1$ -coordination of the  $\text{Li}_2$  molecule to the heteroatom in the ring. However when 1-methyl imidazole intermediates are optimised, a stable  $\pi$ -coordination (**16**) is not found (Scheme 7).

In the  $\eta^1$ -complex **17** the Li–Li bond appears slightly elongated. While free  $\text{Li}_2$  shows a Li–Li distance of 272.3 pm, this distance is found at 278.4 pm in the intermediate **17** (Scheme 8).



Scheme 8. Bond distances in pm for intermediates involving 1-methyl imidazole.

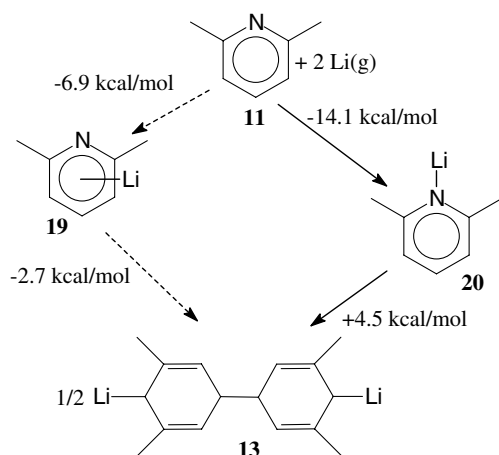


Scheme 7. Calculated reaction mechanism for the cocondensation of lithium atoms with 1-methyl imidazole.

The formation of the second intermediate **18** changes the structure of the ring. The distance between the activated carbon and the nitrogen is elongated by 5.5 pm due to the formation of a three-membered ring involving lithium. There is a clear interaction between the nitrogen and one lithium in this second intermediate, which can be seen from the short bond distance of 189.1 pm.

### 2.2.2. Dimerisation of 2,4,6-collidine, 2,6-lutidine and 2-methoxy pyridine

Methyl or methoxy substituted pyridines lead to a dimeric non-aromatic product upon cocondensation. In order to explain the pathway reaction, the formation of a radical intermediate is required. The dimeric product is explained as a bonding step from two neutral radical intermediates. In contrast to previous cases of C–H



Scheme 9. Calculated reaction mechanism for the cocondensation of lithium atoms with 2,6-lutidine.

activation reactions, the formation of a dilithium species is not required and lithium atoms are bonded towards the aromatic ring.

As previously seen, lithium can show two different coordination modes leading to the formation of a  $\pi$ -complex or a  $\eta^1$ -coordination of lithium with the nitrogen (Scheme 9).

When 2,6-lutidine (**11**) is used the preferred pathway is via the  $\eta^1$ -complex (**20**). An energy difference of 7.2 kcal/mol was found between complex **19** and **20**, showing that the  $\eta^1$ -complex is significantly more stable than the  $\pi$ -complex (**19**) (Scheme 9). The strong interaction between the lithium atom and the lone pair on the nitrogen atom results in a short Li–N distance of 200.7 pm (Table 2); therefore the preferred pathway is by  $\eta^1$ -coordination.

As previously discussed, the next step involves the formation of a radical and its dimerisation is leading to a lithiated dimeric hexadiene **13**.

It is important to note here that the coordination sphere of the lithium is omitted for simplification in the calculations. The THF solvent was not considered in these calculated species and therefore reaction enthalpies are affected. The formation of the dimer product via an  $\eta^1$ -complex shows an endothermic last step; it can be assumed that this is an approximation error.

Table 2  
Selected bond lengths for  $\eta^1$ -intermediates and products

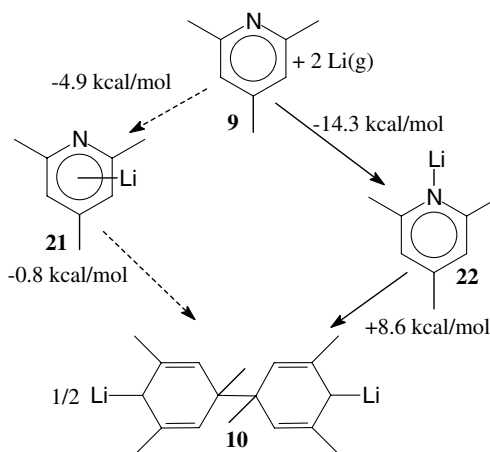
	2,6-Lutidine		2,4,6-Collidine		2-Methoxy pyridine	
	<b>20</b>	<b>13</b>	<b>22</b>	<b>10</b>	<b>24</b>	<b>15</b>
N–Li (pm)	200.7	180.4	201.6	180.5	200.2	183.1
O–Li (pm)					206.5	190.0

The calculated bond length in free  $\text{Li}_2$  is 272.3 pm.

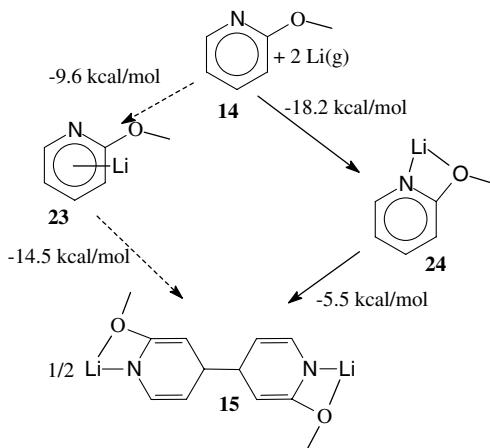
A similar reaction pathway was optimised with a methyl group placed in the *para* position of the aromatic ring. Also for 2,4,6-collidine a  $\eta^1$ -complex **22** is the preferred pathway and the  $\pi$ -complex **21** shows a higher energy of 9.4 kcal/mol.

As Scheme 10 shows, the first stable intermediate **22** shows a similar structure than before. The nitrogen has a strong interaction with the lithium (201.6 pm) stabilizing structure (Table 2). The following step appears as a high energetic barrier (17.1 kcal/mol), which is explained by the omitted coordination sphere.

When the 2-methoxy pyridine pathway is optimised, a similar situation is found. However, the lithium can be coordinated by the oxygen (Scheme 11) and this bond stabilizes the structure and leads a low-energy  $\eta^1$ -intermediate in a highly exothermic process of  $-18.2$  kcal/mol. The dimeric product **15** is also stabilised by this



Scheme 10. Calculated reaction mechanism for the cocondensation of lithium atoms with 2,4,6-collidine.



Scheme 11. Calculated reaction mechanism for the cocondensation of lithium atoms with 2-methoxy pyridine.

O–Li interaction, which is formed in an exothermic step (Table 2).

### 3. Discussion

Previous research in this area showed that aromatic heterocycles react with lithium atoms in the presence of THF under cocondensation conditions [8]. The isolated products were identified as lithiated aromatic compounds. However when the heteroatom in the ring was nitrogen as seen in pyrroles the reactions failed so far. Therefore, this study examines the effect of a second nitrogen atom introduced into the aromatic rings – as in 1-methyl imidazole – towards their C–H activation reaction.

The electron deficient  $\text{Li}_2$  molecule accepts electron density from the aromatic system to form an  $\eta^1$ -complex. Contrary to previously studied reactions, the formation of a stable  $\pi$ -complex intermediate is not found for 1-methyl imidazole.

The next mechanistic step leads to the C–H activation. This involves the double electron transfer from the  $\eta$ -complex bonded  $\text{Li}_2$  to the LUMO of the aromatic ring. If the LUMO energy is too high, as it was for pyrroles (Table 3), it is impossible to place electron density into it, thereby preventing the CH activation reaction from occurring. However, the introduction of second nitrogen into the aromatic pyrrole decreases the calculated LUMO energy.

If the LUMO energy is low enough, as in imidazole or oxygen heterocycles (as shown in Table 3) the reaction proceeds to give an aryl lithium compound and lith-

ium hydride. Table 3 shows calculated LUMO energies of selected heterocycles and pyridine derivatives at the B3LYP/6-31G\*\* level of theory.

When the reaction of substituted pyridines is carried out, the expected C–H activation does not take place. In this case the aromatic ring is reduced and the aromaticity disappears with the formation two double bonds. The reaction of 2,6-lutidine with lithium atoms leads to main product identified as 4,4'-dilutidine. However, the formation of a non-aromatic dimer is a by-product.

The reduction of aromatic rings is leading to hexadienes and was previously reported by Birch [15]. However, in contrast to the *Birch reduction* the cocondensation reactions lead to a dimeric hexadiene and lithium nitrogen bonds. Scheme 12 shows a comparison between a *Birch reduction* and a cocondensation reaction involving 2,4,6-collidine.

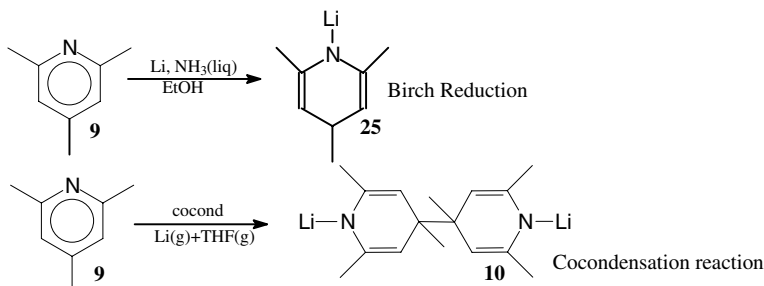
The formation of these reduced dimers is explained by the formation of a calculated intermediate where a lithium atom is  $\eta^1$ -coordinated with respect to the nitrogen. The formation of this intermediate is found to be exothermic in all cases studied. However the last step, in which the dimer is formed via a C–C bond, the reaction energy appears to be endothermic in some cases.

The positive reaction enthalpy can be assumed to be incorrect, since the solvent sphere was omitted. The coordination of the lithium with the THF solvent would stabilise the molecule leading to structures of lower energy. This coordination effect can be seen in the calculated structure of 15. In this dimeric product the two lithium atoms are coordinated to the oxygen of the intramolecular base and an exothermic step is observed in this case.

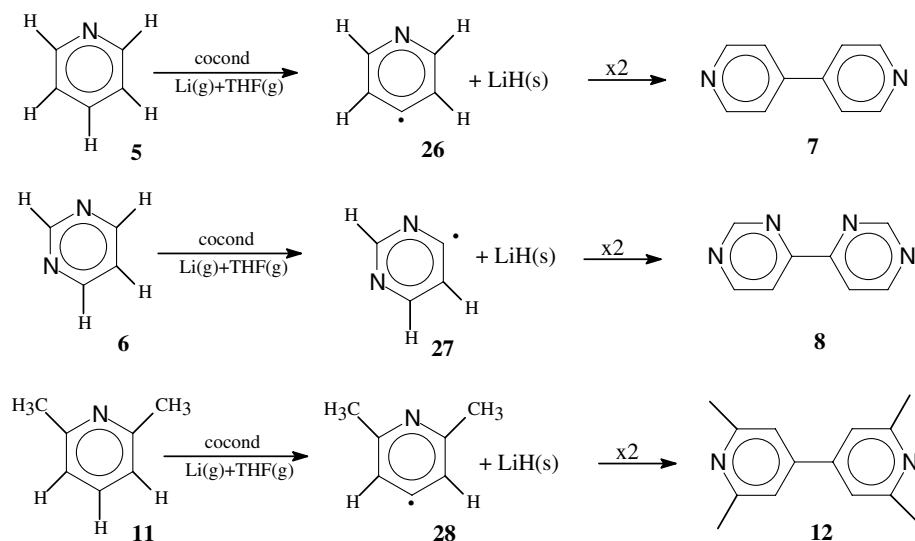
The cocondensation reaction of pyridine, pyrimidine and 2,6-lutidine with lithium atoms leads to dimeric compounds as reported previously. However, the lithium does not appear in the product and the dimer retains its aromaticity. It seems that the reaction proceeds through a radical intermediate (26–28) where the aromatic ring has been dehydrogenated and solid lithium hydride is formed as well (Scheme 13).

Table 3  
Calculated LUMO energies of selected heterocycles (B3LYP/6-31G\*\*)

	LUMO (eV)	Reaction
1-Methyl pyrrole	1.44	No reaction
1,2,5-Trimethyl pyrrole	1.27	No reaction
2-Methoxy furan	0.94	C–H activation
1-Methyl imidazole	0.84	C–H activation
Furan	0.51	C–H activation



Scheme 12. Cocondensation reaction vs. *Birch reduction* of 2,4,6-collidine.



Scheme 13. Proposed mechanism for the cocondensation of lithium atoms with pyridine, pyrimidine and 2,6-lutidine.

#### 4. Conclusions

When aromatic five-membered heterocycles or benzene derivatives are cocondensed with lithium atoms in the presence of THF, an aryl lithium species is formed via a C–H activation reaction. The LUMO energy is interpreted as the main barrier of the reaction. As described for 1-methyl imidazole, the introduction of a new heteroatom in the aromatic ring can decrease the LUMO energy. In this case, the extra nitrogen atom in the ring of imidazole makes the activation reaction possible that it does not occur in pyrroles.

When nitrogen-containing six-membered heterocycles are cocondensed with lithium atoms in the presence of THF, the reaction changes towards the formation of a dimeric product and a lithium carbon bond is not formed.

In the case of pyridine and pyrimidine, the reactions lead to aromatic dimers via the formation of a C–C bond and lithium hydride is found as a by-product.

2,4,6-collidine and 2-methoxy pyridine show the formation of a different species. The dimer identified as product is characterised by the loss of aromaticity, the formation of a C–C bond without losing hydrogen atoms and the formation of two N–Li bonds. In these reactions, the calculated structures show the formation of at least one intermediate where lithium is  $\eta$ -bonded with nitrogen, which stabilises the structure.

The reaction of 2,4-lutidine is a special case: In this cocondensation reaction two products were obtained. The dimerisation of the reactant compound was observed as a main product, but the formation of a non-aromatic lithiated by-product was obtained as well.

#### 5. Experimental

##### 5.1. General

All experimental procedures were performed using standard Schlenk techniques under an atmosphere of dry argon. THF was dried and distilled from sodium benzophenone ketyl under an atmosphere of argon. 1-methyl imidazole, pyridine, 2,4,6-collidine, 2,6-lutidine, 2-methoxy pyridine and pyrimidine were dried and distilled from calcium hydride under an atmosphere of argon. All solvents were then degassed by three freeze–pump–thaw cycles. Celite was stored in an oven at 120 °C overnight and was dried under vacuum for three hours before use. For each filtration a plug of approximately 6 cm of celite was used and each filtration was performed under the vigorous exclusion of air and moisture.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained using either a Varian 300 MHz or a Varian 500 MHz NMR machine. All chemical shifts are reported in ppm and are referenced to TMS. All GC–MS samples were run as liquid samples in ethylacetate using a Finnigan Trace GC–MS, equipped with a RTX-5MS 15 m column.

##### 5.2. A typical cocondensation experiment

Lithium metal (0.53 g, 0.076 mol) was vapourised from an alumina crucible protected by a stainless-steel inlet at around 800 °C over 60 min and cocondensed with a mixture of 5 ml of the aromatic compound and 90 ml of THF. The solution was filtered through a plug of celite in order to remove the solid lithium hydride by-product and unreacted lithium metal. After removal of the solvent mixture in vacuo, a solid was isolated and washed with 20 ml of THF. The lithiated



aromatic compound was identified by derivatisation with  $\text{Me}_3\text{SiCl}$ .

### 5.3. A typical derivatisation of the lithiated aromatic with $\text{Me}_3\text{SiCl}$

To a room temperature solution of around 0.25 g of the lithiated aromatic compound in 20 ml of THF,  $\text{Me}_3\text{SiCl}$  in THF solution was added dropwise with vigorous stirring. The reaction was judged finished when a colour-change from dark red-yellow to pale yellow occurred. To this solution, 10 ml of water was added and the organic phase separated. The aqueous phase was washed three times with 10 ml of dichloromethane. The combined organic extracts were dried over  $\text{MgSO}_4$  and then the solvent was removed under reduced pressure, affording the derivative. GC-MS as well as  $^1\text{H}$  and  $^{13}\text{C}$  NMR were used to identify the product.

### 5.4. Theoretical methods used in this study

DFT calculations were performed using B3LYP and the 6-31G\*\* basis set for C, H, O, N, and Li. For this purpose the program GAUSSIAN 98 [14] was used on a Dell workstation running Red Hat Linux. Harmonic vibrational frequencies, calculated at the same level, characterised stationary points and gave the zero-point energy. The difference in the sum of the electronic and the zero-point energies were interpreted as reaction enthalpies at 0 K. LUMO energies for each aromatic compound were obtained from geometry optimised structures using B3LYP/6-31G\*\*.

### 5.5. X-ray diffraction

X-ray diffraction data were collected on a BRUKER Smart Apex diffractometer at 100 K for the hydrolysed product. A semi-empirical absorption correction on the raw data was performed using the program SADABS [16]. The crystal structure was then solved by direct methods (SHELXS-NT 97) [17] and refined by full matrix least-squares methods against  $F^2$ . Details about the data collection are listed in Table 4 as well as reliability factors. Further details are available free of charge from the Cambridge structural database under the CCDC number 258100 (**10b**).

### 5.6. 2,4,6,2',4',6'-Hexamethyl-1,1'-ditrimethylsilyl-1,4,1',4'-Tetrahydro-[4,4']-bipyridinyl

The general procedure applied to 2,4,6-collidine (**9**) gave 1,1'-dilithio-2,4,6,2',4',6'-hexamethyl-1,4,1',4'-tetrahydro-[4,4']-bipyridinyl (**10**) (red colour) in 35% yield, which was identified as its TMS derivative:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 0.09$  ppm (s),  $\delta = 1.58$  ppm (s),  $\delta = 1.96$

Table 4  
Crystal data and structure refinement of **10b**

Empirical formula	$\text{C}_{32}\text{H}_{46}\text{N}_4$
Molecular formula	$\text{C}_{16}\text{H}_{24}\text{N}_2 \cdot 2\text{C}_8\text{H}_{11}\text{N}$
Formula weight	243.36
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$ (#14)
Unit cell dimensions	
<i>a</i> (Å)	9.0283(16)
<i>b</i> (Å)	7.9751(15)
<i>c</i> (Å)	21.890(4)
$\alpha$ (°)	90
$\beta$ (°)	94.140(5)
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	1572.0(5)
<i>Z</i>	2
Density (calculated) (Mg/m <sup>3</sup> )	1.028
Absorption coefficient (mm <sup>-1</sup> )	0.060
<i>F</i> (000)	532
Crystal size (mm <sup>3</sup> )	0.20 × 0.20 × 0.02
$\Theta$ range for data collection (°)	1.87–20.00
Index ranges	$-8 \leq h \leq 8$ , $-7 \leq k \leq 7$ , $-17 \leq l \leq 21$
Reflections collected	4118
Independent reflections [ <i>R</i> (int)]	1386 [0.0737]
Completeness to theta = 20.00° (%)	94.2
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9988 and 0.9880
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	1386/42/173
Goodness-of-fit on $F^2$	1.063
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.1054$ , $wR_2 = 0.2697$
<i>R</i> indices (all data)	$R_1 = 0.1608$ , $wR_2 = 0.3119$
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.645 and $-0.374$

ppm (s),  $\delta = 4.54$  ppm (s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 0.9$ , 22, 24, 44, 115, 146 ppm.

### 5.7. 2,6,2',6'-Tetramethyl-1,1'-ditrimethylsilyl-1,4,1',4'-tetrahydro-[4,4']-bipyridinyl

The general procedure applied to 2,6-lutidine (**11**) gave 1,1'-dilithio-2,6,2',6'-tetramethyl-1,4,1',4'-tetrahydro-[4,4']-bipyridinyl (**13**) (red colour) in 4% yield, which was identified as its TMS derivative:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 0.09$  ppm (s),  $\delta = 2.55$  ppm (s),  $\delta = 3.28$  ppm (t,  $J = 6$  Hz),  $\delta = 4.35$  ppm (d,  $J = 6$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) due to the low yield of this reaction, the compound could not be identified using  $^{13}\text{C}$  NMR spectroscopy.

### 5.8. 2,2'-Dimethoxy-1,1'-ditrimethylsilyl-1,4,1',4'-tetrahydro-[4,4']-bipyridinyl

The general procedure applied to 2-methoxy pyridine (**14**) gave 1,1'-dilithio-2,2'-dimethoxy-1,4,1',4'-tetrahydro-[4,4']-bipyridinyl (**15**) (dark yellow colour) in 8% yield, which was identified as its TMS derivative: ( $\text{CDCl}_3$   $^1\text{H}$  NMR)  $\delta = 0.08$  ppm (s),  $\delta = 3.47$  ppm (m),



$\delta = 3.64$  ppm (s),  $\delta = 3.87$  ppm (d,  $J = 3$  Hz),  $\delta = 4.78$  ppm (m),  $\delta = 5.15$  ppm (d,  $J = 4$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): due to the low yield of this reaction and the low concentration of the analysed compound, not all carbons could be found in the  $^{13}\text{C}$  NMR spectra,  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 0.9, 28.7, 52.7, 66.9, 119.7$ .

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at [doi:10.1016/j.jorganchem.2005.04.017](https://doi.org/10.1016/j.jorganchem.2005.04.017).

### References

- [1] A.E. Shilov, G.B. Shul'pin, *Chem. Rev.* 97 (8) (1997) 2905.
- [2] B.A. Arndtsen, R.G. Bergmann, T.A. Mobley, T.H. Petersen, *Acc. Chem. Res.* 28 (1995) 154.
- [3] R.H. Crabtree, *Chem. Rev.* 95 (1995) 987.
- [4] M. Tacke, *Chem. Ber.* 128 (1995) 91.
- [5] M. Tacke, *Chem. Ber.* 129 (1996) 1369.
- [6] M. Tacke, *Eur. J. Inorg. Chem.* (1998) 537.
- [7] J.P. Dunne, M. Bockmeyer, M. Tacke, *Eur. J. Inorg. Chem.* (2003) 458.
- [8] M. Tacke, O. Mendoza, F.-J.K. Rehmann, L.P. Cuffe, *Eur. J. Inorg. Chem.* (2004) 4525.
- [9] M. Tacke, O. Mendoza, F.-J.K. Rehmann, L.P. Cuffe, *J. Organomet. Chem.* (2005) 1511.
- [10] F. Effenberger, M. Roos, R. Ahmad, A. Krebs, *Chem. Ber.* 124 (1991) 1639.
- [11] M. Kuroboshi, Y. Waki, H. Tanaka, *J. Org. Chem.* (2003) 3938.
- [12] N. Ple, A. Turck, K. Couture, G. Queguiner, *J. Org. Chem.* (1995) 3781.
- [13] S. Hünig, I. Wehner, *Synthesis* (1989) 552.
- [14] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, *GAUSSIAN 98*, Revision A.7, Gaussian Inc., Pittsburgh, PA, 1998.
- [15] A.J. Birch, *Pure Appl. Chem.* (1996) 553.
- [16] G.M. Sheldrick, *SADABS*. Version 2.03, University of Göttingen, Germany, 2002.
- [17] G.M. Sheldrick, *Sc Shelxs 97* and *SHELXL 97*, University of Göttingen, Germany, 1997.