Optimised synthesis of monoanionic bis(NHC)-pincer ligand precursors and their Li-complexes†

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Herein we report the optimised synthesis of a versatile bis(imidazole)carbazole framework 4, a precursor to our previously reported C=N–C bis(NHC) pincer ligand, bimca. We have also used 4 as a basis for constructing a library of fully characterised bis(imidazolium) salt pre-ligands which vary the steric and electronic parameters of the subsequently formed NHC moieties. Lithium bis(NHC)carbazolide complexes Li(bimca)§ were generated from their parent bis(imidazolium)carbazole salts, and their behavior in solution and the solid state is discussed.

Introduction

Following the seminal work of Moulton and Shaw on pincer-ligands 40 years ago, Peris, Crabtree and coworkers described the first neutral pincer ligand that bears two NHC moieties in 2001 and Douthwaite et al. synthesised the first monoanionic pincer ligand, which connects two NHC moieties via a diethylene amide backbone in 2004. In comparison to bidentate NHC- or classical pincer-ligands, the advantage of NHC derived pincer-ligands lies in the synergy of both the electron donating character of multiple NHCs that can stabilize higher oxidation states and activate metal centres in low oxidation states as well as through the chelating feature of the pincer geometry leading to a thermodynamic stabilization. In some cases the combination of these two features lead to interesting catalytic activity. Our work has seen the development of a rigid, fully sp3-hybridised ligand backbone with a central anionic pyrroldine-derived donor, flanked by two neutral NHC donors; 3,6-di-tert-butyl-1,8-bis(imidazol-2-ylidene)-9-carbazole (bimca)‡ (see Fig. 1).

The synthesis of the metal complexes bearing the bimca ligand is generally conducted via transmetallation from the respective lithium carbazolide carbene complexes Li(bimca)§. The highly air- and moisture sensitive compounds Li(bimca) Me and Li(bimca) Et were in situ generated by deprotonation of the respective imidazolium salts Hbimca Me2HBF4 with lithium bases such as methyl- or butyllithium with full conversion (NMR). Various transition metal complexes bearing the N-methylated ligand bimca Me were synthesised, amongst these a Rh(i) carbonyl complex which was used as an efficient nucleophilic catalyst. Recently, a series of N-protonated bimca complexes was reported by Grotjahn and co-workers.

In a previous publication we reported the synthesis of 3,6-di-tert-butyl-1,8-bis(imidazol-1-yl)-9-carbazole (4) as the base framework for the bimca ligand, starting from 9H-carbazole (1) via a 3-step synthesis in 16% yield (for numbers see Scheme 1). Due to the relatively low overall yield and the time consuming synthesis, the full potential of our bimca ligand (Fig. 1) and its organometallic derivatives remained untapped. To address these limitations, we now present an economic, scalable synthesis of 4 using readily available, air-stable precursors. Starting from compound 4 a small ligand library was prepared and the formation of the respective lithium complexes was studied.
Results and discussion

Improving the synthesis of bis(imidazolyl)carbazole 4

Our previous approach for the alkylation of 1 followed the procedure reported by Gibson and co-workers\(^7\) to access the dialkylated carbazole 2 in moderate yield (50–70%) after 24 to 72 h of reaction time. However, we found that the quality and quantity of the product obtained varied greatly with different batches of commercially obtained AlCl\(_3\) and dichloromethane.

This led us to follow the protocol of Liu \textit{et al.}\(^8\) using anhydrous ZnCl\(_2\) as the Lewis acid catalyst to obtain 2 in short reaction times (8 h) and excellent yields (95%) as a colourless crystalline material. This approach also allowed for large scale syntheses of 2 of up to 20 grams. Recently, Koskinen and co-workers used a related procedure with regard to the synthesis of 1,8-dibromo-3,6-di-tert-butyl-9H-carbazole.\(^9\) When working under non-anhydrous conditions we obtained a grey to bluish powder, which can be purified by column chromatography using n-hexane or petroleum ether to yield 2 in 90% yield. The identity and origin of these coloured impurities remain unknown.

For the synthesis of 3 we initially used the procedure provided by Nakada \textit{et al.}\(^{3,4}\) for 3,6-diphenyl-substituted species.\(^9\) The biggest disadvantages we faced were prolonged reaction times, laborious work up, and poor yields of 30%. Therefore, we screened for more successful iodination methods (Table 1) including variations of the Nakada\(^9\) procedure, as well as reactions with KI/KIO\(_3\),\(^9\) and KI/H\(_2\)O\(_2\)/NaOAc.\(^9\) To our disappointment, all of these synthetic protocols (entries 1–3) were associated with tedious workup, requiring the removal of mixtures of monoiodinated carbazole and other unidentified species. These workups led to poor or immeasurably low yields of the desired product. Fortunately, reactions using BTMA\(_2\)I\(_2\)\(^{9d,e}\) (entry 4) or commercially available iodine monochloride\(^9\) (entry 5) yielded 3 in good to very good yields whilst also providing a simple workup.

Best results were achieved by using iodine monochloride as an iodine source in acetic acid with zinc chloride\(^9\) at 60 to 75 °C (entry 8), whereas higher reaction temperatures led to complete decomposition of the iodine monochloride and no product formation (entry 9). After recrystallization from petroleum ether, we obtained colourless microcrystalline 3 in very good yields (80%).

In an effort to further streamline this portion of the synthesis we developed a stepwise one-pot procedure combining the Friedel–Crafts alkylation of 1 and the iodination of 2 (Scheme 1). Although nitromethane had to be removed after the alkylation step, the resulting di-tert-butyl carbazole 2 was produced in sufficient purity to proceed immediately to the subsequent iodination. After workup, diiodocarbazole 3 was isolated in 60% yield in one pot from carbazole (vs. 76% for the two step reaction).

For the synthesis of bis(imidazole) 4 through an Ullmann coupling, we substituted the costly and air sensitive (CuOTf)\(_2\)-PhH\(_4\) catalyst for Cu\(_2\)O following a report by Tronnier and Strassner.\(^10\) The synthetic benefits of this procedure are two-fold: improved yields of up to 95% were readily achieved in about half the reaction time of our previously reported method, and in our hands this reaction proved to be reliably scalable. The base compound 4 is storable and offers numerous possibilities for further modification at the imidazole moieties, particularly for functionalization at their unsubstituted nitrogen atoms. The overall synthesis of bis(imidazole) 4 can now be

![Scheme 1 General synthesis of the bisimidazolium salts 5a–i and the lithium pincer complexes 6a–l including improved synthesis of bis(imidazole) 4.](image)
performed straightforwardly on a 20 g scale within four days and a total yield of 72%.

**Synthesis and characterization of bis(imidazolium) salts 5**

In general, the electronic and steric properties of NHC ligands play a crucial role in the catalytic activity and/or selectivity of the resulting metal complexes. The most facile approach to tuning these parameters often begins with altering their N-substituents. Therefore, we decided to prepare a small library of imidazo-5h salts (5a–i) derived from 4 (Table 2). The alkylation of 4 works very effectively with typical alkylation agents like Meerwein’s reagents (R₂OBF₄) or iodomethane to yield the N-allyl imidazolium salts Hbimca⁻MC₂HBF₄ (5a) (entry 1), Hbimca⁻MC₂HI (5a') (entry 2) as well as Hbimca⁻MC₂HBF₄ (5b) (entry 3). Treatment with propyl bromide, isopropyl bromide or iodide, allyl bromide and benzyl bromide in acetonitrile gave the corresponding imidazolium salts 5c–e, and 5g in good to excellent yields (Table 2, entries 4–6, 8). We also synthesised the macrocyclic system 5f where both imidazolium moieties are linked via a C₅ allyl chain, by reacting 4 with 1,5-dibromopentane (Table 2, entry 7). Reactions with 1,4-dibromobutane and 1,6-dibromohexane failed to give the desired product under these conditions.

The preparation of imidazolium salts 5h and 5i, which bear N-aryl functionalities, posed a synthetic hurdle since these could not be furnished using a straightforward nucleophilic substitution reaction. Our attempts to react 4 with aryl halides or diazonium salts did not result in the formation of imidazolium products. Instead, we adapted a synthesis reported by Gao and coworkers which comprised the use of highly electrophilic diphenyldesium tetrafluoroborate in the presence of a copper catalyst. In our hands the use of the most efficient catalyst from Gao’s report, Cu(OAc)₂, did not result in product formation. We assume that during the reaction, rapid deprotonation of the nascent imidazolium salt 5h by the basic Cu(OAc)₂ led to deactivation of the catalyst. This problem was overcome by substituting Cu(OAc)₂ for the less basic CuCl₂, which provided a successful route to the diphenyl substituted 5h in 55% isolated yield (Table 2, entry 9).

In contrast to the introduction of aryl groups, electron poor pyridyl moieties can be introduced at high temperature via nucleophilic ipso-substitution of halopyridines. In our case, the reaction of 4 with neat 2-chloropyridine at 190 °C yielded the bis(imidazolium) salt 5i in 63% yield (Table 2, entry 10).

Single crystals of the imidazolium salts 5d–h were obtained by crystallization from an oversaturated solution in dichloromethane or isopropanol (Fig. 2). Due to the various possibilities for hydrogen bonding, co-crystallised solvent is observed in almost every case. Furthermore, all imidazolium salts show short contacts between the carbazole NH and the imidazolium C₂ protons and their respective counterions. In the case of the i-Pr substituted imidazolium salt 5d, this leads to deviations between the N–C–N angles of the two imidazolium moieties, as one i-Pr group exhibits a short contact to the bromide counterion. Various bis(imidazolium) salts are known for their anion recognition abilities. But due to this varying degree of anion binding, no clear trend of the electronic influence of the N-substituent and the N–C–N angle in the solid state could be deduced.

In contrast, a clear dependence of the electronic influence of the N-substituents on the imidazolium C₂⁻H ᵃ⁻C₃ coupling constant was identified in the solution state via ¹H NMR spectra (Table 3). A substituent with a strong electron withdrawing effect (−I) serves to enhance the electron withdrawal of the nitrogen atoms and thus, according to Bent’s rule, gives higher p-character to the N–C–N σ-bonds. As a consequence the s-character of the C–H bond is increased resulting in a larger C–H coupling constant. Although the differences are within a range of only 4 Hz, the trend is clear: the imidazolium moieties of the i-Pr substituted 5d with the weakest −I effect show the smallest coupling constant (222.8 Hz for Br⁻ and 223.0 Hz for I⁻ as counterion) and with an increasing −I effect in the series N-n-propyl (5e), N-ethyl (5b), N-methyl (5a) the coupling constants increase to 224.0 Hz. The electron withdrawing N-aryl (5e), N-phenyl (5h) and N-pyridyl (5i) substituents lead to a further increase of ᵃ⁻C₃ from 224.6 (5e) to 226.4 Hz (5i). The coupling constant appears to be independent of the counter ion (cf. 5a, 5a' and 5d, 5d'). The ¹H NMR chemical shift of the H-2' signals follow the same overall trend. The signal for the most deshielded proton can be found for Hbimca⁻MC₂HCl (5i) at δ = 11.08 ppm. This is in accordance with the higher acidity of the C2'-H group due to the higher s-character of the carbon orbital in this bond. However, the influence of the anion cannot be neglected, as imidazolium salts often show hydrogen bonding interactions to...

### Table 2. Synthesis of the Hbimca⁻2HCl library 5a–i

| Entry | Reagent | Product (Scheme 1) | Yield (%) |
|-------|---------|--------------------|-----------|
| 1ᵃ    | Me₂OBF₄ | 5a                 | 78ᵃ       |
| 2     | Me₂Cl   | 5a'                | 99ᵃ       |
| 3ᵇ    | Et₂OBF₄ | 5b                 | 78ᵇ       |
| 4ᵇ    | Br⁻      | 5c                 | 80ᵇ       |
| 5ᵉ    | I⁻       | 5d                 | 91ᵉ       |
| 5ᵣ    | Br⁻      | 5d'                | 83ᵣ       |
| 6ᵉ    | Br⁻      | 5e                 | 65ᵉ       |
| 7ᵉ    | Br⁻      | 5f                 | 68ᵉ       |
| 8ᵉ    | Br⁻      | 5g                 | 70ᵉ       |
| 9ᵣ    | BF₄⁻     | 5h                 | 55ᵣ       |
| 10ᵣ   | Cl⁻      | 5i                 | 63ᵣ       |

Reagents and conditions: ᵃ MeCN, at room temperature. ᵇ MeCN, 50 °C, 5 d. ᵈ DMF, 70 °C, 5 d. ᵇ MeCN, reflux, 4 d. ʰ MeCN, 80 °C, 24 h. ˢ DMF, 100 °C, 8 h. ʰ Neat, 190 °C, 14 h. ᵃ Over 2 steps. See Experimental section for details.
their counterions not only in the solid state, but also in solution. Nevertheless, as HbimcaMe$_2$HBF$_4$ (5a) shows almost the same shielding as HbimcaMe$_2$HI (5a') for the respective H-2’ proton, this trend coincides nicely with the course of the $J_{\text{C,H}}$ coupling constants, if the influence of the counterion as well as possible steric effects are taken into account. This data provides evidence that bulkier $N$-alkyl groups, e.g. i-Pr in 5d, lead to a lower s-character in the C2’-H bond compared to 5a whereas the $N$-aryl and $N$-heteroaryl substituted imidazolium salts 5h,i show a stronger s-character in the carbon orbital of the C2’-H bond, which is consistent with the –I effect of the respective imidazolium $N$-substituents.

**Synthesis and characterization of Li(bimca$^\text{R}$) complexes 6**

In analogy to the previously reported deprotonation of the imidazolium salt 5a to the corresponding Li(bimca$^\text{Me}$) complex 6a$^1$ the deprotonation of the imidazolium species 5a-f, and h,i with three equivalents of methyllithium or $n$-butyllithium in THF or $n$-hexane results in the formation of a yellow (6a–d), orange (6e,f) or red (6h,i) solution with a strong blue fluorescence under UV light. In the case of 5g, the deprotonation leads to decomposition of the imidazolium salt, which we attribute to side reactions at the benzylic methylene group. This undesired reactivity may be avoided by choosing a more selective base. All Li(bimca$^\text{R}$) complexes are highly air and moisture sensitive so that they are best prepared and characterized in situ.

The $^1$H NMR spectra of the formed Li(bimca$^\text{R}$) complexes 6 show the absence of the carbazole NH and imidazolium C2’-H signals, thus indicating the clean formation of Li(bimca$^\text{R}$) complexes 6. The retention of signals originating from chemically equivalent pairs of nuclei across the whole ligand indicates

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Fig. 2  Molecular structures of the imidazolium salts 5d (top left), 5e (top right), 5f (bottom left) and 5h (bottom right). Atoms are shown with anisotropic atomic displacement parameters at the 50% probability level. Short contacts between selected hydrogen atoms and the respective anions are shown. In all cases co-crystallised solvent molecules are omitted for clarity.
that the symmetry is maintained upon Li coordination in solution. Due to the low electronegativity of the lithium cation, the Li–NHC bond is mostly ionic in character, which is generally reflected by only a small upfield shift of the $^{13}$C NMR carbene signal compared to that observed for free NHCs.$^{17}$

In the literature, $^{13}$C NMR chemical shifts for imidazolin-2-ylidene derived NHCs that contain a monoanionic linker and are coordinated to a lithium cation, can be found just below 200 ppm.$^{16}$ In comparison to those values, the signals for our lithium complexes 6 are less upfield shifted. The chemical shifts for the carbenic carbons of the N-alkylated systems range from 203.7 ppm ($6d$, $R$ = $i$-Pr) to 206.1 ppm ($6a$, $R$ = Me) and from 205.5 ppm ($6h$, $R$ = Ph) to 205.8 ppm ($6i$, $R$ = Py) for the N-arylated systems. These values follow almost the same trend as the coupling constants in the corresponding imidazolium salts 5. The somewhat lower chemical shift of the N-arylated species might be due to additional shielding caused by the aromatic substituents. In comparison with the aforementioned literature compounds we conclude that both NHC moieties are coordinated to one Li atom in solution, which accounts for the less pronounced upfield shift by the incremental effect of the second NHC moiety.

Recently, Hofmann and coworkers described Li–NHC complexes of neutral bis(NHC) ligands coordinating to one lithium center. The $^{13}$C NMR shifts for the carbene atoms range between 206 and 212 ppm depending on the counterion; 211.9, 211.1 ppm (bromide ion), and 205.9 ppm (PF$_6^-$ ion).$^{18}$ These values support an incremental influence on the chemical shift of each coordinated carbene moiety. The chemical shifts of compounds $6a$–$e$ and $h,i$ are in accordance with these reported values for bis(NHC) ligands. The fact that we cannot recognise any dependence of the carbene chemical shift on the former counterion of the imidazolium precursors $5a$–$i$ can be explained by the negative charge already present in the ligand itself and suggests that there is no LiX Li(bimca) interaction in solution, cf. solid state molecular structure of $6d$ (Fig. 3). However, the fact that no Li–C coupling is observed in the $^{13}$C NMR spectrum indicates a fast exchange with the generated Li-salts. This is corroborated by the fact that the $^7$Li NMR spectra of Li complexes show a broad and unspecific signal.

Crystals of freshly prepared $6d$ suitable for X-ray structure analysis were grown from a DME solution as pale yellow rectangular plates. The solid state structure of $6d$ (Fig. 3) shows
each NHC moiety of the pincer ligand coordinated to one of the two crystallographically independent lithium cations. The additional coordination of an iodide as well as a DME molecule to both lithium cations (Li1–N–Li2 angle: 97.3(5)°). This k-N mode of amides is common for lithium, but has been observed only once before for Li–NHC complexes (Li–N–Li = 73.1° (mean)). A Li–iodide coordination in this k-N mode has only been reported once before in a Li–borazole complex.20 The lengths of both carbene–lithium bonds are nearly identical; 2.142(11) Å (C1–Li1), 2.131(11) Å (C7–Li2), and in the range reported for typical NHC lithium interactions.19,21

Characteristic for NHC complexes is that the average N–C–N angle is about 5° smaller compared to the related azolium precursor (103.6(5)° vs. 109.3(7)°) and that the endocyclic N–C bonds are slightly elongated in the lithium complex. In comparison to the respective free carbenes, the N–C–N angle is widened by 2–3°.22 Due to the different coordination sphere of both lithium centers (DME vs. iodide), the complex is unsymmetrical in the solid state. This seems to be in contrast to our observations in solution, wherein the NMR spectroscopic data provides evidence for a symmetrical complex. This can be explained by either the fast exchange of the lithium cation as evidenced by the 13C and the 7Li NMR spectra or the influence of the DME coligand. So far, it cannot be deducted whether in solution a monometalic species with an unfavoured four-coordinated distorted geometry is present, and the solid state structure simply provides a snapshot of the lithium cation exchange intermediate, or whether a bimetallic species that undergoes fast exchange is the favoured species in solution. Attempts to crystallise complex 6d from other ethereal solvents, e.g. THF and diethyl ether were unsuccessful.

All described lithium NHCs 6 are stable for months and good to handle under the strict exclusion of oxygen and moisture. This and the fact that they are easy to prepare in situ makes them highly suitable for the use as transmetallation reagents.

Conclusions

An optimised synthetic route to the carbazole based bis-(imidazolyl) pincer ligand framework 4 is presented. This new route benefits from a streamlined workup and the elimination of air-sensitive techniques to afford the desired intermediate in good yield over a short time frame. We have demonstrated that this framework provides a platform from which N-functionalised derivatives can be easily accessed by general protocols for the N-alkylation, N-arylation, and N-heteroarylation at the imidazolide moieties. Thus, a small ligand library 5a–i and their corresponding lithium complexes 6a–i was constructed and fully characterised (excepting 6g). The donor ability of these ligands, particularly the NHC moieties, reveal a trend on the basis of their solution state behavior. This trend is determined by the electronic properties borne from the N-functionalities of these NHC fragments. It was found that the N-i-Pr substituted 6d appears to be the strongest donor, and N-aryl and N-heteroaryl 6h,i the weakest, respectively. The use of these Li(bimca®) complexes as transmetallation agents for the synthesis of transition metal, s- and p-block metal pincer complexes is underway in our labs.

Experimental

Syntheses

1,8-Diiodo-3,6-di-tert-butylcarbazole (3). 1,8-Diiodo-3,6-di-tert-butylcarbazole (2) (10.0 g, 35.8 mmol, 1 eq.) and ZnCl2 (12.2 g, 89.6 mmol, 2.5 eq.) were dissolved in 700 mL acetic acid and heated to 60 °C. To this solution was added ICl (4.12 mL, 78.7 mmol, 2.2 eq.) dropwise. After stirring the solution at 60 °C for 3 h it was heated to 75 °C for 2 h. The solution was cooled to room temperature and added portionwise to 1 L of water. The precipitate was filtered off, dissolved in 400 mL dichloromethane, washed with a saturated sodium sulfite solution (3 ×, 75 mL) and dried over MgSO4. The solvent was evaporated in vacuo and product 3 remained as a colourless powder. Yield: 80% (15.2 g). The signals of the NMR spectra are consistent with the literature.4

3,6-Di-tert-butyl-1,8-bis(imidazol-1-yl)carbazole (4). 1,8-Diiodo-3,6-di-tert-butylcarbazole (3) (17.0 g, 32.0 mmol, 1 eq.), imidazole (7.63 g, 112 mmol, 3.5 eq.), KOH (6.28 g, 112 mmol, 3.5 eq.) and CuO (0.46 g, 3.2 mmol, 0.1 eq.) were suspended in 50 mL dimethylsulfoxide. The red suspension was heated to 120 °C for 2 days. After reduction of the solvent to 5 mL it was added to a solution of ammonia and ammonium chloride. The precipitate formed was filtered off and recrystallised from ethanol. The raw material was taken up in 100 mL THF and filtered. Removing the solvent in vacuo gives product 4 as a colourless powder. Yield: 95% (12.5 g). The signals of the NMR spectra are consistent with the literature.4

(Hbimca®)ZnBF4 (5b). To a suspension of 3,6-di-tert-butyl-1,8-bis(imidazol-1-yl)carbazole (4) (842 mg, 2.05 mmol) in 20 mL of dry acetonitrile was added triethylamine tetrafluoroborate (Meerwein’s salt) (Et3OBF4) (605 mg, 4.10 mmol), upon which the suspension became a yellow solution. After stirring for one hour, the solvent was removed in vacuo. The residue was washed three times with water (20 mL each) and recrystallised from ethanol to obtain colourless crystals. Yield: 78% (1.03 g). Mp 299–302 °C (dec.). 1H NMR (300.13 MHz, DMSO-d6): δ 1.46 (s, 18H, H-10), 1.56 (t, JHH = 7.4 Hz, 6H, H-13), 4.32 (q, JHH = 7.4 Hz, 4H, H-12), 7.77 (s, 2H, H-2,7), 8.14 (s, 2H, H-4’), 8.28 (s, 2H, H-5’), 8.63 (s, 2H, H-4,5), 9.77 (s, 2H, H-2’), 11.52 (s, 1H, NH). 13C(1H) NMR (75.47 MHz, DMSO-d6): δ 14.8 (C13), 31.6 (C10), 34.9 (C11), 44.7 (C12), 119.1 (C1/8), 119.3 (C4/5), 120.9 (C2/7), 122.5 (C4’), 123.4 (C5’), 125.4 (C4a/ 5a), 132.1 (C1a/8a), 136.9 (C2’), 143.8 (C3/6). MS (ESI+): m/z (%) 556 [M-BF4]+ (60), 469.7 [M-2BF4]+ (13), 235.0 [M-2BF4H]+ (100). IR (KBr, cm−1): 3151 (w), 2957 (s), 2868 (m), 1598 (m), 1573 (m), 1552 (m), 1498 (m), 1450 (m), 1365 (m), 1298 (m), 1265 (m), 1229 (w), 1204 (s), 1144 (vs), 1057 (w), 876 (w), 839 (w), 742 (w), 655 (w), 624 (w). EA: calcd for C30H39N5B2F8: C 56.01, H 5.89; found: C 55.75, H 6.11, N 10.80.
HbimcaBr)2HBr (5c). To a suspension of 3,6-di-tert-butyl-1,8-bis(imidazol-1-yl)carbazole (4) (200 mg, 0.49 mmol, 1 eq.) in dimethylformamide (2 mL) was added 2-bromopropane (0.23 mL, 2.4 mmol, 5 eq.). The mixture was heated to 70 °C for 3 days. 4 mL of diethyl ether were added, the obtained beige solid was filtered and washed with cold diethyl ether (3 × 2 mL). Recrystallisation from ethanol led to compound 5d as a colourless, microcrystalline solid. Yield: 91% (630 mg). Mp 350 °C (dec.). 1H NMR (400.11 MHz, DMSO-d6): δ 1.47 (s, 18H, H-10), 1.62 (d, JHH = 6.8 Hz, 12H, H-13), 4.77 (sept, JHH = 6.8 Hz, 2H, H-12), 7.75 (d, JHH = 1.5 Hz, 2H, H-2,7), 8.26 (t, JHH = 1.8 Hz, 2H, H-5,4), 8.35 (t, JHH = 1.8 Hz, 2H, H-5), 8.62 (d, JHH = 1.5 Hz, 2H, H-4,5), 9.99 (t, JHH = 1.5 Hz, 2H, H-2,7). 13C{1H} NMR (101.61 MHz, DMSO-d6): δ 124.1 (C5), 125.9 (C4a/5a), 120.1 (C4/5), 120.4 (C2/7), 123.5 (C4), 120.3 (C2), 121.1 (C1), 121.4 (C4). 13C{1H} NMR signals were assigned via 1H–13C HSQC spectra due to bad quality of the 13C-NMR spectrum. Signals for the quaternary carbon atoms could not be assigned. MS (FAB+): m/z (%) 576.2 [M-HBr]+ (15), 496.3 [M-2Br-H]+ (100), 454.3 [M-2Br-Pr]+ (18). EA: caled for C32H43Br2N2: C 55.62, H 6.69, N 10.15. The same procedure was suitable to synthesise 3,6-di-tert-butyl-1,8-bis(3-isopropylimidazoliodiazol)carbazole diiodide 5f from 2-iodopropane in 75% yield as a white powder.

HbimcaBr)2HBr (5f). A 50 mL Schlenk tube was charged with 3,6-di-tert-butyl-1,8-bis(imidazol-1-yl)carbazole (4) (150 mg, 0.37 mmol), a large stirring bar and acetonitrile (10 mL). To this reaction mixture was slowly added 1,5-dibromopentane (0.10 mL, 0.74 mmol, 1.1 eq.) After 5 d at 80 °C the beige-coloured solution was concentrated to dryness in vacuo, the residue redissolved in dried ethanol (5 mL) and precipitated by adding the same amount of diethyl ether. The off-white solid was filtered off, washed with hexane (10 mL) and dried in vacuo. Yield: 68% (162 mg). Mp 304 °C (dec.). 1H NMR (400.11 MHz, DMSO-d6): δ 1.46 (s, 18H, H-10), 1.67 (m, 4H, H-14), 1.79 (m, 4H, H-13), 4.36 (m, 4H, H-12), 7.80 (dd, JHH = 1.5 Hz, 2H, H-2,7), 8.08 (t, JHH = 1.6 Hz, 2H, H-4,5), 8.29 (t, JHH = 1.6 Hz, 2H, H-5,4), 8.61 (d, JHH = 1.4 Hz, 2H, H-4,5), 9.76 (s, 2H, H-2,7), 11.20 (s, 1H, NH). 13C{1H} NMR (100.61 MHz, DMSO-d6): δ 134.7 (C14), 158.2 (C15), 26.2 (C3/6). 13C{1H} NMR (100.61 MHz, DMSO-d6): δ 134.7 (C14), 158.2 (C15), 26.2 (C3/6). HRMS (ESI+): m/z (%) 572.2 [M-Br]+ (15), 492.3 [M-2Br-H]+ (100). EA: caled for C32H28N2Br2: 0.5C6H5Cl2: C 55.77, H 6.34, N 10.00; found: C 56.43, H 5.45, N 9.61.
in vacuo to dryness and the crude product was recrystallised from isopropanol to afford the product $5g$ as a white solid. Yield: 61% (366 mg). Mp 309 °C (dec.). 1H NMR (400.14 MHz, DMSO-$d_6$): δ 1.46 (s, 18H, H-10), 5.78 (s, 4H, H-12), 7.35–7.48 (m, 6H, H-14, H-16), 7.59 (d, $J_{HH} = 1.6$ Hz, 2H, H-2/7), 7.66–7.77 (m, 4H, H-15), 7.82 (t, $J_{HH} = 1.7$ Hz, 2H, H-4'), 8.00 (t, $J_{HH} = 1.7$ Hz, 2H, H-5'), 8.36 (d, $J_{HH} = 1.6$ Hz, 2H, H-4/5), 10.87 (br s, 2H, H-2'), 12.12 (br s, 1H, NH). 13C{1H} NMR (100.61 MHz, DMSO-$d_6$): δ 31.7 (C10), 35.0 (C11), 128.3 (C4a/5a), 128.5 (C1/8), 135.6 (C3/6), 143.8 (C3/6). MS (FAB+): m/z (%) 672.3 [M-Br-H]+ (14), 592.3 [M-2Br-H]+ (100). EA: calcd for C$_{48}$H$_{65}$N$_2$Br$_2$: C 62.65, H 5.50, N 9.09.

**Diphenyliodonium tetrafluoroborate**

Chloroperbenzoic acid (81% active oxidant, 610 mg, 2.90 mmol) was dissolved in 7.50 mL of dimethylformamide (100). The suspension was allowed to stir for 30 min, then cooled to 0 °C and then dried. Diphenyliodonium salt. The suspension was allowed to stir for 30 min, then cooled to 0 °C and stored at room temperature for 1 h. After this time hexane (60 mL) was added via cannula to the DME solvato complex as pale yellow rectangular plates. Solvent characterization were grown from a DME solution of 1H NMR (500.13 MHz, THF-$d_8$): δ 1.50 (s, 18H, H-10), 1.58 (s, $J_{HH} = 7.3$ Hz, 6H, H-13), 4.28 (d, $J_{HH} = 7.3$ Hz, 4H, H-12), 7.21 (s, 2H, H-4'), 7.40 (s, 2H, H-2/7), 7.76 (s, 2H, H-5), 8.00 (d, $J_{HH} = 1.5$ Hz, 2H, H-4/5). 13C{1H} NMR (125.77 MHz, THF-$d_8$): δ 17.3 (C3), 32.9 (C10), 35.3 (C11), 46.8 (C12), 111.6 (C27), 114.2 (C45), 118.7 (C4'), 119.5 (C5'), 128.3 (C4a/5a), 128.5 (C1/8), 135.6 (C3/6), 143.8 (C1a/8a), 204.7 (C2').

**Li(bimca$^+$)**

In the glove-box lithium disopropylamide (LDA) (5.2 mg, 49 μmol) was added to a suspension of 1,1,4,4-tetramethyl-1,8-bisimidazol-1-yl)-carbazole (4) (500 mg, 730 μmol) was added to the crude product. The suspension was allowed to settle and the pale amber, fluorescent blue solution was stirred at room temperature for 1 h. After this time hexane (60 mL) was added via cannula to precipitate the beige, extremely moisture sensitive solid. The remaining solid was dried under vacuum to give the desired Li-(bimca$^+$). The product was stable in solution for 1 day, but decomposed upon removal of the solvent in vacuo. 1H NMR (500.13 MHz, THF-$d_8$): δ 1.50 (s, 18H, H-10), 1.58 (s, $J_{HH} = 7.3$ Hz, 6H, H-13), 4.28 (d, $J_{HH} = 7.3$ Hz, 4H, H-12), 7.21 (s, 2H, H-4'), 7.40 (s, 2H, H-2/7), 7.76 (s, 2H, H-5), 8.00 (d, $J_{HH} = 1.5$ Hz, 2H, H-4/5). 13C{1H} NMR (125.77 MHz, THF-$d_8$): δ 17.3 (C3), 32.9 (C10), 35.3 (C11), 46.8 (C12), 111.6 (C27), 114.2 (C45), 118.7 (C4'), 119.5 (C5'), 128.3 (C4a/5a), 128.5 (C1/8), 135.6 (C3/6), 143.8 (C1a/8a), 204.7 (C2').

**Li(bimca$^-$)**

**Li(bimca$^-$)**

Procedure A: A hexane solution of n-butyl lithium (0.26 mL, 0.48 mmol) was added to a stirred THF suspension (20 mL) of the bis(imidazolium) salt $5d'$ (0.120 g, 0.16 mmol), via syringe, to immediately give a yellow then pale amber, fluorescent blue solution which was stirred at room temperature for 1 h. After this time hexane (60 mL) was added via cannula to precipitate the beige, extremely moisture sensitive product. The remaining solid was dried under vacuum to give Li(bimca$^+$)-Li $6d$ as a pale amber. Yield: (48 mg, 47%). Mp 213–214 °C (dec.). Crystals suitable for X-ray structural characterization were grown from a DME solution of $6d$ yielding the DME solvato complex as pale yellow rectangular plates. Solvent included in the solid state is labile under vacuum. 1H NMR (400 MHz, THF-$d_8$): δ 1.49 (s, 18H, H-10), 1.63 (d, $J_{HH} = 6.8$ Hz, 12H, H-13), 4.72 (sept, $J_{HH} = 6.8$ Hz, 2H, H-12), 7.25 (d, $J_{HH} = 1.7$ Hz, 2H, H-4'), 7.39 (t, $J_{HH} = 1.7$ Hz, 2H, H-4/5), 7.77 (d, $J_{HH} = 1.7$ Hz, 2H, H-4/5), 7.98 (t, $J_{HH} = 1.7$ Hz, 2H, H-4/5). 13C{1H} NMR (100 MHz, THF-$d_8$): δ 24.3 (C13), 32.8 (C10), 35.1 (C11), 53.4 (C12), 110.9 (C27), 114.0 (C45), 119.5 (C5'), 119.8 (C5'), 128.0 (C6), 128.1 (C9), 135.2 (C3/6), 143.5 (C1a/8a), 206.2 (C2'). 7Li{1H} NMR
(97.21 MHz, THF-d$_8$): $\delta$ = 1.17. IR (nujol, cm$^{-1}$): 1664 (m), 1574 (m), 1547 (w), 1226 (m), 1169 (m), 1154 (m), 1079 (w), 10718 (w), 892 (w), 844 (m), 723 (m). The elemental analysis of 6d consistently revealed a carbon composition higher than expected for Li(bimca$^{(9)}$)-Li. This outcome is likely due to the inclusion of THF in the solid product. EA: calcd for C$_{32}$H$_{40}$N$_5$Li: C 59.00, H 6.19, N 10.75; found: C 59.70, H 5.53, N 11.46.

Due to their high sensitivity towards air and moisture no elemental analysis of compounds 6 were measured.

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