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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^{R}) 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,[1] Peris, Crabtree and coworkers described the first neutral pincer ligand that bears two NHC moieties in 2001[2a] and Douthwaite *et al.* synthesised the first monoanionic ligand, which connects two NHC moieties *via* a diethylene amide backbone in 2004.[2b] 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[3] as well as through the chelating feature of the pincer geometry[1] leading to a thermodynamic stabilization. In some cases the combination of these two features lead to interesting catalytic activity.[3b–e] Our work has seen the development of a rigid, fully sp^2-hybridised ligand backbone with a central anionic pyrrolide-derived donor, flanked by two neutral NHC donors; 3,6-di-*tert*-butyl-1,8-bis(imidazolin-2-ylidene)-9-carbazolide (bimca)‡ (see Fig. 1).[4]

The synthesis of the metal complexes bearing the bimca ligand is generally conducted *via* transmetallation from the respective lithium carbazolide carbene complexes Li(bimca^{R}). 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^{R}·2HBF$_4$ with lithium bases such as methyl- or butyllithium with full conversion (NMR). Various transition metal complexes bearing the *N*-methylated ligand bimca^{Me} have been synthesised, amongst these a Rh(I) carbonyl complex which was used as an efficient nucleophilic catalyst.[5] Recently, a series of *N*-protonated bimca complexes was reported by Grotjahn and co-workers.[6]

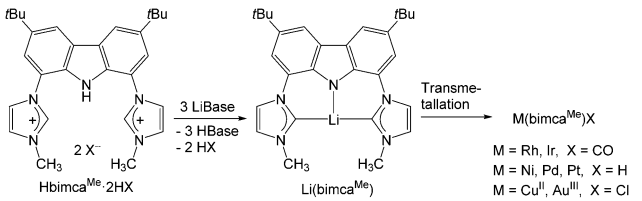

Fig. 1 Synthesis of lithium NHC-pincer complex Li(bimca^{Me}) from the bis(imidazolium) salt Hbimca^{Me}·2HBF$_4$ and its use as a transmetallation agent.

In a previous publication[4] 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 9*H*-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.

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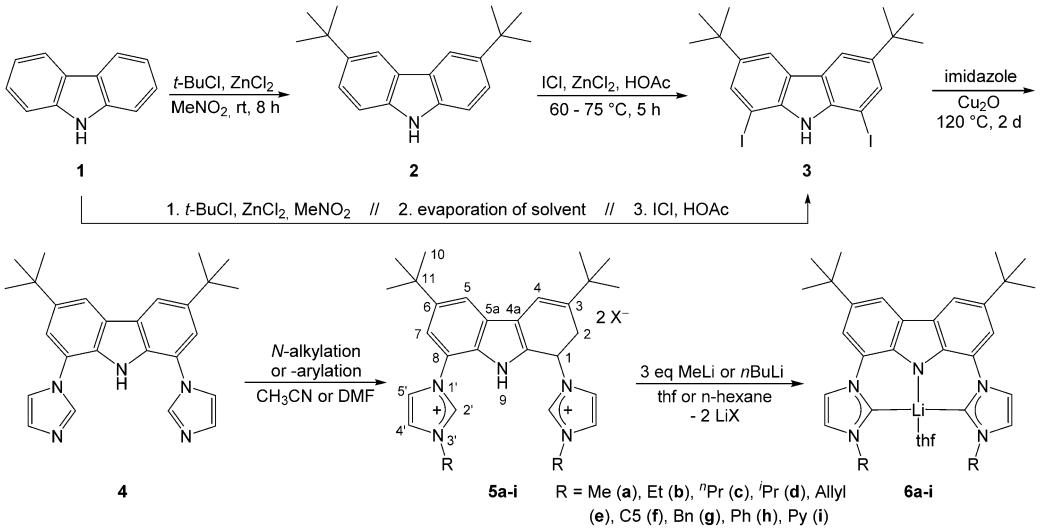
† Electronic supplementary information (ESI) available: CIF files providing experimental and crystal data for compounds **5b**, **5d′**, **5d–5h** and **6d**, as well as NMR spectra of all new compounds. CCDC 1472375 (**5b**), 1472369–1472374 (**5d–h**, and **6d**), and 1501070 (**5d′**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6nj01941b

‡ The acronym bimca is derived from bis(imidazolin-2-ylidene)carbazolide.



Scheme 1 General synthesis of the bisimidazolium salts **5a–i** and the lithium pincer complexes **6a–i** including improved synthesis of bis(imidazole) **4**.

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 *et al.*[8a] 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-9*H*-carbazole.[8b] 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 *et al.* for 3,6-diphenyl-substituted species.[9a] 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[9a] procedure, as well as reactions with KI/KIO_3[9b] and KI/H_2O_2/NaOAc.[9c] 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·ICl_2[9d,e] (entry 4) or commercially available iodine monochloride[9f] (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[9g] 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%).

Table 1 Optimisation of the iodination of carbazole **2** to diiodocarbazole **3**

Entry	Iodine source	Co-reagents	Solvent	T [°C]	t [h]	Yield of **3** [%]
1	I_2	KIO_4, H_2SO_4	AcOH/H_2O	80	8	30
2	KI	KIO_3	AcOH	40	8	0
3	KI	NaOAc, H_2O_2	AcOH	40	8	0
4	BTMA·ICl_2	H_2SO_4	AcOH	60		64–80
5	ICl	—	AcOH	60	5	65
6	ICl	—	1,4-Dioxane	60	5	10
7	ICl	—	$MeNO_2$	40	5	<10
8	ICl	$ZnCl_2$	AcOH	60–75	5	80
9	ICl	$ZnCl_2$	AcOH	90	3	0

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 $(CuOTf)_2 \cdot PhH$[4] catalyst for Cu_2O 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

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.[11] The most facile approach to tuning these parameters often begins with altering their *N*-substituents. Therefore, we decided to prepare a small library of imidazolium salts (**5a–i**) derived from **4** (Table 2). The alkylation of **4** works very effectively with typical alkylating agents like Meerwein's reagents (R_3OBF_4) or iodomethane to yield the *N*-alkyl imidazolium salts Hbimca^{Me}·2HBF$_4$ (**5a**) (entry 1), Hbimca^{Me}·2HI (**5a′**)[4] (entry 2) as well as Hbimca^{Et}·2HBF$_4$ (**5b**) (entry 3). Treatment with propyl bromide, isopropyl bromide or iodide, allyl bromide and benzyl bromide in acetonitrile or in DMF 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 alkyl 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 diphenyliodonium tetrafluoroborate[12] in the presence of a copper catalyst.[13] 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 $CuCl_2$, which provided a successful route to the diphenyl *N*-substituted **5h** in 55% isolated yield (Table 2, entry 9).

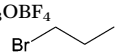
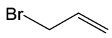
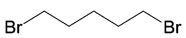
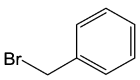
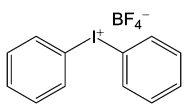
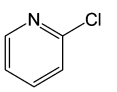
In contrast to the introduction of aryl groups, electron poor pyridyl moieties can be introduced at high temperature *via* nucleophilic *ipso*-substitution of halopyridines.[2a] In our case, the reaction of **4** with neat 2-chloropyridine at 190 °C yielded the bis(imidazolium) salt **5i** in 63% yield (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.[14] 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 $^1J_{CH}$ coupling constant was identified in the solution state *via* ^{1}H or non-decoupled ^{13}C 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,[15] 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 (**5c**), *N*-ethyl (**5b**), *N*-methyl (**5a**) the coupling constants increase to 224.0 Hz. The electron withdrawing *N*-allyl (**5e**), *N*-phenyl (**5h**) and *N*-pyridyl (**5i**) substituents lead to a further increase of $^1J_{CH}$ 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 ^{1}H NMR chemical shift of the H-2′ signals follow the same overall trend.[16] The signal for the most deshielded proton can be found for Hbimca^{Py}·2HCl (**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^R·2HX library **5a–i**

Entry	Reagent	Product (Scheme 1)	Yield (%)
1[a]	Me_3OBF_4	**5a**	78[4]
2	MeI	**5a′**	99[4]
3[a]	Et_3OBF_4	**5b**	78
4[b]		**5c**	80
5[c]		**5d**	91
5[d]		**5d′**	83
6[e]		**5e**	65
7[e]		**5f**	68
8[e]		**5g**	70
9[f]		**5h**	55[h]
10[g]		**5i**	63

Reagents and conditions: [a] MeCN, at room temperature. [b] MeCN, 50 °C, 5 d. [c] DMF, 70 °C, 5 d. [d] MeCN, reflux, 4 d. [e] MeCN, 80 °C, 24 h. [f] DMF, 100 °C, 8 h. [g] Neat, 190 °C, 14 h. [h] Over 2 steps. See Experimental section for details.

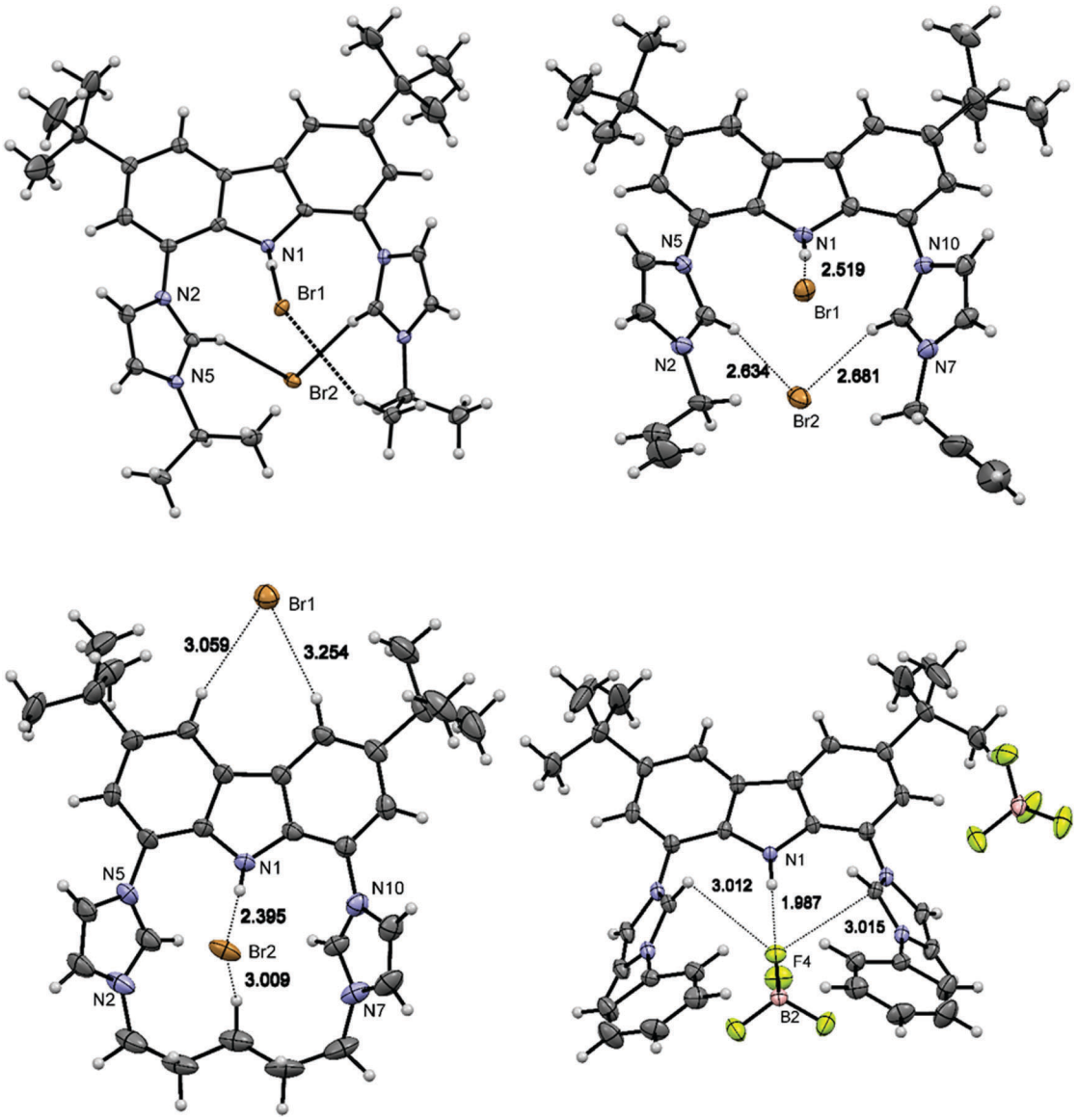


Fig. 2 Molecular structures of the imidazolium salts **5d** (top left), **5e** (top right), **5f** (bottom left) and **5h** (bottom right). Atoms are shown with anisotropic atomic displacement parameters at the 50% probability level. Short contacts between selected hydrogen atoms and the respective anions are shown. In all cases co-crystallised solvent molecules are omitted for clarity.

their counterions not only in the solid state, but also in solution. Nevertheless, as Hbimca^{Me}·2HBF$_4$ (**5a**) shows almost the same shielding as Hbimca^{Me}·2HI (**5a′**) for the respective H-2′ proton, this trend coincides nicely with the course of the $^1J_{CH}$ coupling constants, if the influence of the counter ion 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^R) complexes 6

In analogy to the previously reported deprotonation of the imidazolium salt **5a** to the corresponding Li(bimca^{Me}) complex **6a**[4] 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^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^R) complexes **6** show the absence of the carbazole NH and imidazolium C2′–H signals, thus indicating the clean formation of Li(bimca^R) complexes **6**. The retention of signals originating from chemically equivalent pairs of nuclei across the whole ligand indicates

Table 3 Characteristic analytical data for the Hbimca^R·2HX salts **5a–i** and the respective Li(bimca^R) complexes **6a–i**

Compound **5**/**6**	–R	X$^-$ of **5**	NH $\delta(^1H)$ shifts of **5**^{a} [ppm]	CH $\delta(^1H)$ shifts of **5**^{a} [ppm]	N–C–N angle of **5**^{b} [°]	$^1J_{CH}$ for C2′ in **5**^{a} [Hz]	$\delta(^{13}C)$ carbene signal C2′ of **6**^{c} [ppm]
a[4]	–Me	BF_4^-	11.42	9.81	108.8(3) 109.0(3)	224.0	206.1
a′[4]	–Me	I^-	11.45	9.70	108.7(5)	223.9	206.2
b	–Et	BF_4^-	11.52	9.77	110.0(4), 108.7(4)	223.6	204.7
c	–*n*-Pr	Br^-	11.63	10.02	—	223.5	204.0
d	–i-Pr	Br^-	11.68	9.99	108.0(3), 108.9(3)	222.8	203.7
d′	–i-Pr	I^-	11.56	9.90	109.1(6), 109.4(6)[d]	223.0	203.7
e	–Allyl	Br^-	11.84	10.34	107.9(5), 108.1(5)	224.6	206.3
f	$-(CH_2)_5-$	Br^-	11.20	9.76	108.3(2)	—	—
g	–Bn	Br^-	12.12	10.87	108.2(2)	223.2	decomposition
h	–Ph	BF_4^-	11.76	10.38	108.4(2)	226.0	205.5
i	–Py	Cl^-	12.41	11.08	—	226.4	205.8

[a] Measured in DMSO-d_6, for the influence of water traces and the substrate concentration see ref. 16. [b] See ESI for details. [c] Measured in THF-d_8. [d] Mean of two independent molecules.

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 (**6h**, R = Ph) to 205.8 ppm (**6i**, R = Py) for the *N*-aryl 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 ^7Li 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

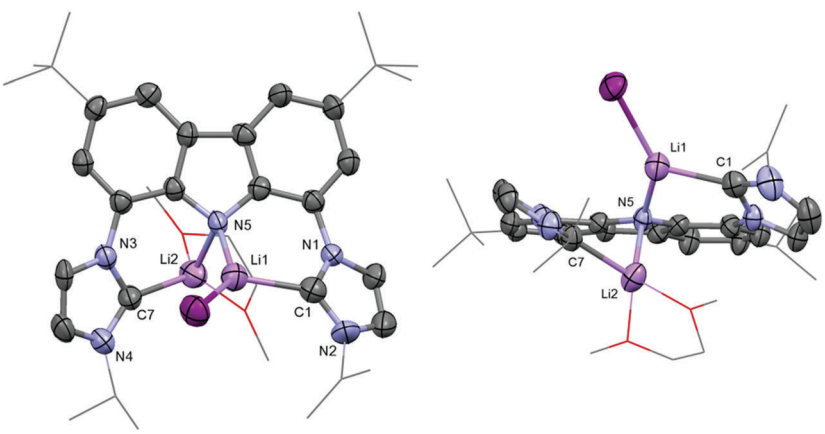


Fig. 3 Molecular structure of the LiI adduct of lithium complex **6d**. Atoms are shown with anisotropic atomic displacement parameters at the 50% probability level. Hydrogen atoms are omitted and the i-Pr and *t*-Bu groups as well as the coordinated DME are depicted as wireframes for clarity. The single crystal was obtained from a DME solution of **6d**.

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 the respective lithium centers is also revealed. Interestingly, the carbazolide nitrogen exhibits bifurcated coordination to both lithium cations (Li1–N5–Li2 angle: 97.3(5)°). This κ-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)).[19] A Li-iodide coordination in this κ-N mode has only been reported once before in a Li–borazide 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 ^{13}C and the ^{7}Li NMR spectra or the influence of the DME coligand. So far, it cannot be deduced whether in solution a monometallic 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(imidazole) 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 imidazole 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^{R}) 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). 3,6-Di-*tert*-butylcarbazole (**2**) (10.0 g, 35.8 mmol, 1 eq.) and $ZnCl_2$ (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 $MgSO_4$. 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 (**4**) (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 Cu_2O (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^{Et})2HBF$_4$ (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 triethyloxonium tetrafluoroborate (Meerwein's salt) ($Et_3O^+BF_4^-$) (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-d_6): δ 1.46 (s, 18H, H-10), 1.56 (t, $^3J_{HH}$ = 7.4 Hz, 6H, H-13), 4.32 (q, $^3J_{HH}$ = 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). $^{13}C\{^1H\}$ NMR (75.47 MHz, DMSO-d_6): 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* (%) 556.6 [M-BF$_4$]$^+$ (60), 469.7 [M-2BF$_4$]$^+$ (13), 235.0 [M-2BF$_4$-H]$^{2+}$ (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 $C_{30}H_{39}N_5B_2F_8$: C 56.01, H 6.11, N 10.89; found: C 55.75, H 6.11, N 10.80.

(Hbimca^{nPr})2HBr (5c). To a suspension of 3,6-di-*tert*-butyl-1,8-bis(imidazol-1-yl)carbazole (**4**) (500 mg, 1.76 mmol, 1 eq.) in 10 mL of dry acetonitrile was added dropwise 1-bromopropane (1.2 mL, 3.5 mmol, 2 eq.). The yellow suspension was stirred for 5 days at 50 °C. After removing the solvent *in vacuo*, the crude product was recrystallised from ethanol to obtain product **5c** as a light yellow solid. Yield: 80% (553 mg). ^{1}H NMR (400.11 MHz, DMSO-d$_6$): δ 1.00 (t, $^3J_{HH}$ = 7.4 Hz, 6H, H-14), 1.47 (s, 18H, H-10), 1.97 (sx, $^3J_{HH}$ = 7.4 Hz, 4H, H-13), 4.27 (t, $^3J_{HH}$ = 7.4 Hz, 4H, H-12), 7.77 (s br, 2H, H-2/7), 8.13 (d, $^3J_{HH}$ = 1.7 Hz, 2H, H-4′), 8.32 (d, $^3J_{HH}$ = 1.7 Hz, 2H, H-5′), 8.63 (s br, 2H, H-4/5), 10.02 (s, 2H, H-2′), 11.63 (s, 1H, NH). MS (FAB$^+$): *m*/*z* (%) = 576.2 [M-Br]$^+$ (15), 496.3 [M-2Br-H]$^+$ (100), 454.3 [M-2Br-^{n}Pr]$^+$ (18). EA: calcd for $C_{32}H_{43}N_5Br_2$: C 58.45, H 6.59, N 10.65; found: C 58.04, H 6.75, N 10.49.

(Hbimca^{iPr})2HBr (5d). To a stirred suspension of 3,6-di-*tert*-butyl-1,8-bis(imidazol-1-yl)carbazole (**4**) (200 mg, 490 μmol, 1 eq.) in dimethylformamide (2 mL) was added 2-bromopropane (0.23 mL, 2.4 mmol, 5 eq.). The solution 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). Recrystallization from ethanol led to compound **5d** as a colourless, microcrystalline solid. Yield: 91% (630 mg). Mp 350 °C (dec.). ^{1}H NMR (400.11 MHz, DMSO-d$_6$): δ 1.47 (s, 18H, H-10), 1.62 (d, $^3J_{HH}$ = 6.8 Hz, 12H, H-13), 4.77 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, H-12), 7.75 (d, $^4J_{HH}$ = 1.5 Hz, 2H, H-2/7), 8.26 (t, $^3J_{HH}$ = 1.8 Hz, 2H, H-4′), 8.35 (t, $^3J_{HH}$ = 1.8 Hz, 2H, H-5′), 8.62 (d, $^4J_{HH}$ = 1.5 Hz, 2H, H-4/5), 9.99 (t, $^4J_{HH}$ = 1.5 Hz, 2H, H-2′), 11.68 (s, 1H, NH). ^{13}C{^{1}H} NMR (101.61 MHz, DMSO-d$_6$): δ 22.2 (C13), 31.6 (C10), 34.9 (C11), 52.9 (C12), 119.2 (C4a/5a), 119.3 (C4/5), 120.8 (C2/7), 121.1 (C4′). ^{13}C NMR signals were assigned *via* ^{1}H-^{13}C-HSQC spectra due to bad quality of the ^{13}C-NMR spectrum. Signals for the quaternary carbon atoms could not be assigned. MS (FAB$^+$): *m*/*z* (%) 576.2 [M-H-Br]$^+$ (15), 496.3 [M-2Br-H]$^+$ (100), 454.3 [M-^{i}Pr-2Br]$^+$ (18). EA: calcd for $C_{32}H_{43}N_5Br_2\cdot 2H_2O$: C 55.42, H 6.83, N 10.10; found: 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-isopropylimidazolium)carbazole diiodide **5d′** from 2-iodopropane in 75% yield as a white powder.

(Hbimca^{iPr})2HI (5d′). 2-Iodopropane (867 mg, 5.10 mmol) was added to a stirred suspension of **4** (700 g, 1.7 mmol) in acetonitrile (20 mL). The reaction mixture was heated to reflux and stirred for 72 h. The clear, dark red reaction mother liquor was concentrated to *ca.* 10 mL and upon cooling (0 °C) **5d′** crystallised out as a white solid. The solid was filtered and washed with cold diethyl ether (3 × 5 mL) to give the title compound as a white, microcrystalline solid. A second crop was isolated by the dropwise addition of diethyl ether to the acetonitrile filtrate. Crystals suitable for single-crystal X-ray diffraction analysis were grown from a saturated solution of **5d′** in dichloromethane layered with hexane (combined yield: 83% (1.06 g)). Mp 262–264 °C (dec.). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 1.48 (s, 18H, H-10), 1.62 (d, $^3J_{HH}$ = 6.6 Hz, 12H, H-13), 4.78 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, H-12), 7.79 (s, 2H, H-2/7), 8.28 (t, $^3J_{HH}$ = 1.5 Hz, 2H, H-4′), 8.37 (t, $^3J_{HH}$ = 1.5 Hz, 2H, H-5′), 8.64 (s, 2H, H-4/5), 9.90 (t, $^4J_{HH}$ = 1.5 Hz, 2H, H-2′), 11.56 (s, 1H, NH). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ 22.3 (C13), 31.7 (C10), 35.0 (C11), 53.0 (C12), 119.2 (C1/8), 119.3 (C4/5), 120.8 (C2/7), 121.2 (C4′), 123.4 (C5′) 125.5 (C4a/5a), 132.0 (C1a/8a), 135.8 (C2′), 143.8 (C3/6). IR (nujol, cm^{-1}): 3067 (m), 1736 (m), 1596 (s), 1561 (s), 1318 (s), 1263 (s), 1144 (s), 1114 (s), 941 (m), 871 (s). Calcd for $C_{32}H_{43}I_2N_5$: C 51.14, H 5.77, I 33.77, N 9.32. Found: C 51.17, H 5.68, N 9.20.

(Hbimca^{Allyl})2HBr (5e). To a stirred suspension of 3,6-di-*tert*-butyl-1,8-bis(imidazol-1-yl)carbazole (**4**) (250 mg, 0.610 mmol) in acetonitrile (2 mL) was added portionwise allylbromide (0.110 mL, 1.20 mmol, 2 eq.) and the suspension was stirred at 80 °C for 24 h. The reaction mixture was concentrated to dryness, the remaining crude product was redissolved in ethanol and diethyl ether was added until a colourless precipitate formed. The suspension was filtered and the residue washed with additional diethyl ether (5 mL). The product was dissolved in dichloromethane, filtered again to get rid of the remaining inorganic salts and dried to afford compound **5e** as a colourless solid. Yield: 65% (262 mg). ^{1}H NMR (400.11 MHz, DMSO-d$_6$): δ 1.47 (s, 18H, H-10), 5.08 (d, $^3J_{HH}$ = 6.3 Hz, 4H, H-12), 5.45 (dd, $^2J_{HH}$ = 1.3 Hz, $^3J_{HH}$ = 10.3 Hz, 2H, H-14*cis*), 5.57 (dd, $^2J_{HH}$ = 1.3 Hz, $^3J_{HH}$ = 17.1 Hz, 2H, H-14*trans*), 6.82 (m, 2H, H-13), 7.78 (d, $^4J_{HH}$ = 1.7 Hz, 2H, H-2/7), 8.10 (d, $^3J_{HH}$ = 1.7 Hz, 2H, H-4′), 8.38 (d, $^3J_{HH}$ = 1.7 Hz, 2H, H-5′), 8.64 (d, $^4J_{HH}$ = 1.7 Hz, 2H, H-4/5), 10.34 (s, 2H, H-2′), 11.84 (s, 1H, NH). ^{13}C{^{1}H} NMR (100.61 MHz, DMSO-d$_6$): δ 31.6 (C10), 34.9 (C11), 51.2 (C12), 118.0 (C1/8), 119.1 (C4/5), 120.8 (C2/7), 121.1 (C14), 122.8 (C4′), 123.3 (C5′) 125.5 (C4a/5a), 131.4 (C13), 132.2 (C1a/8a), 137.4 (C2′), 143.7 (C3/6). MS (FAB$^+$): *m*/*z* (%) 572.2 [M-Br]$^+$ (15), 492.3 [M-2Br-H]$^+$ (100). EA: calcd for $C_{32}H_{39}N_5Br_2\cdot 0.5CH_2Cl_2$: C 55.77, H 6.34, N 10.00; found: C 56.43, H 5.45, N 9.61.

(Hbimca^{C5})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 μmol, 1.1 eq.). After 5 d at 80 °C the beige-coloured suspension 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.). ^{1}H NMR (400.11 MHz, DMSO-d$_6$): δ 1.46 (s, 18H, H-10), 1.67 (m, 2H, H-14), 1.79 (m, 4H, H-13), 4.36 (m, 4H, H-12), 7.80 (d, $^4J_{HH}$ = 1.4 Hz, 2H, H-2/7), 8.08 (t, $^3J_{HH}$ = 1.6 Hz, 2H, H-4′), 8.29 (t, $^3J_{HH}$ = 1.6 Hz, 2H, H-5′), 8.61 (d, $^4J_{HH}$ = 1.4 Hz, 2H, H-4/5), 9.76 (s, 2H, H-2′), 11.20 (s, 1H, NH). ^{13}C{^{1}H} NMR (100.61 MHz, DMSO-d$_6$): δ 18.9 (C14), 28.9 (C13), 32.0 (C10), 35.4 (C11), 50.8 (C12), 120.0 (C1/8), 120.1 (C4/5), 120.4 (C2/7), 123.5 (C4′), 124.1 (C5′), 125.9 (C4a/5a), 134.3 (C1a/8a), 137.7 (C2′), 144.8 (C3/6). HRMS (ESI$^+$): *m*/*z* 480.31217 [M-2Br-H]$^+$ (calcd 480.31257), 560.23833 [M-Br]$^+$ (calcd 560.23858), 240.65972 [M-2Br]$^{2+}$ (calcd 240.65985).

(Hbimca^{Bn})2HBr (5g). To a stirred suspension of 3,6-di-*tert*-butyl-1,8-bis(imidazol-1-yl)carbazole (**4**) (200 mg, 0.49 mmol, 1 eq.) in acetonitrile (5 mL) was added portionwise benzylbromide (0.17 mL, 1.46 mmol, 3 eq.) and the suspension was stirred at 80 °C for 72 h. The reaction mixture was concentrated

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.). ^{1}H 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, $^4J_{HH}$ = 1.6 Hz, 2H, H-2/7), 7.66–7.77 (m, 4H, H-15), 7.82 (t, $^3J_{HH}$ = 1.7 Hz, 2H, H-4′), 8.00 (t, $^3J_{HH}$ = 1.7 Hz, 2H, H-5′), 8.36 (d, $^4J_{HH}$ = 1.6 Hz, 2H, H-4/5), 10.87 (br s, 2H, H-2′), 12.12 (br s, 1H, NH). ^{13}C{^{1}H} NMR (100.61 MHz, DMSO-d_6): δ 31.7 (C10), 35.0 (C11), 52.2 (C12), 119.1 (C1/8), 119.4 (C4/5), 120.9 (C2/7), 122.7 (C4′), 123.7 (C5′), 125.6 (C4a/5a), 129.0 (C14, C16), 129.1 (C15), 132.1 (C1a/8a), 134.5 (C13), 137.3 (C2′), 143.8 (C3/6). MS (FAB$^+$): *m*/*z* (%) 672.3 [M-Br-H]$^+$ (14), 592.3 [M-2Br-H]$^+$ (100). EA: calcd for $C_{40}H_{43}N_5Br_2{\cdot}0.25\ CH_2Cl_2$: C 62.39, H 5.66, N 9.04; found: C 62.55, H 5.50, N 9.09.

Diphenyliodonium tetrafluoroborate[12]. Chloroperbenzoic acid (81% active oxidant, 610 mg, 2.90 mmol) was dissolved in CH_2Cl_2 (10 mL). To the solution was added iodobenzene (531 mg, 2.60 mmol) followed by $BF_3{\cdot}Et_2O$ (0.81 mL, 6.50 mmol) at room temperature. The resulting yellow solution was stirred at room temperature for 30 min, then cooled to 0 °C and phenylboronic acid (400 mg, 2.90 mmol) was added. After 2 h of stirring at room temperature, diethyl ether (2 mL) was added to the crude reaction mixture to induce the precipitation of the diphenyliodonium salt. The suspension was allowed to stir for 15 min and then the organic phase was decanted. The remaining solid was washed twice with ice cold diethyl ether (2 × 10 mL) and then dried *in vacuo* to give the pure diphenyliodonium tetrafluoroborate salt as a colourless solid. Yield: 93% (895 mg). The signals of the NMR spectra are consistent with the literature.

(Hbimca^{Ph})2HBF$_4$ (5h). 3,6-Di-*tert*-butyl-1,8-bis(imidazol-1-yl)carbazole (**4**) (300 mg, 730 μmol, 1 eq.) and Ph_2IBF_4 (806 mg, 2.19 mmol, 3 eq.) were dissolved in 7.50 mL of dimethylformamide and $CuCl_2$ (4.91 mg, 36.5 μmol, 5 mol%) was added. The solution was heated to 100 °C for 6 h. After cooling to room temperature, 30 mL of water was added to the green solution. The precipitate formed was filtered off, washed with water and dried *in vacuo*. The crude product was refluxed in 20 mL of ethanol, filtered while the suspension was still hot and the residue washed with ethanol. After drying *in vacuo*, the product was obtained in 55% (302 mg) yield as a white solid. Mp >360 °C. ^{1}H NMR (400.11 MHz, DMSO-d_6): δ 1.50 (s, 18H, H-10), 7.65–7.71 (m, 6H, H_{Ar}), 7.89–7.94 (m, 6H, H_{Ar}), 8.52 (t, 2H_{Ar}), 8.68–7.72 (m, 4H, H_{Ar}), 10.38 (s, 2H, H-2′), 11.76 (s, 1H, NH).^{13}C{^{1}H} NMR (100.61 MHz, DMSO-d_6): δ 31.6 (C10), 34.9 (C11), 118.8 (C1/8), 119.8 (C4/5), 121.0 (C2/7), 121.5 (C4′), 121.7 (C14/13), 124.3 (C5′), 125.3 (C4a/5a), 130.1 (C15), 130.2 (C13/14), 131.9 (C1a/8a), 134.6 (C12), 136.2 (C2′), 143.8 (C3/6). MS (FAB$^+$): *m*/*z* (%) 652.4 [M-HBF$_4$]$^+$ (8), 548.1 [M-2BF$_4$]$^+$ (100).

(Hbimca^{Py})2HCl (5i). 3,6-Di-*tert*-butyl-1,8-bis(imidazol-1-yl)-carbazole (**4**) (500 mg, 1.21 mmol) were dissolved in 2-chloropyridine (5 mL) and the suspension was stirred for 24 h at 190 °C. Subsequently, the brown solution was slowly added to cold petroleum ether to form a precipitate. The crude product was obtained by filtration and washing the residue several times with hot tetrahydrofuran to afford compound **5i** as a white solid. Yield: 63% (487 mg). Mp 214 °C. ^{1}H NMR (400.11 MHz, DMSO-d_6): δ 1.50 (s, 18H, H-10), 7.67 (m, 2H, Py-H), 7.86 (d, $^4J_{HH}$ = 1.6 Hz, 2H, H-2/7 or H-4/5), 8.23 (m, 2H, Py-H), 8.42 (m, 2H, Py-H), 8.51 (m, 2H, H-5′), 8.68 (m, 2H, Py-H), 8.70 (d, $^4J_{HH}$ = 1.6 Hz, H-4/5 or H-2/7), 8.76 (m, 2H, H-4′), 11.08 (s, 2H, H-2′), 12.41 (s, 1H, NH). ^{13}C{^{1}H} NMR (100.61 MHz, DMSO-d_6): δ 31.6 (C10), 34.9 (C11), 115.2 (C_{Py}), 118.8 (C1/8), 119.3 (C4′), 119.7 (C2/7 or C4/5), 121.1 (C4/5 or C2/7), 124.4 (C5′), 125.2 (4a/5a), 125.3 (C_{Py}), 132.2 (C1a/8a), 136.9 (C2′), 140.4 (C_{Py}), 143.4 (C3/6), 146.4 (C_{Py}), 149.1 ($C_{Py,ipso}$). MS (FAB$^+$): *m*/*z* (%) 566.4 [M-2Cl-H]$^+$ (100), 283.8 [M-2Cl]$^{2+}$ (100). Elemental analysis of **5i** consistently returned CHN values inconsistent with its anticipated composition. Therefore, the anion was exchanged to BPh_4^- and the crude product was recrystallised from isopropanol to obtain **5i′** as an off-white solid. Elemental analysis of **5i′** showed significantly better values. EA: calcd for $C_{84}H_{77}B_2N_7{\cdot}LiCl$: C 80.80, H 6.22, N 7.85; found: C 80.34, H 6.66, N 7.96. This outcome is likely due to the inclusion of one equivalent of lithium chloride in the solid product.

Li(bimca^{Et}) (6b). In the glove-box lithium diisopropylamide (LDA) (5.2 mg, 49 μmol) was added to a suspension of 1,1′-(3,6-di-*tert*-butyl-9*H*-carbazol-1,8-diyl)bis(3-ethyl-1*H*-imidazolium)-ditetrafluoroborate (**5b**) (10.0 mg, 16.5 μmol) in 0.5 mL of THF-d_8. The ^{1}H-NMR spectrum of the yellow solution, which was blue fluorescent in the UV-light, showed quantitative conversion to the desired Li-(bimca^{Et}) **6b**. The product was stable in solution for days, but decomposed upon removal of the solvent *in vacuo*. ^{1}H NMR (500.13 MHz, THF-d_8): δ 1.50 (s, 18H, H-10), 1.58 (t, ^3J(HH) = 7.3 Hz, 6H, H-13), 4.28 (q, ^3J(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, ^4J(HH) = 1.5 Hz, 2H, H-4/5). ^{13}C{^{1}H} NMR (125.77 MHz, THF-d_8): δ 17.3 (C13), 32.9 (C10), 35.3 (C11), 46.8 (C12), 111.6 (C2/7), 114.2 (C4/5), 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^{iPr}) (6d). 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 suspension was allowed to settle and the pale yellow, blue fluorescent supernatant was filtered off *via* filter cannula. The remaining solid was dried under vacuum to give Li(bimca^{iPr})·LiI **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. ^{1}H NMR (400 MHz, THF-d_8): δ 1.49 (s, 18H, H-10), 1.63 (d, $^3J_{HH}$ = 6.8 Hz, 12H, H-13), 4.72 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, H-12), 7.25 (d, $^3J_{HH}$ = 1.7 Hz, 2H, H-4′), 7.39 (t, $^3J_{HH}$ = 1.7 Hz, 2H, H-2/7), 7.77 (d, $^3J_{HH}$ = 1.7 Hz, 2H, H-5′), 7.98 (t, $^3J_{HH}$ = 1.7 Hz, 2H, H-4/5). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 24.3 (C13), 32.8 (C10), 35.1 (C11), 53.4 (C12), 110.9 (C2/7), 114.0 (C4/5), 119.5 (C4′), 119.8 (C5′), 128.0 (C_q), 128.1 (C_q), 135.2 (C3/6), 143.5 (C1a/8a), 206.2 (C2′). ^{7}Li{^{1}H} NMR

(97.21 MHz, THF-d_8): δ = 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^{iPr})·LiI. This outcome is likely due to the inclusion of THF in the solid product. EA: calcd for $C_{32}H_{40}N_5Li$·(LiI)(THF): C 59.00, H 6.19, N 10.75; found: C 59.70, H 5.53, N 11.46. Procedure B: Solid methyllithium (3 eq.) was added to a stirred, yellow suspension of the imidazolium salt **5** in THF-d_8 (0.5 mL) to immediately give a pale amber, blue fluorescent solution, which was kept at room temperature for 1 h. A nearly quantitative conversion of the imidazolium precursors **5** and formation of the lithium complexes **6** was monitored by NMR spectroscopy. Due to their high sensitivity towards air and moisture no elemental analysis of compounds **6** were measured.

Li(bimca^{nPr}) (6c). ^{1}H NMR (400.11 MHz, THF-d_8): δ 1.53 (s, 18H, H-10), 1.60–1.70 (br m, 10 H, H13/14), 4.74 (m, 4H, H-12) 7.51 (br s, 2H, H-4′), 7.65 (br s, 2H, H-2/7), 7.98 (br s, 2H, H-5′), 8.08 (br s, 2H, H-4/5). $^{13}C\{^1H\}$ NMR (100.61 MHz, THF-d_8): δ 24.2 (C14), 32.8 (C10), 35.1 (C11), 53.3 (C12), 111.2 (C2/7), 113.9 (C4/5), 116.1 (C4′), 119.4 (C5′), 127.9 (C4a/5a), 128.3 (C1/8), 135.2 (C3/6), 143.5 (C1a/8a), 203.6 (C2′). The C13 signal is covered by the THF signal.

Li(bimca^{Allyl}) (6e). ^{1}H NMR (400.11 MHz, THF-d_8): δ 1.49 (s, 18H, H-10), 4.89 (br s, 2H, H-12), 5.20–5.35 (m, 4H, H-14), 6.20 (m, 2H, H-13), 7.15 (br s, 2H, H-4′), 7.41 (br s, 2H, H-2/7), 7.79 (br s, 2H, H-5′), 8.00 (br s, 2H, H-4/5). $^{13}C\{^1H\}$ NMR (100.61 MHz, THF-d_8): δ 32.5 (C13), 32.7 (C10), 35.0 (C11), 54.5 (C12), 111.3 (s, C2/7), 114.0 (C4/5), 117.3 (C14), 118.9 (C4′), 119.6 (C5′), 128.1 (C4a/5a and C1/8), 135.4 (C3/6), 136.4 (C13), 143.9 (C1a/8a), 205.7 (C2′).

Li(bimca^{Ph}) (6h). ^{1}H NMR (400.11 MHz, THF-d_8): δ 1.49 (s, 18H, H-10), 7.25 (br s, 2H, H-4′), 7.20–7.30 (m, 6H, H_{Ph}), 7.39 (br s, 2H, H-2/7), 7.67–7.70 (m, 4H, H_{Ph}), 7.76 (s br, 2H, H-5′), 7.98 (br s, 2H, H-4/5). $^{13}C\{^1H\}$ NMR (100.61 MHz, THF-d_8): δ 32.8 (C10), 35.1 (C11), 111.8 (C2/7), 114.5 (C4/5), 118.7 (C4′), 120.9 (C5′), 122.3 (C_{Ph}), 126.8 (C_{Ph}), 127.8 (C4a/5a), 128.1 (C1/8), 130.2 (C_{Ph}), 135.6 (C3/6), 143.2 (C1a/8a), 143.5 (C_{Ph}), 205.1 (C2′). $^7Li\{^1H\}$ NMR (97.21 MHz, THF-d_8): δ = 0.59.

Li(bimca^{Py}) (6i). ^{1}H NMR (400 MHz, THF-d_8): δ 1.53 (s, 18H, H-10), 7.27–7.31 (m, 2H, H_{Py}), 7.54 (d, $^3J_{HH}$ = 1.7 Hz, 2H, H-4′), 7.60–7.70 (m, 2H, H_{Py}), 8.00 (d, $^4J_{HH}$ = 1.7 Hz, 2H, H-2/7), 8.10 (d, $^3J_{HH}$ = 1.7 Hz, 2H, H-5′), 8.19 (d, $^4J_{HH}$ = 1.7 Hz, 2H, H-4/5), 7.20–8.23 (m, 2H, H_{Py}), 8.48–8.50 (m, 2H, H_{Py}). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 32.7 (C10), 35.0 (C11), 112.4 (C2/7), 114.6 (C4/5 or C_{Py}), 114.8 (C4/5 or C_{Py}), 117.3 (C4′), 121.0 (C5′), 122.1 (C_{Py}), 127.7 (C4a/5a), 128.2 (C1/8), 135.5 (C3/6), 139.5 (C_{Py}), 143.5 (C1a/8a), 149.3 (C_{Py}), 154.4 (C_{Py}), 205.5 (C2′).

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