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s-Block-Metal-Mediated Hydroamination of Diphenylbutadiyne with Primary Arylamines Using a Dipotassium Tetrakis(amino)calciate Precatalyst

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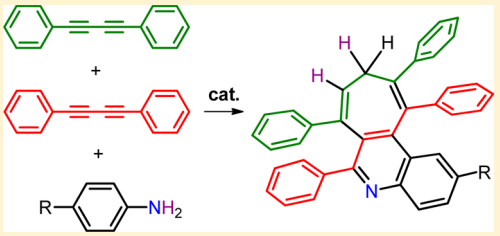
Supporting Information

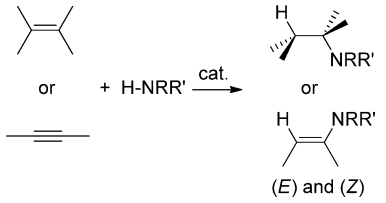
ABSTRACT: The hydroamination of diphenylbutadiyne with primary arylamines requires a reactive catalyst. In the presence of heterobimetallic $K_2[Ca\{N(H)Dipp\}_4]$ (Dipp = 2,6-diisopropylphenyl) the performance of this reaction in THF yields 2-*tert*-butyl-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]-quinoline (**1a**) and 2-fluoro-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]quinoline (**1b**) within 3 days at room temperature when 4-*tert*-butyl- and 4-fluoroaniline, respectively, have been used. During this catalysis *o*-CH activation occurs and quinoline derivatives are formed. Blocking the *o*-CH positions by methyl groups and use of 2,4,6-trimethylaniline under similar reaction conditions leads to the formation of *N*-mesityl-7-(*E*)-((mesitylimino)(phenyl)methyl)-2,3,6-triphenylcyclohepta-1,3,6-trienylamine (**2**) containing a *β*-diketimine unit with a N−H···N hydrogen bridge. NMR experiments with labeled 4-*tert*-butylaniline verify the transfer of N-bound hydrogen atoms to the newly formed cycloheptatriene ring. If the s-block-metal-mediated hydroamination of diphenylbutadiyne is performed in refluxing THF for 6 days, *N*-aryl-2,5-diphenylpyrroles **3a**−**d** (**3a**, R = tBu, R′ = H; **3b**, R = F, R′ = H; **3c**, R = R′ = Me; **3d**, R = R′ = H) are obtained regardless of the substitution pattern of the arylamines.



INTRODUCTION

Metal-mediated hydroamination of C═C and C≡C multiple bonds with amines (Scheme 1) represents an atom-economical procedure to prepare substituted amines by addition of N−H bonds to alkenes or alkynes.[1] Generally, this process has to overcome certain challenges such as unfavorable entropic effects, electrostatic repulsion between a strongly Lewis basic amine and an electron-rich multiple bond, and lack of significant exothermic reaction enthalpy. Due to these facts several strategies have been developed to support the addition of N−H functionalities to C−C multiple bonds. On the one hand, activation of alkenes and alkynes often succeeds in the vicinity of late transition metals by back-donation of charge from the metal-centered d orbitals into π^* orbitals of the alkenes and alkynes, in agreement with the Dewar−Chatt−Duncanson model. On the other hand, the amines can be activated by oxidative addition to transition-metal complexes or by deprotonation and formation of the much more aggressive and nucleophilic amides (R_2N^-) or even imides (RN^{2-}) of early transition metals or s-block metals. The disadvantageous entropy value can be minimized by an intramolecular hydroamination reaction, leading to cyclic amines.

Scheme 1. Hydroamination of Alkenes (Top) and Alkynes (Bottom) Yielding Alkylamines and *E*/*Z*-Alkenylamines



Alkali-metal and alkaline-earth-metal complexes represent less common catalysts for diverse reasons. Organometallics of these s-block metals contain very heteropolar metal−carbon or metal−nitrogen bonds, and saltlike ionic contributions dominate the reaction pattern. In contrast to covalent bonds, electrostatic forces are nondirectional and hence control of stereochemistry has to be performed with a definite and particularly designed ligand sphere. The larger alkaline-earth-metal ions are isoelectronic with trivalent ions of the scandium group as well as tetravalent ions of the titanium group, and such d^0 metal ions are able to use d orbitals in bonding situations.[2] Due to this fact, the heavier alkaline-earth metals combine the advantageous properties of typical s-block metals (strongly ionic and highly heteropolar bonds, high reactivity, and nucleophilicity) and early transition metals (d orbital participation, Lewis acidity, catalytic behavior), with calcium being the ideal element because it is also globally abundant, available worldwide, inexpensive, and nontoxic.[3−5]

For about ten years, intramolecular calcium-mediated hydroamination of alkenes has been investigated intensely by several research groups, often employing heteroleptic com-

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plexes with one bulky protecting anion in order to partially shield the catalyst.[6−13] Intermolecular hydroamination reactions catalyzed by calcium-based complexes are much more challenging. Therefore, amines have been added to activated alkenes such as styrenes[14,15] or carbodiimides[16] as well as alkynes[14,17,18] catalyzed by amidocalcium species. These studies showed that the reactivity of the catalyst can be enhanced by using heterobimetallic potassium tetrakis(amido)calciates of the type $K_2[Ca(NRR')_4]$ in ethereal solvents. However, side-products have been observed that result from an *o*-hydrogen activation and abstraction followed by C−C bond formation (Figure 1, top).[18] Thus, the addition of diphenylamine to

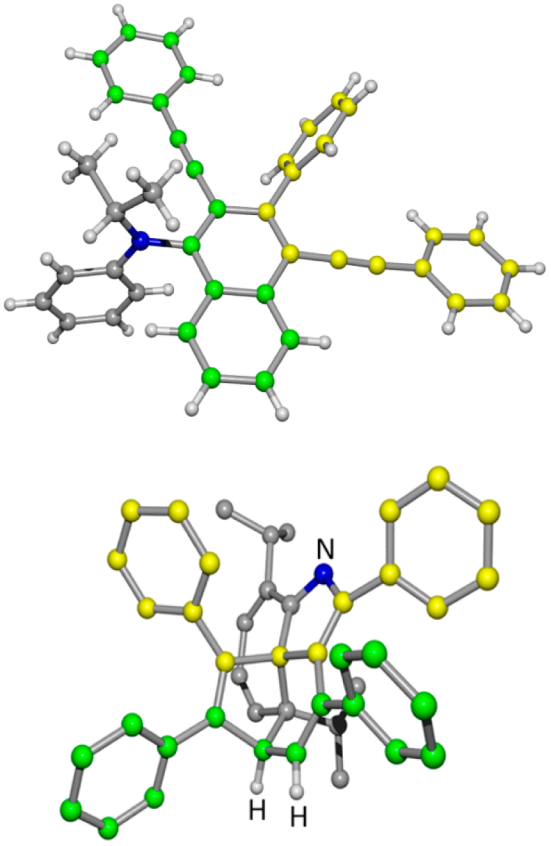


Figure 1. Products of the s-block-metal-mediated hydroamination of diphenylbutadiyne with *N*-diisopropylaniline (top) and 2,6-diisopropylaniline (bottom; only the formerly *N*-bound H atoms are depicted), containing 2 equiv of butadiyne (yellow and green) and 1 equiv of amine (C, gray; N, blue).

diphenylbutadiyne required a heterobimetallic s-block-metal catalyst, whereas the addition of more nucleophilic *N*-isopropylaniline to this butadiyne can be promoted by homometallic s-block-metal amides. In contrast to this "simple" addition of a N−H bond of a secondary amine to diphenylbutadiyne, the reaction of primary 2,6-diisopropylaniline with diphenylbutadiyne at room temperature in the presence of catalytic amounts of $K_2[Ca\{N(H)Dipp\}_4]$ (Dipp = 2,6-diisopropylphenyl) proceeds via multiple reaction steps involving ring expansion of the 2,6-diisopropylphenyl ring to a seven-membered-ring system (Figure 1, bottom).[17] Here, 2 equiv of diphenylbutadiyne (distinguished by the colors yellow and green) react with 1 equiv of H_2N-Dipp, regardless of the applied stoichiometry.

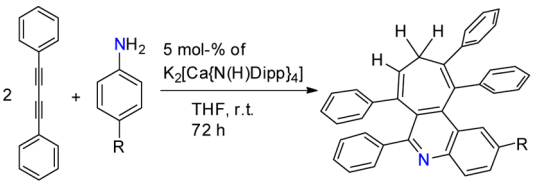
The copper-catalyzed addition of primary amines to diphenylbutadiyne gives pyrroles in high yields. This reaction requires high catalyst loads such as 25 mol % of copper(I) halide and enhanced reaction temperatures.[19]

These results initiated a detailed investigation of the reaction of primary anilines with diphenylbutadiyne in the presence of the same approved precatalyst $K_2[Ca\{N(H)Dipp\}_4]$ under variation of the reaction conditions and the substitution pattern of the primary arylamine. We decided to maintain this precatalyst because (i) its preparation is straightforward from the metathesis reaction of KN(H)Dipp with CaI_2 (eq 1) and (ii) its purification easily succeeds by recrystallization. Furthermore, (iii) this compound crystallizes free of solvent, thus avoiding aging of the solid by uncontrolled loss of solvent molecules; hence, stoichiometric requirements (addition of a specified mole percent of $K_2[Ca\{N(H)Dipp\}_4]$ to the substrates) can easily be achieved.

$$4KN(H)Dipp \xrightarrow[-2KI]{+CaI_2} K_2[Ca\{N(H)Dipp]_4 \quad (1)$$

RESULTS AND DISCUSSION

Synthesis. In a typical procedure, equimolar amounts of diphenylbutadiyne and substituted amine were combined in tetrahydrofuran (THF) in the presence of 5 mol % of $K_2[Ca\{N(H)Dipp\}_4]$ and stirred for 3 days at room temperature. Depending on the substitution pattern, different reaction pathways have been observed. The use of 4-*tert*-butylaniline in this reaction and a hydrolytic workup procedure yields product **1a** regardless of the applied stoichiometry. This product is based on α-deprotonation steps of 4-*tert*-butylaniline and formation of a C−C bond leading to 2-*tert*-butyl-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]quinoline (**1a**); very poor yields were obtained under similar reaction conditions for the reaction of diphenylbutadiyne with 4-fluoroaniline leading to 2-fluoro-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]quinoline (**1b**). The fluoro substituent withdraws electron density via the aromatic ring from the nitrogen atom, reducing the nucleophilicity of the amino functionality. Compensation of reduced reactivity by more drastic reaction conditions proved to be disadvantageous because at raised temperatures another reaction pathway was observed as discussed below, yielding a pyrrole. Nevertheless, derivatives **1a,b** both represent quinoline derivatives with annelated seven-membered rings. The reaction is depicted in eq 2, and only hydrogen atoms that are involved in the conversion are explicitly shown.



1a (R = *t*Bu; 72 %)
1b (R = F, < 5 %)

(2)

The reaction of 2,4,6-trimethylaniline with diphenylbutadiyne must proceed via a different pathway, because the ortho positions are blocked by methyl groups. In this case, a 1:1 ratio of both substrates was observed at room temperature in THF with a precatalyst load of 5 mol % of $K_2[Ca\{N(H)$-$Dipp\}_4]$ according to eq 3, yielding *N*-mesityl-7-(*E*)-((mesitylimino)-

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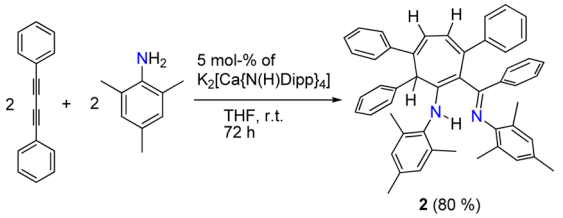
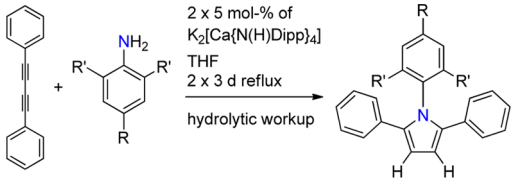


(3)

(phenyl)methyl)-2,3,6-triphenylcyclohepta-1,3,6-trienylamine (**2**). Only those hydrogen atoms are depicted that were bound at the nitrogen atom of the amine substrate. Again, a seven-membered cycloheptatriene moiety was found; however, the mesityl substituents remain intact during this transformation, in contrast to earlier findings with 2,6-diisopropylaniline yielding product **B** (Figure 1, bottom).[17]

In order to study the influence of the reaction temperature, in a typical procedure diphenylbutadiyne was dissolved in THF and an equimolar amount of arylamine and 5 mol % of the catalyst $K_2[Ca\{N(H)Dipp\}_4]$ were added. This reaction mixture was stirred and refluxed for 3 days. Then another 5 mol % of $K_2[Ca\{N(H)Dipp\}_4]$ was added and heating was continued for a further 3 days. A standard workup procedure including hydrolysis with distilled water, extraction with diethyl ether, drying with sodium sulfate, and recrystallization from pentane or toluene at 5 °C yielded colorless crystals of *N*-aryl-2,5-diphenylpyrroles **3** according to eq 4 (**3a**, R = *t*Bu, R′ = H; **3b**, R = F, R′ = H; **3c**, R = R′ = Me; **3d**, R = R′ = H).

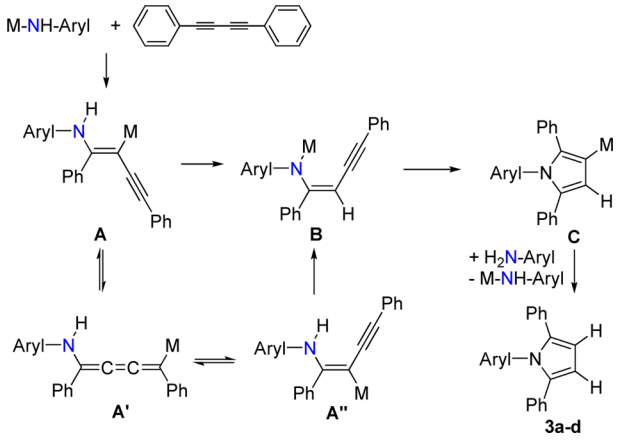


(4)

Proposed Mechanism. In all cases, with the exception of **1b**, moderate to good yields were obtained. The precatalyst $K_2[Ca\{N(H)Dipp\}_4]$ reacts with the primary aniline substrate, and NMR spectroscopic investigations of THF solutions containing $K_2[Ca\{N(H)\text{-}Dipp\}_4]$ and the 4-fold stoichiometric amount of 2,4,6-trimethylaniline verified the quantitative ligand exchange and formation of 2,6-diisopropylaniline. A 1:2 ratio of $K_2[Ca\{N(H)Dipp\}_4]$ and mesitylamine led to heteroleptic calciates of the general formula $K_2[Ca\{N(H)Dipp\}_{4-x}\{N(H)\text{-}Mes\}_x]$. Due to the fact that all aniline derivatives might exhibit comparable pK_a values, it can be concluded that the bulkier amide is replaced by the smaller amide in order to minimize intramolecular strain of the calciate anion mainly provoked by the ortho substituents.

The catalytic reaction starts with the addition of a metal−nitrogen bond to one C≡C triple bond as shown in Scheme 2 (nucleophilic attack of an amide at an alkyne) yielding intermediate **A**. In this scheme, M symbolizes the s-block metal and hence the anionic site. The reactivity of homometallic calcium amides is not sufficient to mediate this hydroamination. Therefore, we employed the already known strategy to significantly enhance the reactivity by formation of a

Scheme 2. Proposed Mechanism of the s-Block-Metal-Mediated Hydroamination of Diphenylbutadiyne with Primary Arylamines at High Temperatures Yielding *N*-Aryl-2,5-diphenylpyrroles



heterobimetallic catalyst system.[17,18] *E*/*Z* isomerization is possible via the cumulene isomer **A**′, which can isomerize to either a trans (**A**) or a cis orientation (**A**″) of the anionic site and the remaining alkyne moiety. Such cumulene systems have also been suggested during calcium-mediated hydrophosphanylation of diphenylbutadiyne with diphenylphosphane in order to explain isomer mixtures.[20] After the initial reaction step, intramolecular metalation transfers the *N*-bound hydrogen to the alkenyl moiety and amide **B** is formed. During the high-temperature route an intramolecular addition to the second alkyne unit occurs and the pyrrole derivative **C** is formed. The reaction of this intermediate species with another arylamine regenerates the catalyst, and the formation of pyrroles **3a**−**d** is completed.

In contrast to this straightforward pathway for the synthesis of pyrroles **3a**−**d**, the low-temperature route proceeds via an insertion of another diphenylbutadiyne molecule into the metal−carbon bond of the primary reaction product (carbometalation step, Scheme 3) yielding intermediate **D**. For the sake of clarity the diphenylbutadiyne units are distinguished by different colors in this scheme. An intramolecular metalation reaction forms amide **E**. Now, two reaction routes seem to be feasible to explain the formation of **1** (via *o*-CH activation) and **2** (via addition of a second arylamine). These compounds are depicted in Figure 2, also clarifying the origin of the structural moieties. The closed-shell ionic mechanism involves the formation of the 1,2,4,6-cycloheptatetraene intermediate **F**. Such species exhibit ring strain; nevertheless, unsaturated ring systems of this kind have already been studied in a solid matrix[21] and by quantum chemical investigations, also considering other isomers such as phenylcarbene, bicyclo[3.2.0]hepta-1,3,6-triene, bicyclo[3.2.0]-hepta-3,6-diene-2-ylidene, bicyclo[3.2.0]hepta-2,3,6-triene, and bicyclo[4.1.0]heptatriene.[22] Furthermore, a cyclotetramer of such a strained cycloheptatetraene derivative has been characterized by an X-ray crystal structure determination.[23] Despite the fact that ring strain is present in cycloheptatetraenes, these derivatives also represent $4n$ π-Möbius aromatic systems.[24] Intermolecular metalation by an arylamine regenerates the catalyst and leads to the formation of **G**.

In this bicyclic intermediate **G** the allene moiety attacks the *o*-CH group leading to compound **1**. Absence of *o*-CH

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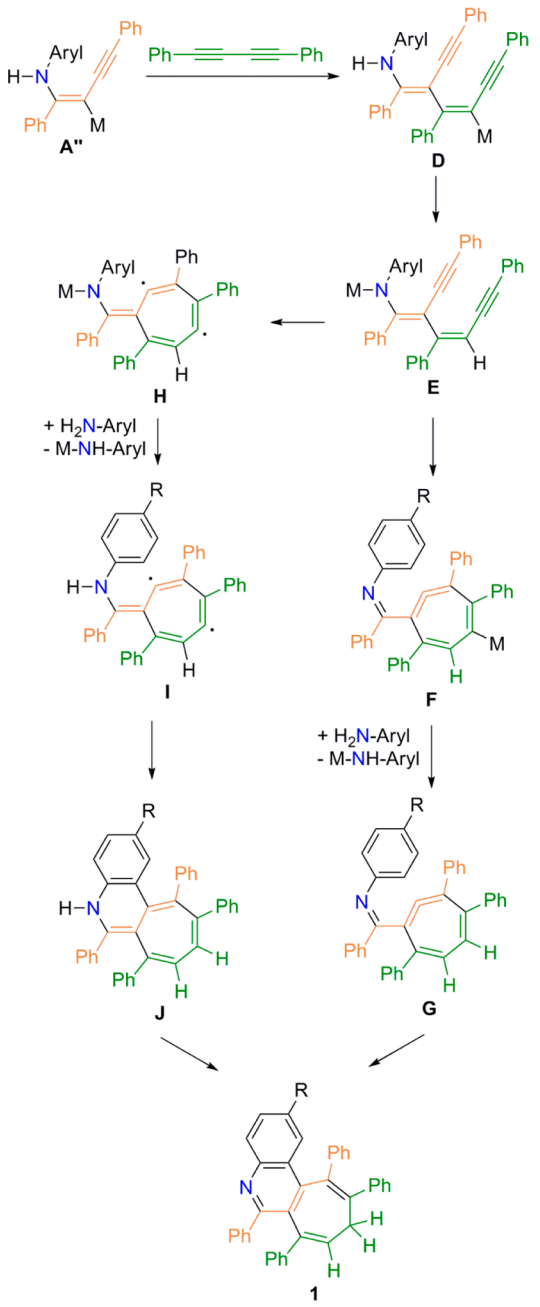
Scheme 3. Proposed Mechanism of the s-Block-Metal-Mediated Hydroamination of Diphenylbutadiyne with Primary Arylamines at Room Temperature via a 1,2,4,6-Cycloheptatetraene Intermediate and via a Bergman Cyclization Route[a]



[a]The diphenylbutadiyne units are distinguished by the colors orange and green.

fragments and bulkier N-bound aryl groups favor the formation of isomer **G′** (Scheme 4), leading to an alternative reaction pattern. Here, the 1,4-addition of an arylamine to the cycloheptatetraene ring leads to the formation of compound **2**.

An alternative pathway contains the Bergman cyclization leading to diradical **H**. Again the catalyst is re-formed by an intermolecular reaction with an arylamine yielding intermediate **I**. This radical can attack either at a *o*-CH group (yielding **1**) or—in the case that such a functionality is absent—another amine substrate, leading to compound **2** as shown in Scheme 4.

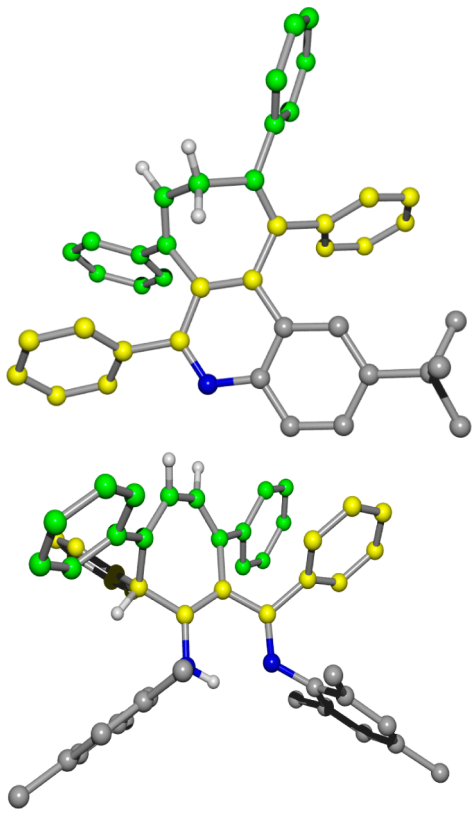
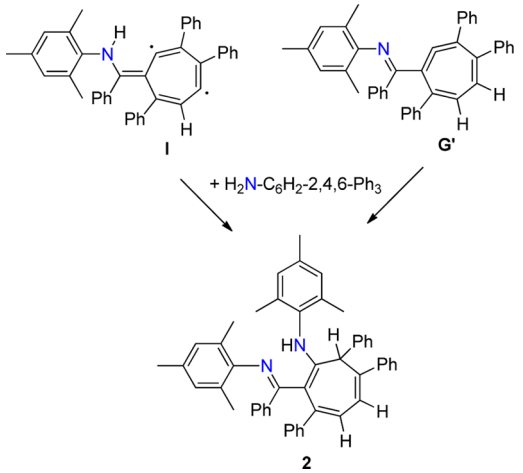


Figure 2. Stick-and-ball presentations of **1** (top) and **2** (bottom). The structural building blocks are distinguished by different colors: the initial diphenylbutadiyne moieties are shown in yellow and green and the arylamines in gray (C atoms) and blue (N atom). Only those H atoms are drawn (light gray) that are involved in chemical transformations or are bound at a nitrogen atom.

Scheme 4. Proposed Final Mechanistic Steps for the Formation of 2 Starting from I or G′[a]



[a]**G′** is the *E* isomer of **G**.

The fact that homometallic calcium bis(amide) does not mediate these hydroamination reactions raises the question of the cooperation of potassium and calcium in the catalyst system. In the solid state $K_2[Ca\{N(H)Dipp\}_4]$ forms a coordination polymer consisting of $[Ca\{N(H)Dipp\}_4]^{2-}$ anions interconnected by potassium cations.[17] It can be assumed that in solution the calciate anions are maintained.

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In these calciate anions electrostatic repulsion between the amido substituents enhances the Ca−N bond lengths and, hence, the nucleophilicity and reactivity of the amido groups. This consideration suggests that M in the schemes might be a calciate fragment. The role of the potassium ions remains unclear and speculative. Potassium ions are considered as soft Lewis acids, being able to coordinate to rather hard (such as ethers) and preferably to soft Lewis bases such as aromatics and extended π systems. Nevertheless, it remains speculative to what extent this coordination behavior of K^+ supports the catalytic hydroamination via coordination to any of the reported intermediates. Due to the fact that rather high yields of the products were obtained and that cycloheptatetraene derivatives have already been accessible experimentally, we favor the mechanism via the cycloheptatetraene intermediates. In addition, we would expect diverse derivatives for the radical mechanism due to reactions of the radical with solvent molecules and still present arylamine substrates.

NMR Experiments. The ^{1}H NMR spectrum of **1a** (R = *t*Bu) clearly shows a characteristic ABX coupling pattern for the hydrogen atoms at the seven-membered ring leading to three doublets of doublets (Figure 3) with a pseudotriplet for the CH

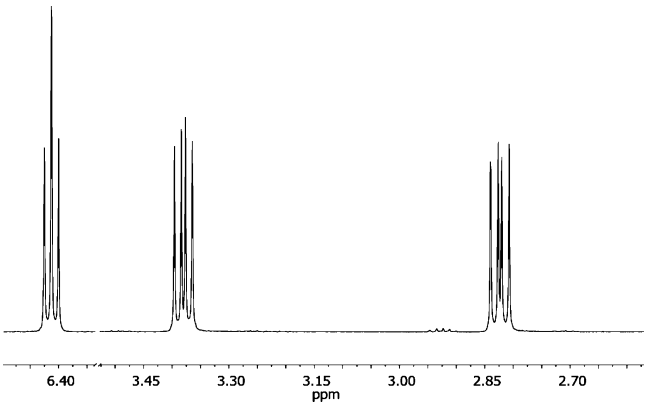

Figure 3. ^{1}H NMR resonances of the newly formed methylene unit of the seven-membered ring of compound **1a**. The coupling pattern clearly verifies the magnetic nonequivalence of the H atoms.

resonance at δ 6.41 ppm due to very similar vicinal coupling constants. The H atoms of the methylene fragment are magnetically inequivalent with a geminal coupling constant of $^2J_{HH}$ = 11.6 Hz, verifying the nonplanarity of the cycloheptatriene unit.

In order to support the reaction mechanism, we repeated the preparation of this compound with partially N-deuterated 4-*tert*-butylaniline with a deuteration degree of 75%. This approach should yield **1a** in addition to its partially deuterated derivatives. The coupling pattern in the ^{1}H NMR spectrum at the CH signal at δ = 6.41 ppm enables the assignment and determination of the positions of deuterium atoms (Figure 4). The coupling pattern of the endocyclic =CH−CH_2− fragment allows the assignment to the moieties CH−CH_2, CH−CHD, and CH−CDH. The intensity ratio of the resonances excludes the formation of CH−CD_2 units, which would suggest a bimolecular reaction mechanism. This coupling pattern and the resonances of the neighboring methylene group (see the Supporting Information) clearly show that there exists no preference for deuteration at either position and hence no stereocontrol for the transfer of the *o*-hydrogen atom of the 4-

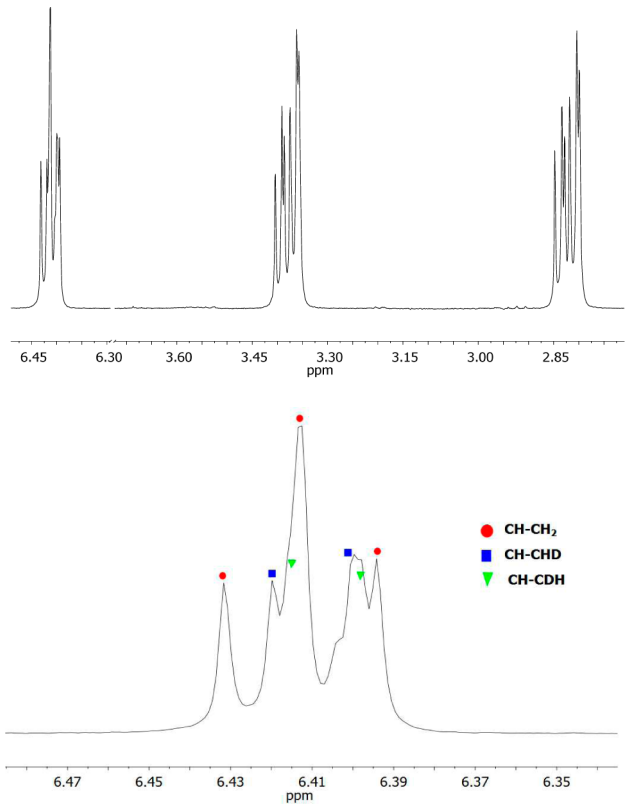

Figure 4. ^{1}H NMR spectrum of the CH fragment of the seven-membered ring of partially deuterated **1a** (top), with assignment to differently deuterated derivatives (bottom).

tert-butylphenyl group to the seven-membered ring yielding the methylene group.

Compound **2** represents a β-diketimine derivative with an annelated unsaturated seven-membered ring. This structural fragment gives rise to a low-field-shifted resonance for the N−H···N hydrogen bridge with a chemical shift of δ 12.85 ppm. In Figure 5 the ^{1}H NMR spectrum of the methyl region is

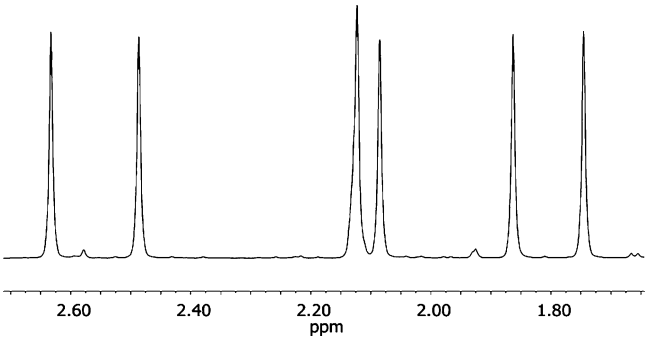

Figure 5. ^{1}H NMR resonances of the methyl substituents of the mesityl groups, showing that the 2,6-positions are magnetically nonequivalent, which suggests a hindered rotation of the mesityl groups around the N−C bonds.

depicted. All methyl groups are chemically different, which has been explained by hindered rotation around the C−N bonds. The nonequivalence of the *o*-methyl groups of each mesityl substituent is a consequence of the chiral carbon atom of the seven-membered cycloheptatriene ring.

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Molecular Structures. The molecular structure and numbering scheme of *N*-mesityl-2,5-diphenylpyrrole (**3c**) are depicted in Figure 6. Due to steric reasons the N-bound aryl group is oriented nearly perpendicular to the pyrrole ring with an angle of 69.2° between these planes. Expectedly, the π system of the pyrrole ring leads to short bonds and charge delocalization to a large extent. Endocyclic C1−C2, C2−C3, and C3−C4 bond lengths differ by less than 3 pm and have an average value of 138.9 pm. The exocyclic C1−C20 and C4−C5 bond lengths, with an average distance of 147.2 pm, are characteristic for single bonds between sp^2-hybridized carbon atoms. 1,2,5-Triphenylpyrrole (**3d**) exhibits crystallographic C_2 symmetry and shows very similar structural parameters (see the Supporting Information). This measurement at −140 °C leads to results very similar to those of the crystal structure determination at room temperature.[25]

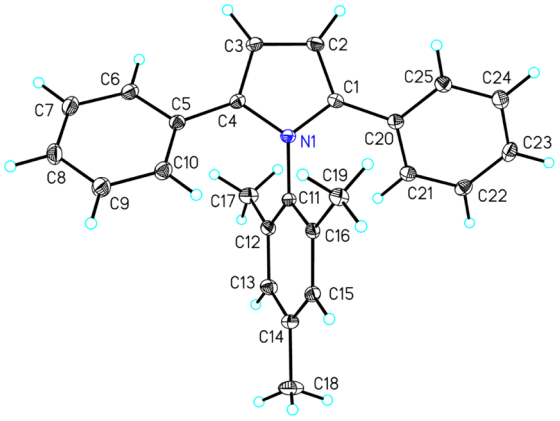

Figure 6. Molecular structure and numbering scheme of **3c**. The ellipsoids represent a probability of 30%, and H atoms are shown with arbitrary radii. Selected bond lengths (pm): N1−C1 139.1(2), N1−C4 139.3(2), N1−C11 144.4(2), C1−C2 138.1(2), C2−C3 140.7(2), C3−C4 137.8(2), C1−C20 147.6(2), C4−C5 146.8(2). Selected bond angles (deg): C1−N1−C4 109.0(1), N1−C1−C2 107.5(1), C1−C2−C3 107.9(1), C2−C3−C4 108.4(1), N1−C4−C3 107.3(1), C1−N1−C11 125.6(1), C4−N1−C11 125.1(1), N1−C1−C20 124.7(1), C2−C1−C20 127.8(1), N1−C4−C5 125.3(1), C3−C4−C5 127.4(1).

Verification of the compositions of **1a**,**b** and **2** as shown in Figure 2 was also successful by X-ray diffraction experiments on single crystals. Molecular structures and numbering schemes of **1a**,**b** are presented in Figures 7 and 8, respectively. The numbering schemes of both compounds are identical, and a comparison of selected bond lengths is given in Table 1. These compounds are built from two butadiyne molecules (atoms C1A−C16A and C1B−C16B) and one 4-*tert*-butylaniline (N1A, C17A−C26A) or 4-fluoroaniline molecule (N1A, F1A, C17A−C22A), respectively. The quinoline fragments show balanced bond lengths which are comparable to those of unsubstituted quinoline.[26] Substituents at the quinoline nucleus of **1a**,**b** lead to a slight lengthening between those carbon atoms carrying substituents. The phenyl groups are oriented nearly perpendicular to the ring systems; hence, no interaction between the aromatic phenyl groups and the π-systems of the seven-membered ring can be expected and characteristic C−C single bond values around 149 pm were observed.

The molecular structure and numbering scheme of compound **2** are shown in Figure 9. This compound is built from two butadiyne (atoms C1A−C4A and C1B to C4B) and two 2,4,6-trimethylaniline molecules (N1A and C17A−C25A as well as N1B and C17B−C25B). Compound **2** contains the chiral C4B atom, but due to the centric monoclinic space group the crystalline state consists of a racemate. The structure-dominating moiety is the N1A−C1B−C2B−C3B−N1B fragment with significant charge delocalization and a N1B−H···N1A hydrogen bridge (N1A···N1B distance 265.7(3) pm). The C1A−C2B bond length shows a characteristic single-bond value for sp^2-hybridized carbon atoms excluding π interaction between the β-diketimine unit and the remaining π bonds of the seven-membered ring. This hydrogen bridge also explains why only the *E* isomer of the N1A═C1B imine unit is observed.

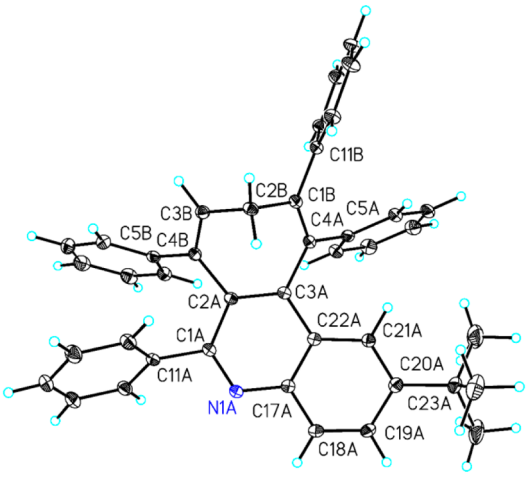

Figure 7. Molecular structure and numbering scheme of **1a**. The ellipsoids represent a probability of 30%, Hand atoms are shown with arbitrary radii. Selected bond lengths are given in Table 1.

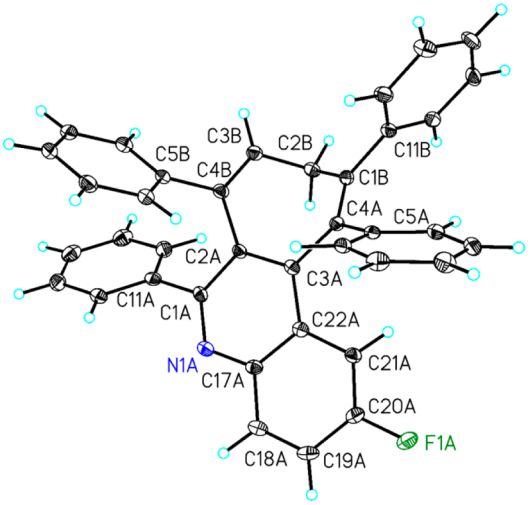

Figure 8. Molecular structure and numbering scheme of **1b**. The ellipsoids represent a probability of 30%, and H atoms are shown with arbitrary radii. Selected bond lengths are given in Table 1.

CONCLUSION

The s-block-metal-mediated hydroamination of diphenylbutadiyne with primary amines in THF requires the presence of 5−10 mol % of heterobimetallic $K_2[Ca\{N(H)Dipp\}_4]$; homometallic calcium bis(amides) did not initiate the hydroamination under similar reaction conditions. The substitution pattern of the arylamines and the reaction conditions strongly influence the reaction pathway. At high temperatures in

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Table 1. Comparison of Selected Bond Lengths (pm) of 2-*tert*-Butyl-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]quinoline (1a) and 2-Fluoro-6,7,10,11-tetraphenyl-9*H*-cyclohepta[*c*]quinoline (1b)

bond	**1a** (R = *t*Bu)	**1b** (R = F)
N1A−C1A	131.4(2)	131.4(3)
N1A−C17A	137.1(2)	138.0(3)
C17A−C18A	140.8(2)	141.5(3)
C17A−C22A	141.6(2)	141.5(3)
C18A−C19A	137.0(2)	137.5(4)
C19A−C20A	141.4(2)	138.7(4)
C20A−C21A	138.5(2)	136.4(3)
C20A−R	153.2(2)	136.3(3)
C21A−C22A	141.6(2)	141.9(3)
C1A−C2A	144.4(2)	144.2(3)
C1A−C11A	149.1(2)	149.6(3)
C2A−C3A	139.5(2)	139.5(3)
C2A−C4B	148.6(2)	148.3(3)
C3A−C4A	149.2(2)	148.6(3)
C3A−C22A	144.6(2)	146.2(3)
C4A−C5A	149.4(2)	149.4(3)
C4A−C1B	135.6(2)	135.8(3)
C1B−C2B	151.8(2)	151.1(3)
C1B−C11B	149.0(2)	149.3(3)
C2B−C3B	150.3(2)	150.5(3)
C3B−C4B	133.8(2)	132.8(3)
C4B−C5B	149.0(2)	149.2(3)

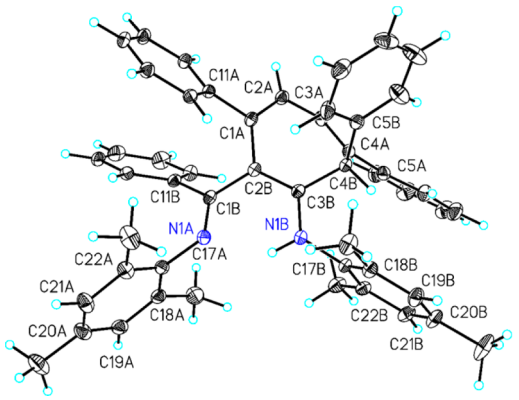

Figure 9. Molecular structure and numbering scheme of **2**. The ellipsoids represent a probability of 30%, and selected H atoms are shown with arbitrary radii. Selected bond lengths (pm): N1A−C17A 142.9(3), N1A−C1B 129.5(3), N1B−C17B 143.2(3), N1B−C3B 135.7(3), N1B−H 88(3), C1A−C2A 135.8(3), C1A−C2B 147.2(3), C1A−C11A 149.0(3), C2A−C3A 143.9(3), C3A−C4A 134.7(3), C4A−C5A 148.4(3), C4A−C4B 152.8(3), C1B−C2B 146.9(3), C1B−C11B 150.6(3), C2B−C3B 139.1(3), C3B−C4B 151.6(3), C4B−C5B 153.9(3).

refluxing THF the formation of *N*-aryl-2,5-diphenylpyrroles succeeds with moderate to high yields. A 2-fold addition of metal−nitrogen bonds to both C≡C triple bonds yields pyrrole rings with an aromatic character.

In contrast to the high-temperature route, the s-block-metal-mediated reaction of diphenylbutadiyne with arylamines at room temperature strongly depends on the substituents in ortho positions. During this reaction an amide reacts with two diphenylbutadiyne molecules. Cyclization leads either to a cyclohepta-1,2,4,6-tetraene intermediate or, via Bergman cyclization, to a methylidene−cycloheptatrienediyl radical. These highly reactive intermediates attack *o*-CH functionalities of the arylamine unit, leading to a quinoline derivative with a 2:1 ratio of butadiyne to arylamine. If *o*-CH groups are not available, another reaction pathway is pursued and the reactive intermediate traps another 1 equiv of arylamine, yielding a *β*-diketimine derivative which is annelated to a seven-membered ring. This *β*-diketimine crystallizes in the ene−amine form with a N−H···N hydrogen bridge and shows no significant conjugation with the attached multiple bonds of the annelated seven-membered ring. The performance of this s-block-metal-mediated hydroamination of diphenylbutadiyne at room temperature allows the synthesis of quinolone derivatives in the presence of *o*-CH functionalities.

Special attention has to be given to the advantageous properties of the catalyst system. The reaction of 4 equiv of KN(H)Dipp with calcium iodide in THF yields solvent-free $K_2[Ca\{N(H)Dipp\}_4]$.[17] The potassium ions bind to the amido anions and to the *π* systems of the aryl groups, leading to a coordination polymer in the solid state. Nevertheless, this complex is soluble in ethers. On the one hand, the rather bulky isopropyl groups in ortho positions prevent formation of ether adducts which commonly tend to slowly lose these neutral coligands upon standing and handling. Partial loss of coligands leads to weathering of the crystalline material and makes it difficult to exactly meet the stoichiometry. On the other hand, these isopropyl groups enhance intramolecular steric strain which can be released by a ligand exchange reaction and, therefore, in solution a fast substitution of the 2,6-diisopropylanilide anion by smaller amide ligands occurs. This initial amide exchange, which is much faster than the addition to the alkyne moieties, is the reason that $K_2[Ca\{N(H)Dipp\}_4]$ represents an ideal precatalyst for any hydroamination of diphenylbutadiyne with sterically less demanding primary arylamines. It is a common observation that heterobimetallic s-block-metal compounds often adopt reactivities different from those of their homometallic constituents.[5,27−30] These mixed-metal complexes form metalates[27,28] which are in some cases addressed as inverse crowns[29] and turbo Grignard or turbo Hauser reagents.[30]

In conclusion, thermodynamic control (in boiling THF) of s-block-metal-mediated hydroamination of diphenylbutadiyne with primary arylamines employing $K_2[Ca\{N(H)Dipp\}_4]$ yields *N*-aryl-2,5-diphenylpyrroles regardless of the bulkiness of the N-bound aryl groups, whereas kinetic control (at room temperature) leads to rather complex reaction pathways depending on the ortho substituents of the arylamines, where the formation of unsaturated seven-membered rings represents a key feature.

EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. The solvent was dried over KOH and subsequently distilled over sodium/benzophenone under a nitrogen atmosphere prior to use. Deuterated solvents were dried over sodium, degassed, and saturated with nitrogen. The yields given are not optimized. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AC 400 and AC 600 spectrometers. Chemical shifts are reported in parts per million relative to $SiMe_4$ as an external standard. The residual signals of the deuterated solvents $[D_8]$THF and CD_2Cl_2 were used as internal standards. The solvent-free and recrystallized precatalyst $K_2[Ca\{N(H)Dipp\}_4]$ was prepared according to a literature procedure.[17] A specific amount of this compound was dissolved in anhydrous THF, and aliquots of this solution were added to the reaction mixtures. This procedure allowed

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us to easily add definite amounts of precatalyst to the substrates under strictly anaerobic conditions. All substrates were purchased from Sigma-Aldrich, Merck, or Alfa Aesar and used without further purification.

General Procedure for the Synthesis of 2-Substituted 6,7,10,11-Tetraphenyl-9*H*-cyclohepta[*c*]quinolone (1; R = tBu, F). A 2 equiv amount of diphenylbutadiyne was dissolved in THF. Thereafter, 1 equiv of 4-*tert*-butylaniline and 5 mol % (with respect to the butadiyne) of the catalyst $K_2[Ca\{N(H)Dipp\}_4]_\infty$ were added. This solution was stirred for 3 days at room temperature. After hydrolysis with distilled water, extraction with diethyl ether, drying with sodium sulfate, and recrystallization from a mixture of dichloromethane and pentane at 5 °C, colorless crystals were isolated from an orange mother liquor.

Synthesis of 2. Diphenylbutadiyne (0.3 g 1.48 mmol) was dissolved in 15 mL of THF. Then, 0.21 mL of 2,4,6-trimethylaniline (0.2 g, 1.48 mmol) and 5 mol % of the calciate catalyst $K_2[Ca\{N(H)Dipp\}_4]_\infty$ were added. This reaction mixture was stirred for 3 days at oom temperature. A standard workup procedure included hydrolysis with 15 mL of distilled water, extraction with diethyl ether, drying with sodium sulfate, and recrystallization from a mixture of dichloromethane and pentane at 5 °C, yielding colorless crystals in a reddish brown mother liquor. Yield: 0.4 g, 0.59 mmol, 80%.

General Procedure for the Synthesis of *N*-Aryl-2,5-diphenylpyrroles 3. Diphenylbutadiyne (0.3 g 1.48 mmol) was dissolved in 17 mL of THF before 4-fluoraniline (0.164 g, 1.48 mmol) and 10 mol % of the calciate $K_2[Ca\{N(H)Dipp\}_4]_\infty$ (5 mol % at the beginning and 5 mol % after 3 days) were added, and the reaction mixture was heated for 6 days at 60 °C. Thereafter, the solution was hydrolyzed with 15 mL of distilled water and extracted with diethyl ether and the separated ether phase dried with sodium sulfate. Recrystallization from pentane at 5 °C yielded a colorless solid (0.40 g, 1.27 mmol, 85.8%) in an orange mother liquor.

X-ray Structure Determination. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semiempirical basis using multiple scans.[31−33] The structures were solved by direct methods (SHELXS)[34] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[34] The hydrogen atoms (with the exception of methyl groups C24, C25, and C26 of **1a** and **2**) were located by difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically.[34] Crystallographic data as well as structure solution and refinement details are summarized in the Supporting Information. The programs XP (Siemens Analytical X-ray Instruments, Inc.)[35] and POV-Ray[36] were used for structure representations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, a table, and CIF files giving preparative details and physical data of all reported compounds and crystallographic data of the crystal structure determinations as well as the NMR spectra of all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00449. Crystallographic data (excluding structure factors) have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-1062187 for **1a**, CCDC-1062188 for **1b**, CCDC-1062189 for **2**, CCDC-1062190 for **3c**, and CCDC-1062191 for **3d**. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail deposit@ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

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