Cocondensation Reactions of Five-Membered Heterocycles with Lithium Atoms at 77 K

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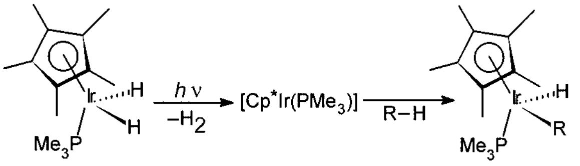
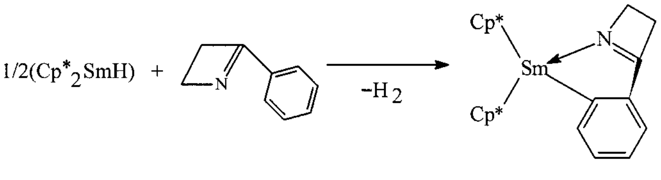
Lithium atoms were cocondensed with eight aromatic five-membered heterocycles in the presence of THF at 77 K. In the case of the oxygen- and sulfur-containing heterocycles (furans and thiophenes), the reaction resulted in C–H bond activation and led to the corresponding aryllithium compound. The other heterocycles (pyrroles) failed to react with lithium atoms in the presence of THF. A special case was found when oxazole was reacted under these cocondensation conditions; here a dilithiated product was obtained. DFT (B3LYP/6-31G**) calculations were carried out in order to interpret the pathways of the reactions and the possible intermediates. For all the reactions π- and σ-complexes between lithium clusters and the heterocycles were found as stable intermediates.

Introduction

The activation of carbon−hydrogen bonds has been a major topic of research for the last thirty years.[1,2,3] Numerous methods have been developed to perform these reactions. Most of these have centred on the oxidative addition of the hydrocarbon moiety to a highly sub-coordinated metal complex as shown below.[4,5]



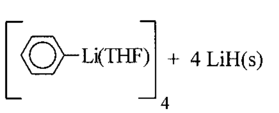
However, C−H bond activation is not limited just to transition metal chemistry. Another commonly used method is σ-bond metathesis using extremely electrophilic lanthanide centres as outlined below.[6]



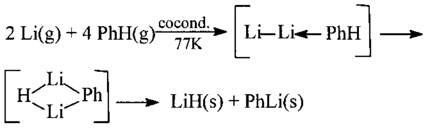
To date there has been very little preparative-scale work using metal atoms to perform oxidative addition reactions. Many metals are known to activate methane in a matrix under photochemical conditions.[3,7] However, these types of reactions are of no use in preparative-scale metal vapour synthesis (MVS). For example, iron atoms react with methane to form CH_3FeH at 10 K when photolysed in an argon matrix.[8]

$$\mathrm{Fe} + \mathrm{CH_4} \xrightarrow[\mathrm{Ar,\ 10K}]{h\nu} \mathrm{HFeCH_3}$$

Work performed by this group in the nineties showed that lithium atoms could selectively activate the C−H bond of benzene and toluene in the presence of THF without photochemical excitation.[9,10,11] This result led to the direct preparation of aryllithium compounds on a synthetic scale.



One of the key intermediates in this reaction is a Li_2-benzene π-complex. This complex is capable of undergoing two single-electron transfers from the Li_2 cluster to the LUMO of the aromatic ring, resulting in the activation of the aromatic C−H bond.



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The work has been expanded to +I-substituted (CMe_3, $SiMe_3$, *o*- and *m*-xylene) and donor-substituted (OMe, NMe_2, SMe) benzene derivatives recently.[12]

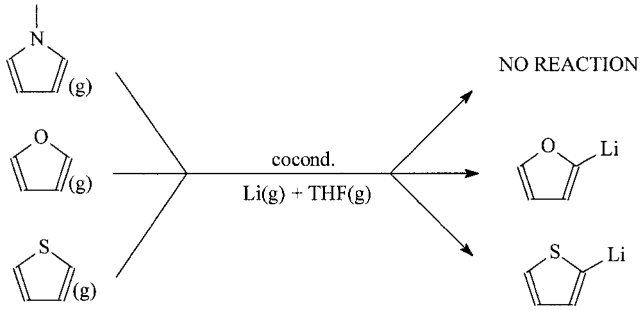
The aim of this paper was to perform cocondensation reactions with furans, thiophenes, pyrroles and oxazole in order to find similarities to and differences from benzene derivatives.

Results

1. Experimental Studies

A variety of five-membered heterocyclic compounds were cocondensed with lithium atoms at 77 K in the presence of THF.

When methylpyrrole, furan and thiophene were cocondensed, a reaction was observed in the case of furan and thiophene only. The products of these reactions were monolithiated compounds[13,14] in which the heterocyclic ring showed a C−H activation in the *ortho* position as shown in Scheme 1. In the case of furan and thiophene, the yields were 35% (2.15 g) and 55% (3.55 g) respectively.

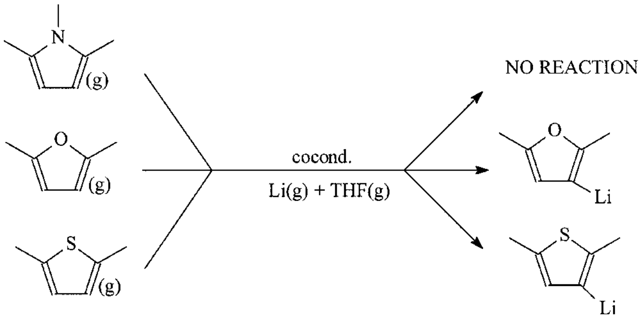


Scheme 1. Cocondensation reaction of lithium atoms with heterocycles at 77 K

A derivatisation reaction with Me_3SiCl was carried out, yielding products stable in air in order to identify the position of the lithium in the aromatic ring. The TMS-substituted compound was identified from NMR spectroscopic data and GC-MS data.[15,16]

A similar reaction series was carried out with the *ortho* position blocked. Methyl groups were placed in the *ortho* positions of the aromatic rings, and cocondensation experiments were carried out.

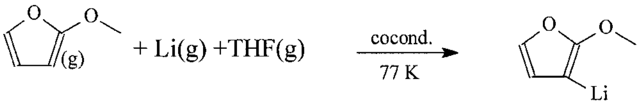
1,2,5-Trimethylpyrrole, 2,5-dimethylfuran and 2,5-dimethylthiophene were condensed with lithium at 77 K, and lithiated products were obtained in the case of 2,5-dimethylfuran and 2,5-dimethylthiophene.[17] As shown in Scheme 2, in this case C−H activation was observed in the *meta* position with respect to the heteroatom. Again, no reaction was observed for the pyrrole compound. The lithiated compound was identified from the TMS-substituted derivative.[18]



Scheme 2. Cocondensation reaction of lithium atoms with *ortho*-dimethyl heterocycles at 77 K

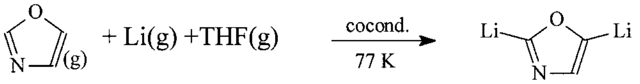
Earlier reports showed that lithium atoms were able to activate aromatic hydrocarbons selectively under these cocondensation conditions.[9,10,11] When a methoxy group was added to the aromatic hydrocarbons, activation was always found in an *ortho* position with respect to the methoxy group.[12] Thus methoxy groups can be considered as useful tools to activate the *ortho* position on hydrocarbon aromatic rings.

When a methoxy group was placed on a heterocycle, the same behaviour was observed. 2-Methoxyfuran was used for this reaction and a C−H activation was observed in an *ortho* position with respect to the methoxy group instead of the heteroatom.



Scheme 3. Cocondensation reaction of lithium atoms with 2-methoxyfuran

Oxazole presents a special case. When oxazole was cocondensed with lithium atoms the reaction yielded a dilithiated compound. In this unusual reaction sequence two lithium atoms were able to activate two C−H bonds in this compound, both in an *ortho* position with respect to the oxygen.

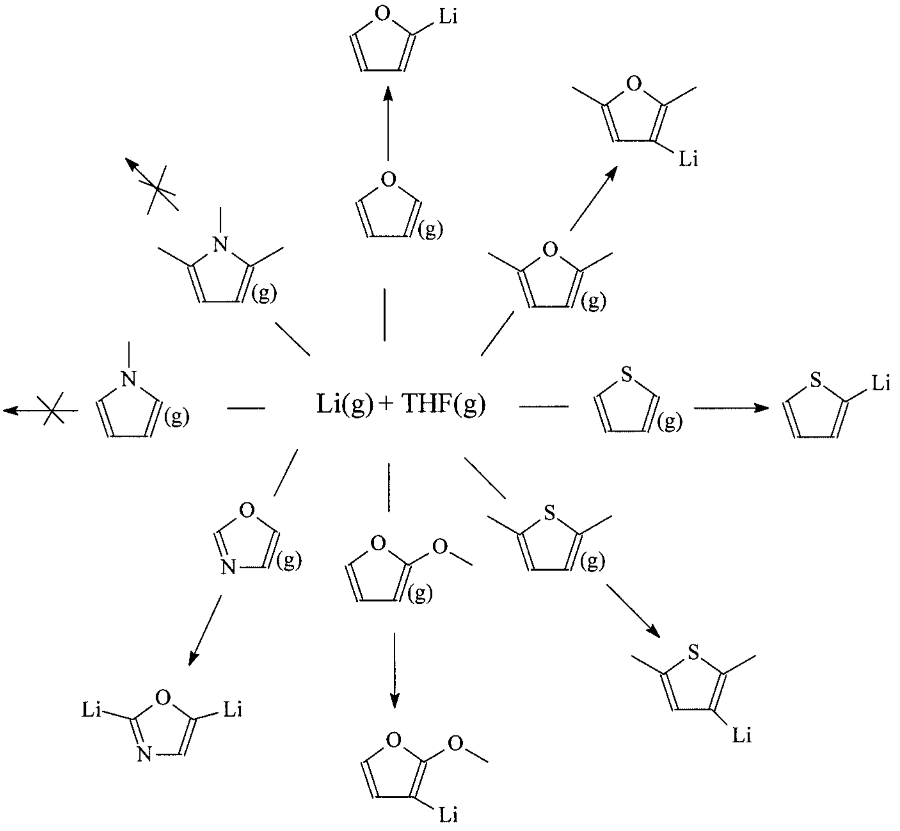


Scheme 4. Cocondensation reaction of lithium atoms with oxazole

In order to facilitate an overview, all cocondensation reactions are summarised in Scheme 5.

2. Theoretical Studies

The aim of this work was to identify, by calculation, plausible intermediate species for all these heterocycle cocondensation reactions, thereby identifying the reaction



Scheme 5. Summary of the reactions of lithium atoms with five-membered heterocycles in the presence of THF at 77 K

mechanism. Calculations were performed using the GAUSSIAN 98[19] and the B3LYP DFT functional with the 6−31G** set basis.

The C−H activation involves at least two steps, the coordination of the lithium cluster with the aromatic compound, and then the insertion of the Li_2 cluster into the C−H bond by a double electron transfer via the aromatic system.[9,10]

Two different possibilities were found for the coordination of the dilithium cluster (Figure 1). Please note that in some cases the lines on the diagrams only have topological significance. The first possibility is the coordination of the Li_2 cluster to the aromatic system to form a π-complex, and the second possibility is η^1-coordination of the Li_2 cluster to the heteroatom in the ring.[12]

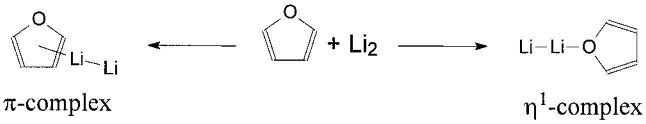


Figure 1. Principal coordination modes of the dilithium cluster to a heterocyclic aromatic compound like furan

When furan is used the preferred pathway is via the η^1-complex. An energy difference of 2.7 kcal/mol was found between the two complexes, showing that the η^1-complex is more stable than the π-complex. The strong interaction between the lithium cluster and the oxygen results in a short Li−O distance of 197.4 pm and supports this pathway. As described previously, the next step is a double electron transfer step from the Li_2 cluster to the LUMO of the aromatic ring. For the furan cocondensation, this step has a larger reaction enthalpy of −29.0 kcal/mol and there is still a strong interaction between the lithium and the oxygen in the second intermediate [*d*(LiO):184.5 pm]. The optimised structure of this second intermediate shows an elongation in the C−O bond of the lithiated carbon. In uncoordinated furan the distance is 136.4 pm; in the second intermediate this distance is 145.7 pm.

When methyl groups are placed in the two *ortho* positions in the furan, a similar situation is found. The η^1-complex is the more stable intermediate with a small energy difference of 2.7 kcal/mol from the π-complex. Furan gives a similar energy for the first step, while there is a less exothermic second step (−18.7 kcal/mol instead of −29.9 kcal/mol found in furan). The distance between the Li_2 and the oxygen in the η^1-complex is the same in both complexes (196.9 pm).

For heterocycles containing sulfur, like thiophene or 2,5-dimethylthiophene, the situation changes and the favoured pathway is via the π-complex.

In the thiophene calculation, a difference in energy of 5.7 kcal/mol in favour of the π-complex was found between the π- and the η^1-coordinated intermediates.

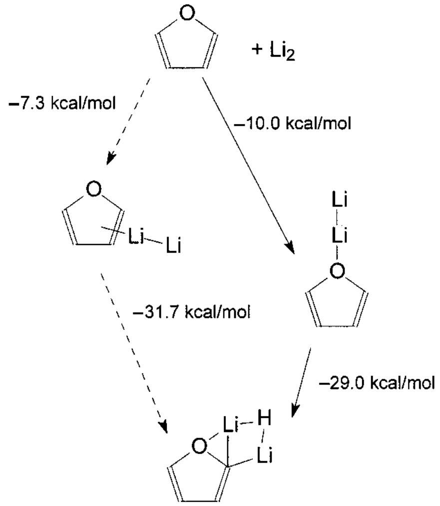


Figure 2. Calculated reaction mechanism for the cocondensation of lithium atoms with furan

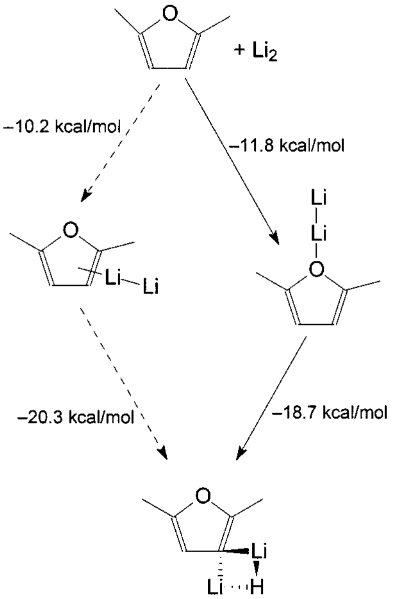


Figure 3. Calculated reaction mechanism for the cocondensation of lithium atoms with 2,5-dimethylfuran

As shown in Figure 4, the C−H activation step for thiophene is a highly exothermic process, as was also the case for furan. There is no interaction between the sulfur and the lithium in the second intermediate and the Li_2H plane is found to be perpendicular to the thiophene plane. The corresponding intermediate in the furan calculation is almost planar (Figure 5). There is a small elongation in the C−S bond by 2.9 pm compared to the uncoordinated thiophene. In furan, the extra coordination to the oxygen atom in the C−H-activated second intermediate leads to an elongation of the C−O bond by 9.3 pm compared to the uncoordinated furan.

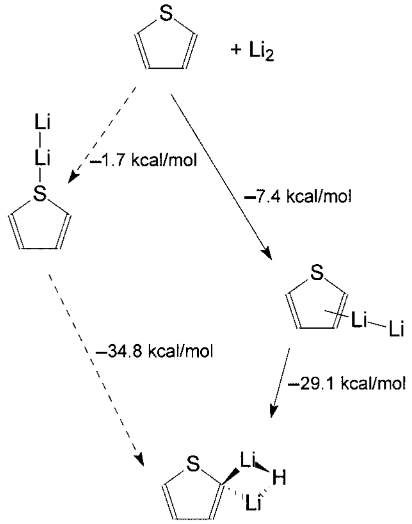


Figure 4. Calculated reaction mechanism for the cocondensation of lithium atoms with thiophene

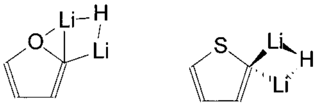


Figure 5. Second intermediate calculations for furan and thiophene

A similar theoretical study was performed on 2,5-dimethylthiophene where a π-complex pathway was shown to be more stable as well. As shown in Figure 6, there is a difference of 7.5 kcal/mol between the η^1- and the π-complex, favouring the latter.

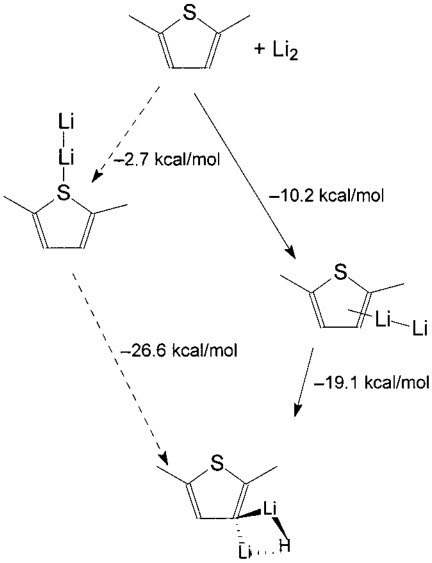


Figure 6. Calculated reaction mechanism for the cocondensation of lithium atoms with 2,5-dimethylthiophene

When there is a methoxy substituent on the aromatic ring functioning as an additional Lewis base, the reaction pathway is more complicated. A theoretical study of 2-methoxyfuran was carried out, and two different pathways were found.

The first possibility is the formation of a π-complex, as found in the previous calculations. The second pathway involves the coordination of the Li_2 cluster to the methoxy group. A third possibility can be ruled out, since the coordination of the Li_2 cluster to the oxygen in the furan forming an η^1-complex does not lead to a stable intermediate on the energy hypersurface of this system.

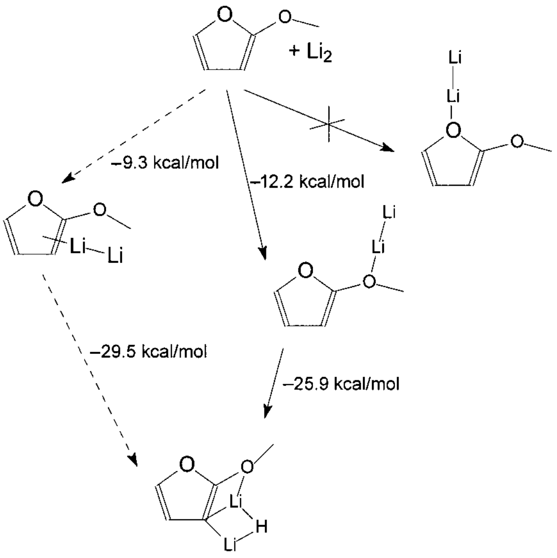


Figure 7. Calculated reaction mechanism for the cocondensation of lithium atoms with 2-methoxyfuran

As Figure 7 shows, the preferred pathway is via an η^1-complex involving the methoxy group. The η^1-complex is more stable than the π-complex by 2.9 kcal/mol. This η^1-complex shows a strong interaction between the lithium and the oxygen in the methoxy group, resulting in a Li−O bond length of 193.1 pm. As in previous mechanisms the next step is a double electron transfer from the Li_2 cluster to the LUMO of the aromatic ring forming a hydride and a carbanion. In this second intermediate a strong bond is still present between oxygen and lithium (194.0 pm).

The theoretical study of the oxazole reaction pathway presents a special case. The presence of two heteroatoms gives oxazole the possibility of forming two η^1-complexes: one in which the lithium cluster is bonded to the nitrogen and one in which it is bonded to the oxygen. The cocondensation reaction of oxazole in the presence of THF gives a dilithiated product; however, only the formation of the monolithiated oxazole is considered in this calculation.

In the first step, the η^1-complex is the more stable intermediate when nitrogen is the donor. The η^1-complex with the oxygen is also a stable intermediate, but in this case the reaction is about 9 kcal/mol less exothermic, as shown in Figure 8. No stable π-complex was found.

Both η^1-complexes lead to a C−H-activated second intermediate where the interaction between the heteroatom and the lithium is still present. These second steps are highly exothermic processes, both for the nitrogen η^1-complex (−37.6 kcal/mol) and for the oxygen η^1-complex (−33.1 kcal/mol).

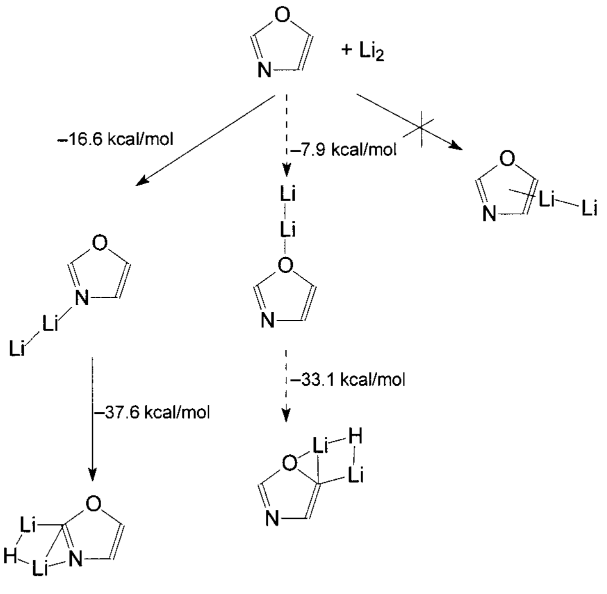
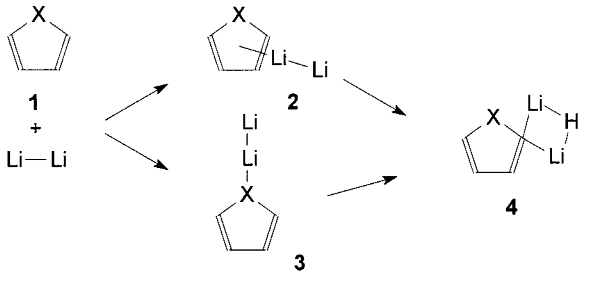


Figure 8. Calculated reaction mechanism for the first lithiation of oxazole

Discussion

Previous research in this area showed that aromatic hydrocarbons react with lithium atoms in the presence of THF under cocondensation conditions.[9,10] The isolated products were identified as monolithiated aromatic compounds. This study examines the effect of heteroatoms introduced into the aromatic rings on the C−H activation reactions.

A delicate balance between enhancing complex formation ability and lowering LUMO energy, which allows reductive cleavage of the aromatic C−H bond, is needed for a successful C−H activation. As shown in Scheme 6, the electron-deficient Li_2 cluster **1** accepts electron density from the aromatic system to form an unusual main group element π-complex **2**, or from the heteroatom to form an η^1-complex **3**. C−H activation follows this step, leading to **4**.



Scheme 6. Key mechanistic steps in heteroaromatic C−H bond activation using lithium atoms

When the heteroatom in the aromatic ring donates electron density to the lithium cluster, the interaction between the two lithium atoms is strengthened. This can be observed by comparing the calculated Li−Li bond lengths for the π- and η^1-complexes as shown in Table 1. For example, the biggest difference is observed in the case of 2,5-dimethylthiophene, where the Li−Li distance decreases from 277.5 pm to 273.7 pm, whereas for furan there is only a decrease of 0.9 pm. However, when the heterocycle contains sulfur, as in thiophene and 2,5-dimethylthiophene, the π-complex is found to be more stable than the η^1-complex. In all other cases the opposite behaviour is found.

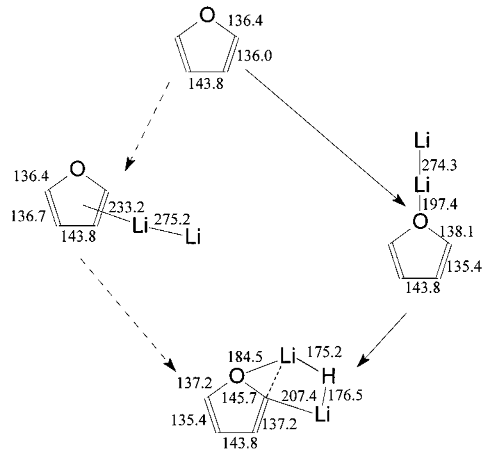
Table 1. Selected Li−Li bond lengths for all calculated intermediates; the calculated Li−Li bond length for free Li_2 is 272.3 pm

	d(LiLi) [pm] π-complex	*d*(LiLi) [pm] η^1-complex	*d*(LiLi) [pm] C−H-activated intermediate
furan	275.2	274.3	238.5
2,5-dimethylfuran	276.3	275.7	228.4
thiophene	276.0	272.9	231.4
2,5-dimethylthiophene	277.5	273.7	229.1
2-methoxyfuran	276.5	275.2	236.0
oxazole		(N) 276.4 (O) 273.3	254.5

The next mechanistic step is crucial. It involves the double electron transfer from the π- or η-complex-bonded Li_2 cluster (**2**,**3**) to the LUMO of the aromatic ring. If the LUMO energy is too high, as it is for pyrroles (as outlined in Table 2), it is impossible to place electron density into it, thereby preventing the C−H-activation reaction from occurring. It can be seen in Schemes 1 and 2 that lithium does not react with 1-methylpyrrole or 1,2,5-trimethylpyrrole. If the LUMO energy is low enough, as in furan or thiophene (as shown in Table 2) the reaction proceeds to give an aryllithium compound and lithium hydride.

Table 2. LUMO energies of selected reactants calculated with B3LYP/6-31G**

	LUMO (eV)	Reaction
1-methylpyrrole	1.44	no reaction
1,2,5-trimethylpyrrole	1.27	
2-methoxyfuran	0.94	C−H activation
2,5-dimethylfuran	0.76	
furan	0.51	
2-lithiooxazole	0.21	
5-lithiooxazole	0.12	
2,5-dimethylthiophene	0.00	
oxazole	−0.03	
thiophene	−0.22	



Scheme 7. Bond lengths in pm for furan reaction intermediates

Scheme 7 shows all the bond lengths of the calculated species in the furan study. The formation of the first intermediate does not change the structure of the furan ring significantly. The Li−Li distance is slightly elongated. In the uncoordinated dilithium species *d*(Li−Li) is 272.3 pm, which changes to 274.3 and 275.2 pm in the η^1-complex and π-complex.

The formation of the second intermediate changes the structure of the ring. The distance between the activated carbon and the oxygen is elongated by 9.3 pm by the formation of a three-membered ring involving lithium. Furan, methoxyfuran and oxazole show a clear interaction between the heteroatom and one lithium in this second intermediate, which can be seen from the short bond lengths of 184.5, 194.0 and 192.4 pm, respectively.

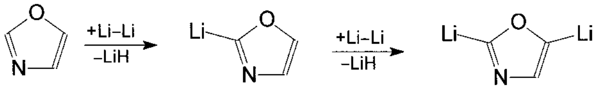
For 2,5-dimethylfuran, 2,5-dimethylthiophene and thiophene the second intermediates exhibit a symmetrical four-membered CLi_2H ring, as shown in Table 3.

Table 3. Bond lengths for C−Li−H rings on second intermediates

	2,5-Dimethylfuran	Thiophene	2,5-Dimethylthiophene
C−Li	210.1	211.7	210.6
Li−H	177.5	177.2	176.8

When an oxygen-donor group is placed in the heterocyclic ring, as in the case of methoxyfuran, the NMR spectroscopic data indicate an *ortho* lithiated product with respect to the methoxy group. In furan and 2,5-dimethylfuran, the η^1-complex is a more stable first intermediate than the π-complex, but, in contrast, the Li−Li is bonded to the methoxy group in the η^1-complex formed.

For the reaction of oxazole with lithium atoms in the presence of THF, a different reaction sequence with respect to the other heterocyclic compounds was observed. The ability to develop a second lithiation reaction, as shown in



Scheme 8. Reaction of oxazole with lithium atoms in the presence of THF

Scheme 8, is the governing factor here. The first intermediate is characterised by the nitrogen, which is able to stabilise the Li−Li cluster more than the oxygen η^1-complex. However, no π-complex was found as a stable intermediate.

Once the first C−H activation has occurred, the monolithiated oxazole is still able to react further. As Scheme 8 shows, this second lithium is also observed in an *ortho* position with respect to the oxygen.

From the calculated LUMO energies of the reactants (Table 2), a comparison can be made in relation to the dilithiated species. The calculation of LUMO energies of the monolithiated compounds was carried out considering solvent interaction with the lithium. For this purpose, three molecules of ammonia were taken to fill the coordination sphere of lithium instead of THF, in order to simplify the process. The calculated LUMO energies for the monolithiated species 2-lithiooxazole and 5-lithiooxazole are 0.21 and 0.12 eV respectively. These LUMO energies can be considered within the range of species that can be activated. It follows that a further activation with addition of lithium to the lithiated oxazole can readily occur during the cocondensation reaction.

Conclusion

Lithium atoms are able to activate heterocyclic aromatic compounds like furan and thiophene, which have a relatively low-lying LUMO energy. The only product of this selective C−H-activation process is 2-lithiofuran or 2-lithiothiophene. If the LUMO energy is considerably higher as in pyrrole, no C−H activation can be observed. If the normally activated *ortho* position is blocked, as in 2,5-dimethylfuran or thiophene, the cocondensation reaction in the presence of THF leads to a selective monolithiation at the *meta* position. The corresponding 1,2,5-trimethylpyrrole fails to react because of its high-lying LUMO energy. Interestingly, oxazole cocondensed with lithium atoms results in 2,5-dilithiooxazole in a novel reaction variation, but the exact mechanism of the dilithiation of oxazole remains unclear. For all the furans in this study and the oxazole, an η^1-complex was calculated to be the most stable intermediate in the early phase of the C−H activation reaction, while thiophenes preferred π-complexes with the intermediate dilithium cluster.

Experimental Section

General: All experimental procedures were performed using standard Schlenk techniques under dry argon. THF was dried and distilled from sodium/benzophenone under argon. Furan, thiophene, 1-methylpyrrole, 2,5-dimethylfuran, 2,5-dimethylthiophene, 1,2,5-trimethylpyrrole, 2-methoxyfuran and oxazole were dried and distilled from calcium dihydride under 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}H and ^{13}C NMR spectra were obtained with 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 ethyl acetate on a Finnigan Trace GC-MS, equipped with an RTX-5MS 15 m column.

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 90 minutes and cocondensed with a mixture of the aromatic compound (15 mL) and THF (80 mL, 1.12 mol). The solution was filtered through a plug of Celite in order to remove the solid lithium hydride by-product and unchanged lithium metal. After removal of the solvent mixture in vacuo, a solid was isolated and washed with THF (20 mL). The lithiated aromatic compound was identified by derivatisation with Me_3SiCl.

A Typical Derivatisation of the Lithiated Aromatic with Me_3SiCl: Me_3SiCl in THF solution was added dropwise with vigorous stirring to a solution of the lithiated aromatic compound (about 0.25 g) in THF (20 mL) at room temperature. The reaction was judged to be finished when a colour change from dark red-yellow to pale yellow occurred. Water (10 mL) was added to this solution, and the organic phase was separated. The aqueous phase was washed three times with dichloromethane (10 mL). The combined organic extracts were dried with $MgSO_4$ and then the solvent was removed under reduced pressure, affording the derivative. GC-MS, ^{1}H and ^{13}C NMR were used to identify the product.

Theoretical Methods Used in This Study: DFT calculations were performed with B3LYP and the 6−31G** basis set for C, H, O, N, S, and Li. For this purpose the program GAUSSIAN 98[19] 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 Kelvin. LUMO energies for each aromatic compound were obtained from geometry-optimised structures using B3LYP/6-31G**.

2,5-Dimethyl-3-(trimethylsilyl)furan: The general procedure applied to 2,5-dimethylfuran gave 3-lithio-2,5-dimethylfuran (red) in 25% yield (0.8 g), identified as its TMS derivative. ^{1}H NMR ($CDCl_3$): δ = 5.7 (s), 2.1 (s) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.0, 106.9, 99.8, 14.5, 12.1, 2.9 ppm.

2,5-Dimethyl-3-(trimethylsilyl)thiophene: The general procedure applied to 2,5-dimethylthiophene gave 3-lithio-2,5-dimethylthiophene (brown) in 45% yield (5.8 g), identified as its TMS derivative. ^{1}H NMR ($CDCl_3$): δ = 6.5 (s), 2.4 (s) ppm. ^{13}C NMR ($CDCl_3$): δ = 137.0, 126.0, 123.7, 14.2, 13.0, 2.1 ppm.

2-Methoxy-3-(trimethylsilyl)furan: The general procedure applied to 2-methoxyfuran gave 3-lithio-2-methoxyfuran (red) in 35% yield (2.7 g), identified as its TMS derivative. ^{1}H NMR ($CDCl_3$): δ = 7.5 (d, J = 5.3 Hz), 6.1 (d, J = 5.3 Hz), 3.7 (s) ppm. ^{13}C NMR ($CDCl_3$): δ = 172.7, 151.8, 120.6, 98.0, 67.0, 0.9 ppm.

2,5-Bis(trimethylsilyl)oxazole: The general procedure applied to oxazole gave 2,5-dilithiooxazole (red/orange) in 29% yield (1.5 g), identified as its TMS derivative. ^{1}H NMR ($CDCl_3$): δ = 7.2 (s) ppm. ^{13}C NMR ($CDCl_3$): δ = 149.0, 137.5, 125.9, 2.0 ppm.

Supporting Information: Coordinates, electronic and zero-point energies of all optimised species.

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