Modular Trimethylene-Linked Bisimidazol(in)ium Salts

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Abstract: A short and modular synthesis of symmetrically and non-symmetrically substituted bisimidazolinylene N-heterocyclic carbene precursors is described. Two methods to establish dicopper(I) complexes of these compounds depending on the steric shielding of the carbene are reported.

Key words: alkylations, copper, carbene complexes, ligands, N-heterocyclic carbenes

Wanzlick and Öfele published the first metal complexes of N-heterocyclic carbenes (NHCs) more than 40 years ago. However, it took nearly three decades until NHCs were established in organometallic chemistry and catalysis.[1] The field remained more or less dormant until 1991, when Arduengo and co-workers were able to isolate the first NHC in substance.[2] Nowadays, NHC complexes and their catalytic activity have become an important area of research.[3,4]

The favorable stability of metal NHC complexes towards heat, oxygen, and moisture represents a significant advantage over the analogous phosphine-containing compounds.[5] Strong σ-donating ability, wide functional group compatibility, and the fact that they do not readily undergo ligand dissociation, combine to make NHCs unique ancillary ligands. N-Heterocyclic carbenes are a good choice not only for olefin metathesis reactions and aryl cross-couplings, but also for polymerizations,[6] hydrogenations,[7] hydrosilylations,[8] hydroborations,[9] hydroformylations,[10] allylic substitutions,[11] cycloadditions ('click' chemistry),[12] methenylations, and others.[13]

The literature comprises many examples of mononuclear complexes of bidentate NHC ligands (type **A**) or bimolecular NHC metal complexes.[14] However, there is a growing number of dinuclear bis-NHC complexes of late transition metals of type **B**.[15] We intended to prepare flexible and stable homodinuclear complexes of nonchelating alkylene-linked bis-NHCs. Of particular interest are bis-NHC precursor salts containing different heterocycles in one molecule. They can provide different electronic and steric coordination sites for homobimetallic complexes (type **C**) and may prove to be helpful to rationally and specifically prepare heterobimetallic bis-NHC complexes (type **D**) (Figure 1).

The general procedure for the preparation of NHC complexes relies on simple ligand exchange. Therefore, synthetic strategies leading to the corresponding highly stabilized five-membered carbene rings as a discrete or a transient species are in demand. In 2004, Marshall et al. reported a suitable route to aryl-substituted, alkyl-linked bisimidazolinium salts, but neither isolated nor characterized the free biscarbenes or metal complexes thereof.[16] It was reported that bisimidazolinium salts with 2,4,6-trimethylphenyl substituents form tetraaminoethene derivatives after deprotonation. Only the deprotonation of a 2,6-diisopropylphenyl-substituted bis-NHC precursor led to an air-sensitive oil, which contained free carbene species according to NMR data.

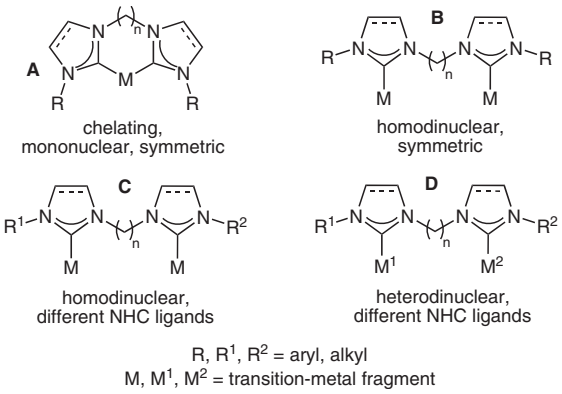

Figure 1 Examples of NHC metal complexes

We optimized this procedure and found a short, modular route to symmetrically as well as non-symmetrically alkyl and aryl substituted bis-NHC precursors and transition metal complexes. Our procedure starts from the inexpensive compounds 2-bromoethylamine hydrobromide and an aniline derivative. In a simple S_N2 reaction, *N*-arylethylenediamines **1a–c** were obtained in good yields on the gram scale (Scheme 1).

Condensation of diamines **1** with triethyl orthoformate in the presence of *p*-toluenesulfonic acid monohydrate gave *N*-arylimidazolines **2a–c** as nucleophilic building blocks in good yields. Imidazolines **2** reacted with 0.5 equivalent of 1,3-dibromopropane to give symmetrical bisimidazolinium dibromides **3**, as depicted in Scheme 1. The molecular structure of bis-NHC precursor **3a** was confirmed by X-ray crystallography (Figure 2).

In some cases, exchange of counterions was beneficial to improve the solubility of the bis-NHC precursors in a cer-

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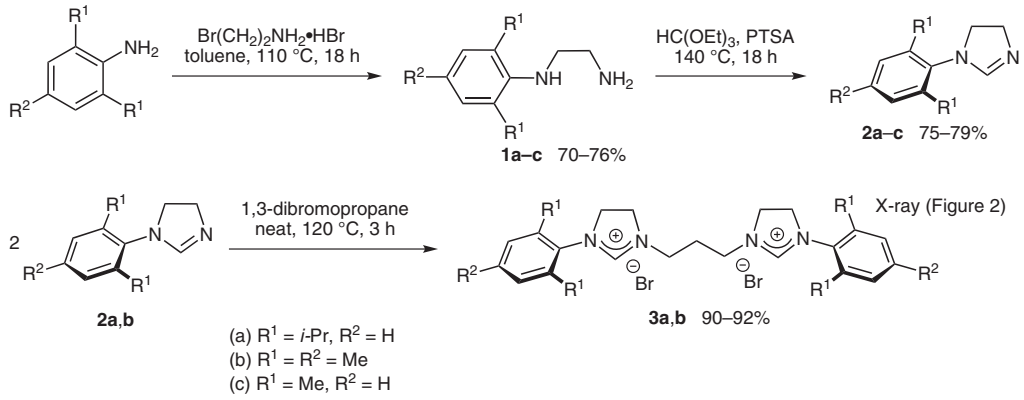


Scheme 1 Synthesis of symmetric bis-NHC precursors

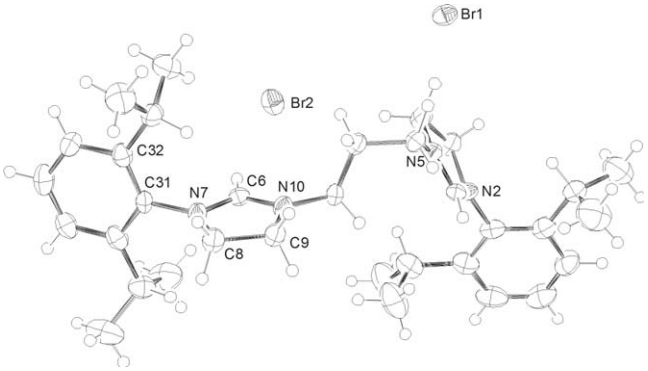
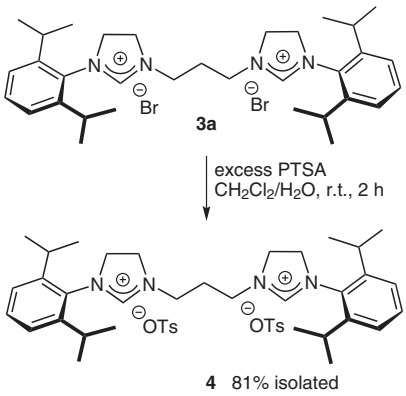


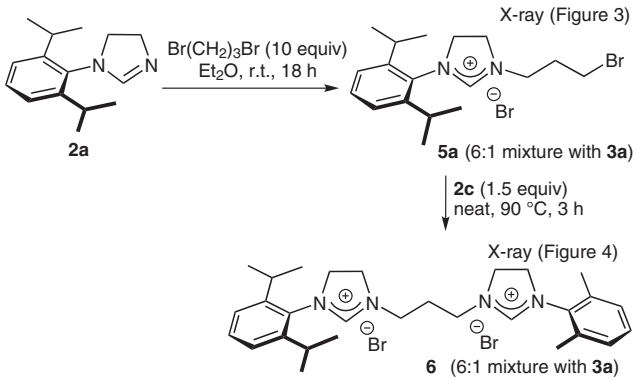
Figure 2 ORTEP plot of the molecular structure of bis-NHC precursor **3a**. Bond lengths [Å]: C6–H6, 0.871; C6–N7, 1.307; C6–N10, 1.291; C9–N10, 1.469; C8–C9, 1.537; C8–N7, 1.482; H6–Br2, 2.786; angles [°]: C8–N7–C31, 123.63; C8–N7–C31–C32, 86.26. Solvent molecules have been omitted for clarity.



Scheme 2 Anion exchange on bis-NHC precursor **3a**

tain solvent or tune coordination characteristics of the anions referring to metals in later complexes. For example, the bis-NHC dibromide **3a** was converted into the ditosylate **4** by stirring a solution of **3a** in CH_2Cl_2 with an excess of an aqueous solution of *p*-toluenesulfonic acid monohydrate (Scheme 2). This procedure is widely used in ionic liquid chemistry.

Monoimidazolinium salts such as **5a** are useful building blocks for the synthesis of non-symmetrically substituted bis-NHC precursors. Unfortunately, both bromoalkyl groups were found to react rapidly by stirring imidazoline **2a** with a 10-fold excess of 1,3-dibromopropane in Et_2O. Therefore, monoimidazolinium salt **5a** was obtained as a 6:1 mixture with **3a** and could not be purified any further (Scheme 3). Even though we were not able to obtain analytical data of pure **5a**, we have proved its existence by the X-ray structure depicted in Figure 3.



Scheme 3 First attempt to synthesize non-symmetrically substituted bis-NHC precursors

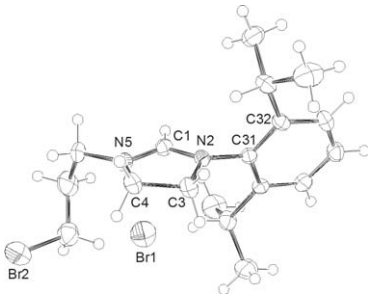


Figure 3 ORTEP plot of the molecular structure of **5a**. Bond lengths [Å]: C1–N5, 1.298; C1–N2, 1.309; N2–C3, 1.484; C3–C4, 1.533; C4–N5, 1.472; angles [°]: C3–N2–C31–C32, 118.93; N2–C3–C4–N5, 12.12.

Reaction of monoimidazolinium salt **5a** (as a 6:1 mixture with **3a**) with imidazoline **2c** yielded the non-symmetrically substituted bis-NHC precursor **6**. Due to the contamination of **5a** with **3a**, we were not able to obtain clean

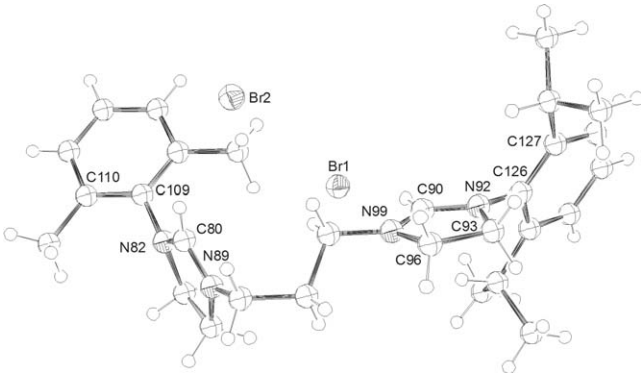
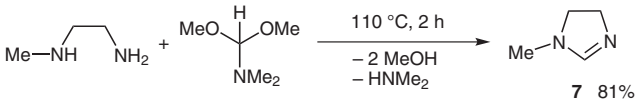


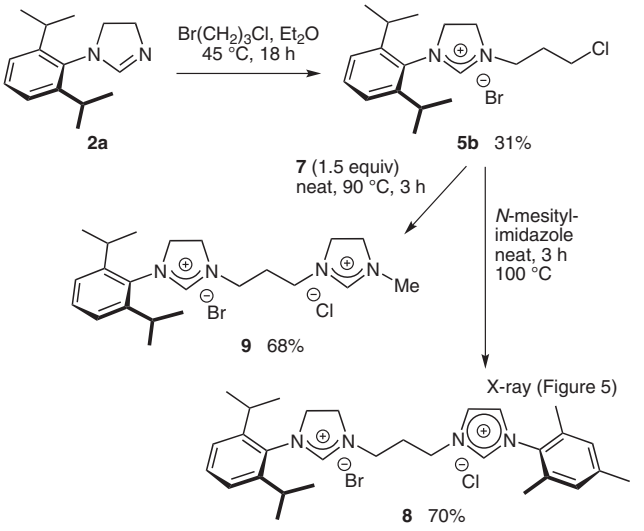
Figure 4 ORTEP plot of the molecular structure of **6**. Bond lengths [Å]: N92–C90, 1.315; C93–C96, 1.528; C90–N99, 1.278; C93–N92, 1.485; N99–C96, 1.493; angles [°]: N92–C93–C96–N99, 8.55; C127–C126–N92–C90, 96.69; C110–C109–N82 –C80, 119.29. Solvent molecules have been omitted for clarity.

analytical data for **6**. The structure of **6** is apparent from a single-crystal X-ray structure analysis (Figure 4).

The reaction of imidazoline **2a** with 1-bromo-3-chloropropane in refluxing Et_2O afforded the monoimidazolinium salt **5b** in moderate yield. The electrophilic building block **5b** reacted with 1-methylimidazoline (**7**), prepared from commercially available *N*-methylethylenediamine by condensation with *N*,*N*-dimethylformamide dimethyl acetal as described by Cetinkaya et al.[17] (Scheme 4), to form the non-symmetrically substituted bis-NHC precursor **9** (Scheme 5).



Scheme 4 Preparation of 1-methylimidazoline (**7**)



Scheme 5 General approach to synthesize non-symmetrically substituted bis-NHC precursors

On the other hand, reaction of imidazolinium salt **5b** with *N*-mesitylimidazole yielded the mixed functional bis-NHC precursor **8** (Scheme 5).[18] Crystallization and purification led to substances with varying chloride to bromide ratios, as seen in Figure 5.

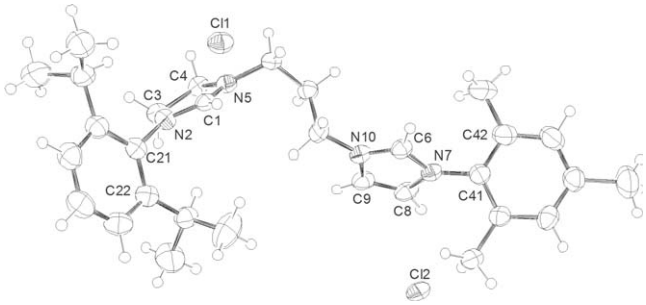
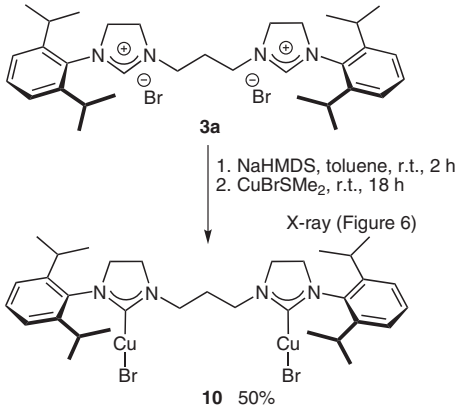


Figure 5 ORTEP plot of the structure of mixed functional bis-NHC precursor **8**. Bond lengths [Å]: C1–N5, 1.295; C1–N2, 1.309; N2–C3, 1.473; C3–C4, 1.525; C6–N10, 1.322; C6–N7, 1.331; N7–C8, 1.383; C8–C9, 1.340; C9–N10, 1.375; angles [°]: C8–N7–C41–C42, 118.45; C3–N2–C21–C22, 118.05.

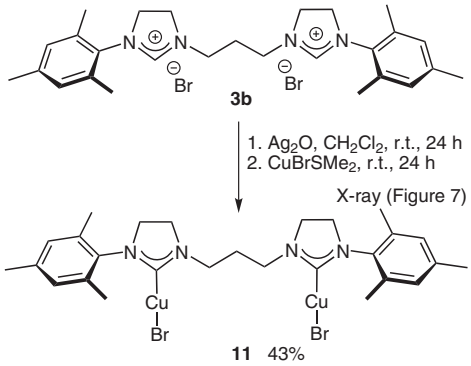
Using this modular approach, we tuned the properties of bis-NHC precursors by the size of the substituent, the nature of the NHC, the length and rigidity of the linker moiety, and the counterion.

We developed two reliable pathways to dicopper(I) bis-NHC complexes depending on the steric demand of the aryl substituent of our bisimidazolinium salts **3a** and **3b**. Deprotonation of the ligand precursor **3a** with sodium hexamethyldisilazide (NaHMDS) in anhydrous toluene in the presence of a copper(I) salt led to complex **10** in moderate yields (Scheme 6).



Scheme 6 Synthesis of dicopper(I)-NHC complex **10** with sterically demanding diisopropylphenyl substituents

After deprotonation with NaHMDS or DBU, bis-NHC precursor **3b** with its medium-sized substituents reacted by intramolecular dimerization to form tetraaminoethenes, as described by Marshall et al.[16] These compounds react with copper(I) salts by formation of black metal copper precipitate. However, synthesis of dicopper(I) complex **11** was achieved via transmetalation from an in situ generated silver NHC species. It is well known that silver(I) NHC complexes easily transfer the ligand to other metals and form silver halides or silver metal.[19]



Scheme 7 Synthetic approach to dicopper(I)-NHC complex **11** with aryl groups of medium size

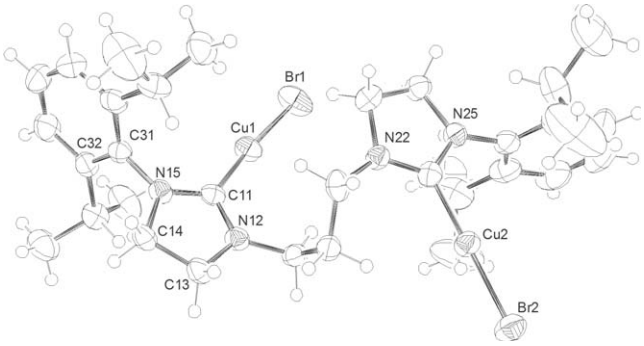


Figure 6 ORTEP plot of the molecular structure of dicopper(I) complex **10**. Bond lengths [Å]: Cu1–Br1, 2.235; Cu1–C11, 1.887; C13–C14, 1.516; C14–N15, 1.477; N12–C13, 1.468; C11–N15, 1.344; C11–N12, 1.340; angles [°]: Br1–Cu1–C11, 174.4; C32–C31–N15–C11, 92.8; C31–N15–C11–Cu1, 0.1; N15–C11–Cu1–Br1, 170.6.

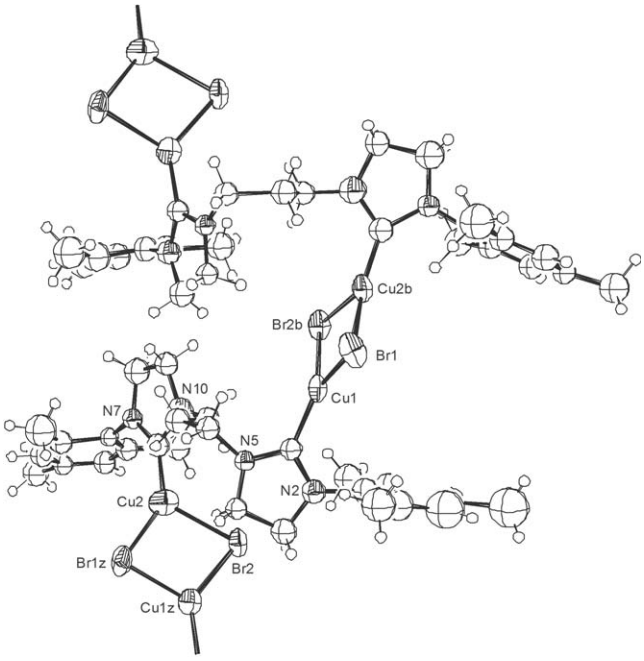


Figure 7 ORTEP plot of the molecular structure of **11** as coordination polymer in the solid state. The crystal quality was only sufficient for constitutional evidence.

Deprotonation of **3b** was carried out in situ using Ag_2O as a base to form a labile and light-sensitive silver(I) NHC species that was not isolated. This silver(I) NHC complex reacted with copper(I) salts by transmetalation of the bis-NHC ligand to form the desired homodinuclear dicopper(I) bis-NHC complex **11** (Scheme 7).

The general influence of the size of aryl groups in bis-NHC-copper complexes **10** and **11** is depicted by X-ray structure drawings in Figures 6 and 7.

Strong steric shielding by aryl groups leads to linearly coordinated copper(I) in complex **10** in the solid state. With decreasing bulk of the aryl groups, the NHC-copper(I) bromide fragments form intermolecular coordination bonds. This is displayed by Figure 7 showing complex **11** as a coordination polymer in the solid state. This fact makes no statement regarding the behavior of the complexes in solution. However, the influence of steric modifications on the accessibility of the copper centers is illustrated.

Starting materials were used as supplied by Acros Organics, Aldrich Chemical Company, and TCI without further purification. Reactions involving air-sensitive reagents were carried out in an atmosphere of N_2 or argon using standard Schlenk techniques. Anhydrous solvents were dried in an MBraun MB SCS-800 solvent purification system. NMR spectra were recorded using Bruker ARX-250 and Bruker Avance 300 spectrometers. Chemical shifts are reported in ppm relative to TMS and were determined by reference to the residual ^1H or ^{13}C solvent peaks. Melting points were determined using a Gallenkamp hot-stage microscope and are uncorrected.

N-(2,6-Diisopropylphenyl)-1,2-diaminoethane (1a); Typical Procedure

This synthesis was carried out according to the method of Marshall et al.,[16] but in a larger scale and with a more time-efficient workup procedure. To a stirred solution of 2,6-diisopropylaniline (80.1 g, 0.452 mol) in toluene (500 mL) was added 2-bromoethylamine hydrobromide (46.4 g, 0.226 mol) and the mixture was heated under reflux conditions for 18 h. The cooled suspension was poured into aq 2 M KOH (500 mL) and stirred until the organic layer became a homogeneous brown oil. The layers were separated and the aqueous layer was extracted with Et_2O (2 × 80 mL). All extracts were combined, washed with brine (100 mL), dried ($MgSO_4$), and filtered. The filtrate was concentrated by rotary evaporation and the residual brown oil was distilled in vacuum over a 15 cm Vigreux column to give the diamine as a nearly colorless oil; yield: 34.9 g (70%, 0.158 mol); bp 106 °C/0.5 mbar; $n_D^{20} = 1.531$.

^1H NMR (300.131 MHz, $CDCl_3$): δ = 7.13 (m, 3 H, CH_{aryl}), 3.37 (sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, 2 × Me_2CH), 2.99 (m, 4 H, NCH_2), 1.28 [d, $^3J_{H,H}$ = 6.8 Hz, 12 H, 2 × $(CH_3)_2CH$].

$^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ = 142.5 ($C_{ipso\text{-aryl}}$), 123.6 ($CH_{p\text{-aryl}}$), 123.6 ($C_{o\text{-aryl}}$), 123.4 ($CH_{m\text{-aryl}}$), 54.3 (NCH_2), 42.5 (NCH_2), 27.5 (Me_2CH), 24.2 [$(CH_3)_2CH$].

MS (EI+): *m/z* (%) = 220.27 (20), 190.22 (100), 175.19 (20), 160.16 (20).

Anal. Calcd for $C_{14}H_{24}N_2$ (220.27): C, 76.31; H, 10.98; N, 12.71. Found: C, 76.12; H, 11.00; N, 12.67.

N-(2,4,6-Trimethylphenyl)-1,2-diaminoethane (1b)

Prepared analogously as described for **1a** from 2,4,6-trimethylaniline (80.1 g, 0.592 mol), 2-bromoethylamine hydrobromide

(60.6 g, 0.296 mol), and toluene (500 mL). A large amount of yellowish precipitate occurred after a few hours of heating. The mixture was worked up as above; colorless oil; yield: 40.1 g (76%, 0.225 mol); bp 84–92 °C/0.6 mbar; n_D^{20} = 1.549.

^{1}H NMR (300.131 MHz, $CDCl_3$): δ = 6.83 (s, 2 H, $CH_{m\text{-aryl}}$), 2.97 (t, $^3J_{H,H}$ = 4.5 Hz, 2 H, NCH_2), 2.89 (t, $^3J_{H,H}$ = 4.5 Hz, 2 H, NCH_2), 2.29 (s, 6 H, 2 × *o*-ArCH_3), 2.24 (s, 3 H, *p*-ArCH_3).

^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ = 143.4 ($C_{ipso\text{-aryl}}$), 131.0 ($C_{p\text{-aryl}}$), 129.6 ($C_{o\text{-aryl}}$), 129.3 ($CH_{m\text{-aryl}}$), 51.1 (NCH_2), 42.4 (NCH_2), 20.4 (*o*-Ar*C*H_3), 18.2 (*p*-Ar*C*H_3).

MS (EI+): *m/z* (%) = 178.21 (30), 148.1 (100).

Anal. Calcd for $C_{11}H_{18}N_2$ (178.15): C, 74.11; H, 10.18; N, 15.71. Found: C, 74.07; H, 10.26; N, 15.69.

N-(2,6-Dimethylphenyl)-1,2-diaminoethane (1c)

Prepared analogously as described for **1a** from 2,6-trimethylaniline (47.4 g, 0.391 mol), 2-bromoethylamine hydrobromide (40.0 g, 0.195 mol), and toluene (500 mL) to give the diamine **1c** as a colorless oil; yield: 23.1 g (72%, 0.141 mol); bp 78–84 °C/0.6 mbar; n_D^{20} = 1.556.

^{1}H NMR (250.133 MHz, $CDCl_3$): δ = 6.97 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, $CH_{m\text{-aryl}}$), 6.80 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, $CH_{p\text{-aryl}}$), 3.01 (t, $^3J_{H,H}$ = 5.2 Hz, 2 H, NCH_2), 2.87 (t, $^3J_{H,H}$ = 5.2 Hz, 2 H, NCH_2), 2.29 (s, 6 H, 2 × *o*-ArCH_3).

^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ = 146.1 ($C_{ipso\text{-aryl}}$), 129.5 ($CH_{p\text{-aryl}}$), 128.7 ($C_{o\text{-aryl}}$), 121.6 ($CH_{m\text{-aryl}}$), 50.8 (NCH_2), 42.4 (NCH_2), 18.4 (Ar*C*H_3).

MS (EI+): *m/z* (%) = 164.20 (40), 134.15 (100), 105.1 (30).

Anal. Calcd for $C_{10}H_{16}N_2$ (164.13): C, 73.13; H, 9.82; N, 17.06. Found: C, 72.72; H, 9.91; N, 17.05.

1-(2,6-Diisopropylphenyl)-4,5-dihydro-1*H*-imidazole (2a); Typical Procedure

This synthesis was carried out according to the method of Marshall et al.,[16] but in larger scale and with a more time-efficient workup procedure. A solution of **1a** (64.9 g, 0.294 mol) in triethyl orthoformate (180 mL, 1.08 mol) and PTSA monohydrate (1.0 g) was heated over 18 h under reflux conditions. The cooled mixture was dissolved in H_2O (300 mL), extracted with Et_2O (3 × 100 mL), and the combined extracts were dried ($MgSO_4$). After filtration and concentration by evaporation in vacuo, the orange crude product eventually crystallized. It was distilled in a Büchi glass oven (190 °C/5 mbar) to yield the product as colorless crystals; yield: 54.1 g (79%, 0.233 mol); mp 79 °C.

^{1}H NMR (300.131 MHz, $CDCl_3$): δ = 7.31 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_{p\text{-aryl}}$), 7.19 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_{m\text{-aryl}}$), 6.82 (s, 1 H, NCHN), 4.08 (t, $^3J_{H,H}$ = 8.8 Hz, 2 H, NCH_2), 3.58 (t, $^3J_{H,H}$ = 8.8 Hz, 2 H, NCH_2), 3.11 (sept, $^3J_{H,H}$ = 7.5 Hz, 2 H, 2 × Me_2CH), 1.22 [d, $^3J_{H,H}$ = 7.5 Hz, 6 H, $(CH_3)_2CH$], 1.19 [d, $^3J_{H,H}$ = 7.5 Hz, 6 H, $(CH_3)_2CH$].

^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ = 156.1 ($C_{ipso\text{-aryl}}$), 148.4 ($CH_{p\text{-aryl}}$), 134.3 (N*C*HN), 128.6 ($C_{o\text{-aryl}}$), 124.1 ($CH_{m\text{-aryl}}$), 55.2 (N*C*H_2), 51.6 (N*C*H_2), 28.1 (Me_2CH), 24.9 [(*C*H_3)$_2$CH], 24.1 [(*C*H_3)$_2$CH].

MS (EI+): *m/z* (%) = 230.25 (100), 215.22 (35), 186.18 (80).

Anal. Calcd for $C_{15}H_{22}N_2$ (230.35): C, 78.21; H, 9.63; N, 12.16. Found: C, 78.25; H, 9.71; N, 11.92.

1-(2,4,6-Trimethylphenyl)-4,5-dihydro-1*H*-imidazole (2b)

Prepared analogously as described for **2a** from **1b** (78.0 g, 0.438 mol) and triethyl orthoformate (290 mL, 1.742 mol); colorless crystals; yield: 65.1 g (79%, 0.346 mol); mp 76 °C.

^{1}H NMR (250.133 MHz, $CDCl_3$): δ = 6.93 (s, 2 H, $CH_{m\text{-aryl}}$), 6.85 (s, 1 H, NCHN), 4.07 (t, $^3J_{H,H}$ = 9.7 Hz, 2 H, NCH_2), 3.57 (t, $^3J_{H,H}$ = 9.7 Hz, 2 H, NCH_2), 2.30 (s, 3 H, *o*-ArCH_3), 2.24 (s, 6 H, 2 × *p*-ArCH_3).

^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ = 155.9 (NCHN), 137.3 ($C_{ipso\text{-aryl}}$), 136.9 ($C_{o\text{-aryl}}$), 134.8 ($C_{p\text{-aryl}}$), 129.3 ($CH_{m\text{-aryl}}$), 55.3 (NCH_2), 48.8 (NCH_2), 20.9 (*o*-Ar*C*H_3), 18.1 (*p*-Ar*C*H_3).

MS (EI): *m/z* (%) = 188.20 (100), 148.13 (50), 132.1 (30).

Anal. Calcd for $C_{12}H_{16}N_2$ (188.27): C, 76.55; H, 8.57; N, 14.88. Found: C, 76.39; H, 8.54; N, 14.84.

1-(2,6-Dimethylphenyl)-4,5-dihydro-1*H*-imidazole (2c)

Prepared analogously as described for **2a** from **1c** (26.0 g, 0.159 mol) and triethyl orthoformate (95 mL, 0.64 mol); colorless crystals; yield: 22.1 g (79%, 0.127 mol); mp 64 °C.

^{1}H NMR (250.133 MHz, $CDCl_3$): δ = 7.09 (m, 3 H, CH_{aryl}), 6.84 (s, 1 H, NCHN), 4.06 (t, $^3J_{H,H}$ = 10.2 Hz, 2 H, NCH_2), 3.57 (t, $^3J_{H,H}$ = 10.2 Hz, 2 H, NCH_2), 2.26 (s, 6 H, 2 × *o*-ArCH_3).

^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ = 155.4 (N*C*HN), 137.2 ($C_{ipso\text{-aryl}}$), 136.8 ($C_{o\text{-aryl}}$), 128.4 ($CH_{p\text{-aryl}}$), 127.3 ($CH_{m\text{-aryl}}$), 55.0 (NCH_2), 48.4 (NCH_2), 17.9 (*o*-Ar*C*H_3).

MS (EI+): *m/z* (%) = 174.19 (100), 146.16 (45), 134.16 (65).

Anal. Calcd for $C_{12}H_{16}N_2$ (174.24): C, 75.82; H, 8.10; N, 16.08. Found: C, 75.54; H, 8.10; N, 16.06.

1,3-Propanediylbis-1-[3-(2,6-diisopropylphenyl)-4,5-dihydro-1*H*-imidazolium] Dibromide (3a); Typical Procedure

This synthesis was carried out according to the method of Marshall et al.[16] In a round-bottomed flask were heated **2a** (20.3 g, 88.2 mmol) and 1,3-dibromopropane (8.76 g, 43.4 mmol) and the mixture was stirred until a homogeneous mass was formed. After some min at 100 °C, the mixture hardened to an orange glass. The glass was heated for 2 h and then cooled to r.t. Then, the glass was dissolved in CH_2Cl_2 (50 mL) and the crude product was precipitated by adding Et_2O. Filtration gave the product as a colorless solid, which was recrystallized from CH_2Cl_2 and Et_2O; yield: 26.0 g (90%, 39.4 mmol). Crystals for X-ray structure determination were collected from a CH_2Cl_2–Et_2O solution at r.t.; mp 256 °C.

^{1}H NMR (300.131 MHz, $CDCl_3$): δ = 9.63 (s, 2 H, NCHN), 7.33 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, $CH_{p\text{-aryl}}$), 7.13 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, $CH_{m\text{-aryl}}$), 4.52 (t, $^3J_{H,H}$ = 9.8 Hz, 4 H, NCH_2), 4.34 (t, $^3J_{H,H}$ = 6.9 Hz, 4 H, NCH_2CH_2), 4.15 (t, $^3J_{H,H}$ = 9.8 Hz, 4 H, NCH_2), 2.90 (pseudo sept, $^3J_{H,H}$ = 6.8 Hz, 4 H, 4 × Me_2CH), 2.38 (quint, $^3J_{H,H}$ = 6.9 Hz, 2 H, $CH_2CH_2CH_2$), 1.21 [d, $^3J_{H,H}$ = 6.8 Hz, 12 H, 2 × $(CH_3)_2CH$], 1.17 [d, $^3J_{H,H}$ = 6.8 Hz, 12 H, 2 × $(CH_3)_2CH$].

^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ = 158.5 (NCHN), 146.4 ($C_{o\text{-aryl}}$), 130.8 ($CH_{p\text{-aryl}}$), 129.7 ($C_{ipso\text{-aryl}}$), 124.7 ($CH_{m\text{-aryl}}$), 53.2 (NCH_2), 49.4 (NCH_2), 45.3 (NCH_2CH_2), 28.5 (Me_2CH), 25.0 [(CH_3)$_2$CH], 24.8 ($CH_2CH_2CH_2$), 23.9 [(CH_3)$_2$CH].

MS (FAB+): *m/z* (%) = 581.45 (50, $[M - Br]^+$), 501.51 (50), 271.3 (100).

Anal. Calcd for $C_{33}H_{50}Br_2N_4$ (662.58) + CH_2Cl_2: C, 57.07; H, 7.29; N, 7.95. Found: C, 57.07; H, 7.55; N, 8.00.

Crystal Data and Structure Refinement for 3a[20]

Empirical formula $C_{35.50}H_{55}Br_2Cl_5N_4$; crystal system: triclinic; space group: $P\bar{1}$; Z = 2; unit cell dimensions: *a* = 9.0161 Å, α = 72.850°, *b* = 15.3247 Å, β = 83.340°, *c* = 16.4048(19) Å, γ = 82.965°; goodness-of-fit on F^2: 1.01; final *R* indices [$I > 2\sigma(I)$]: *R*1 = 0.049, *wR*2 = 0.109; largest difference peak and hole 1.20 and –0.48 eÅ^{-3}.

1,3-Propanediylbis-1-[3-(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-imidazolium] Dibromide (3b)

The procedure for the synthesis of **3a** was followed using **2b** (16.3 g, 86.6 mmol) and 1,3-dibromopropane (8.7 g, 43.1 mmol); white solid; yield: 23.1 g (92%, 39.9 mmol); mp 306 °C.

^{1}H NMR (300.131 MHz, $CDCl_3$): δ = 9.49 (s, 2 H, NCHN), 6.83 (s, 4 H, $CH_{m\text{-aryl}}$), 4.46 (t, $^3J_{H,H}$ = 9.0 Hz, 4 H, NCH_2), 4.25 (t, $^3J_{H,H}$ = 6.1 Hz, 4 H, NCH_2), 4.17 (t, $^3J_{H,H}$ = 9.0 Hz, 4 H, NCH_2), 2.35 (quint, $^3J_{H,H}$ = 6.1 Hz, 2 H, $CH_2CH_2CH_2$), 2.25 (s, 12 H, 4 × *o*-ArCH_3), 2.17 (s, 6 H, 2 × *p*-ArCH_3).

^{13}C{^{1}H} NMR (75.467 MHz, $CDCl_3$): δ = 158.8 (NCHN), 140.0 ($C_{ipso\text{-aryl}}$), 135.1 ($C_{o\text{-aryl}}$), 130.4 ($C_{p\text{-aryl}}$), 129.8 ($CH_{m\text{-aryl}}$), 51.0 (NCH_2), 49.2 (NCH_2), 45.4 (NCH_2CH_2), 24.9 ($CH_2CH_2CH_2$), 20.8 (*o*-ArCH_3), 18.1 (*p*-ArCH_3).

MS (ESI+): *m/z* (%) = 499.23 (100, [M – Br]$^+$).

1,3-Propanediylbis-1-[3-(2,6-diisopropylphenyl)-4,5-dihydro-1*H*-imidazolium] Bis(*p*-toluenesulfonate) (4)

A solution of **3a** (1.0 g, 1.5 mmol) in CH_2Cl_2 (20 mL) and a solution of PTSA monohydrate (0.8 g, 4.6 mmol) in distilled H_2O (20 mL) were mixed and vigorously stirred for 1 h. Then the layers were separated, the organic layer was washed with H_2O (20 mL), dried ($MgSO_4$), and filtered. The product was precipitated by dropwise addition of Et_2O to the filtrate. Recrystallization from CH_2Cl_2 and Et_2O afforded **4** as colorless crystals; yield: 1.0 g (81%, 1.2 mmol); mp 218 °C.

^{1}H NMR (300.131 MHz, $CDCl_3$): δ = 9.02 (s, 2 H, NCHN), 7.55 (d, $^3J_{H,H}$ = 5.0 Hz, 4 H, $CH_{m\text{-aryl}}$), 7.37 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_{p\text{-aryl}}$), 7.17 (d, $^3J_{H,H}$ = 7.5 Hz, 4 H, $CH_{m\text{-aryl}}$), 6.98 (d, $^3J_{H,H}$ = 5.0 Hz, 4 H, $CH_{o\text{-aryl}}$), 4.50 (t, $^3J_{H,H}$ = 10.0 Hz, 4 H, NCH_2), 4.20 (t, $^3J_{H,H}$ = 5.0 Hz, 4 H, NCH_2), 4.10 (t, $^3J_{H,H}$ = 10.0 Hz, 4 H, NCH_2), 2.87 (pseudo sept, $^3J_{H,H}$ = 5.0 Hz, 4 H, 4 × Me_2CH), 2.57 (quint, $^3J_{H,H}$ = 5.0 Hz, 2 H, $CH_2CH_2CH_2$), 2.25 (s, 6 H, 2 × ArCH_3, tosylate), 1.21 [d, $^3J_{H,H}$ = 5.0 Hz, 12 H, 2 × $(CH_3)_2CH$], 1.17 [d, $^3J_{H,H}$ = 5.0 Hz, 12 H, 2 × $(CH_3)_2CH$].

^{13}C{^{1}H} NMR (75.475 MHz, $CDCl_3$): δ = 155.0 (NCHN), 146.7 ($C_{o\text{-aryl}}$), 143.5 ($C_{ipso\text{-aryl}}$, tosylate), 139.1 (*p*-ArCH_3), 130.9 ($C_{p\text{-aryl}}$), 130.1 ($C_{ipso\text{-aryl}}$), 128.5 ($CH_{o\text{-aryl}}$, tosylate), 125.7 ($CH_{m\text{-aryl}}$, tosylate), 124.8 ($CH_{m\text{-aryl}}$), 53.5 (NCH_2), 49.2 (NCH_2), 45.5 (NCH_2CH_2), 28.7 (Me_2CH), 25.8 ($CH_2CH_2CH_2$), 24.8 [$(CH_3)_2CH$], 24.1 [$(CH_3)_2CH$], 21.2 (ArCH_3, tosylate).

MS (ESI+): *m/z* (%) = 673.5 (100, [M – OTs]$^+$).

Anal. Calcd for $C_{47}H_{64}N_4O_6S_2$ (845.17): C, 66.79; H, 7.63; N, 6.63. Found: C, 66.74; H, 7.61; N, 6.60.

3-Bromopropyl-1-[3-(2,6-diisopropylphenyl)-4,5-dihydro-1*H*-imidazolium] Bromide (5a)

To a stirred solution of **2a** (2.0 g, 8.7 mmol) in Et_2O (15 mL) was added dropwise a solution of 1,3-dibromopropane (17.6 g, 87.0 mmol) in Et_2O (15 mL). The mixture was heated for 18 h at reflux. During reaction the product precipitated as a fine white solid. After cooling to r.t., the precipitate was filtered off and recrystallized from CH_2Cl_2 and Et_2O. The crude product contained 85% (determined by ^{1}H NMR spectroscopy) of the desired monoimidazolinium salt **5a** contaminated with 15% of **3a**. All attempts of purification were of no avail. Crystals for X-ray structure determination were collected from a CH_2Cl_2–Et_2O solution at r.t.

^{1}H NMR (250.133 MHz, $CDCl_3$): δ = 9.49 (s, 1 H, NCHN), 7.43 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, $CH_{p\text{-aryl}}$), 7.22 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, $CH_{m\text{-aryl}}$), 4.46 (t, $^3J_{H,H}$ = 11.4 Hz, 2 H, NCH_2), 4.25 (m, 4 H, NCH_2), 3.64 (t, $^3J_{H,H}$ = 5.9 Hz, 2 H, CH_2CH_2Br), 2.95 (sept, $^3J_{H,H}$ = 6.9 Hz, 2 H, 2 × Me_2CH), 2.40 (pseudo quint, $^3J_{H,H}$ = 6.3 Hz, 2 H, $CH_2CH_2CH_2$), 1.26 [pseudo d, $^3J_{H,H}$ = 6.9 Hz, 12 H, 2 × $(CH_3)_2CH$].

^{13}C{^{1}H} NMR (75.467 MHz, $CDCl_3$): δ = 158.7 (NCHN), 146.4 ($C_{o\text{-aryl}}$), 130.9 ($CH_{p\text{-aryl}}$), 129.7 ($C_{ipso\text{-aryl}}$), 124.7 ($CH_{m\text{-aryl}}$), 53.4 (NCH_2), 49.1 (NCH_2), 47.1 (NCH_2CH_2), 45.3 (CH_2CH_2Br), 29.9 ($CH_2CH_2CH_2$), 28.6 (Me_2CH), 25.0 [$(CH_3)_2CH$], 23.9 [$(CH_3)_2CH$].

MS (ESI+): *m/z* (%) = 351.14 (100, [M – Br]$^+$).

Crystal Data and Structure Refinement for 5a[20]

Empirical formula $C_{18}H_{28}Br_2N_2$; crystal system: monoclinic; space group: $P2_1/n$; Z = 4; unit cell dimensions: a = 14.4324 Å, α = 90°, b = 9.0217 Å, β = 90.193°, c = 15.0491(19) Å, γ = 90°; goodness-of-fit on F^2: 1.26; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.051, $wR2$ = 0.163; largest difference peak and hole 0.87 and –1.18 eÅ^{-3}.

3-Chloropropyl-1-[3-(2,6-diisopropylphenyl)-4,5-dihydro-1*H*-imidazolium] Bromide (5b)

To a stirred solution of **2a** (4.0 g, 17 mmol) in Et_2O (15 mL) was added dropwise a solution of 1-bromo-3-chloropropane (2.7 g, 17 mmol) in Et_2O (15 mL). The mixture was heated for 18 h at reflux. During reaction the product precipitated as a fine white solid. After cooling to r.t., the precipitate was filtered off and recrystallized from CH_2Cl_2 and Et_2O; yield: 2.1 g (31%, 5.4 mmol); mp 174 °C.

^{1}H NMR (300.130 MHz, $CDCl_3$): δ = 9.53 (s, 1 H, NCHN), 7.43 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_{p\text{-aryl}}$), 7.23 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_{m\text{-aryl}}$), 4.44 (t, $^3J_{H,H}$ = 10.9 Hz, 2 H, NCH_2), 4.29 (t, $^3J_{H,H}$ = 5.6 Hz, 2 H, NCH_2), 4.22 (t, $^3J_{H,H}$ = 10.9 Hz, 2 H, NCH_2), 3.85 (t, $^3J_{H,H}$ = 5.6 Hz, 2 H, CH_2CH_2Cl), 2.95 (pseudo sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, 2 × Me_2CH), 2.33 (quint, $^3J_{H,H}$ = 5.6 Hz, 2 H, $CH_2CH_2CH_2$), 1.26 [pseudo d, $^3J_{H,H}$ = 6.8 Hz, 12 H, 2 × $(CH_3)_2CH$].

^{13}C{^{1}H} NMR (75.475 MHz, $CDCl_3$): δ = 159.0 (NCHN), 146.6 ($C_{o\text{-aryl}}$), 131.2 ($CH_{p\text{-aryl}}$), 129.8 ($C_{ipso\text{-aryl}}$), 125.0 ($CH_{m\text{-aryl}}$), 53.4 (NCH_2), 49.1 (NCH_2), 46.6 (NCH_2CH_2), 42.3 (CH_2CH_2Cl), 29.4 ($CH_2CH_2CH_2$), 28.8 (Me_2CH), 25.2 [$(CH_3)_2CH$], 24.2 [$(CH_3)_2CH$].

MS (ESI+): *m/z* (%) = 307.36 (100, [M – Br]$^+$).

1,3-Propanediyl-1-[3-(2,6-dimethylphenyl)-4,5-dihydro-1*H*-imidazolium]-1-[3-(2,6-diisopropylphenyl)-4,5-dihydro-1*H*-imidazolium] Dibromide (6)

A stirred mixture of **5a** (0.4 g as a 6:1 mixture with **3a**) and **2c** (0.65 g, 3.7 mmol)] was heated at 100 °C until a homogeneous mixture was formed. After some min, the mixture hardened as an orange glass. The glass was heated for 2 h and then cooled to r.t. Then, the mixture was dissolved in CH_2Cl_2 (50 mL) and addition of Et_2O to the solution precipitated the crude product as a colorless solid. The product contained 85% (determined by ^{1}H NMR spectroscopy) of the desired nonsymmetrically substituted bisimidazolinium salt **6** along with 15% of **3a**. Crystals for X-ray structure determination were collected from a CH_2Cl_2–Et_2O solution at r.t.

^{1}H NMR (300.130 MHz, $CDCl_3$): δ = 9.71 (s, 1 H, NC*H*NAryl), 9.68 (s, 1 H, NC*H*NAryl), 7.42 [t, $^3J_{H,H}$ = 9.0 Hz, 1 H, $CH_{p\text{-aryl}}$ (diisopropylphenyl)], 7.25 [d, $^3J_{H,H}$ = 9.0 Hz, 2 H, $CH_{m\text{-aryl}}$ (diisopropylphenyl)], 7.23 [t, $^3J_{H,H}$ = 6.0 Hz, 1 H, $CH_{p\text{-aryl}}$ (dimethylphenyl)], 7.11 [d, $^3J_{H,H}$ = 6.0 Hz, 2 H, $CH_{m\text{-aryl}}$ (dimethylphenyl)], 4.62–4.18 (m, 8 H, NCH_2), 2.96 (sept, $^3J_{H,H}$ = 6.0 Hz, 2 H, 2 × Me_2CH), 2.45 (quint, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_2CH_2CH_2$), 2.40 (s, 6 H, 2 × *o*-ArCH_3), 1.29 [pseudo t, $^3J_{H,H}$ = 6.0 Hz, 12 H, 2 × $(CH_3)_2CH$].

^{13}C{^{1}H} NMR (75.467 MHz, $CDCl_3$): δ = 158.9 (N*C*HN), 158.8 (N*C*HN), 146.6 ($CH_{m\text{-aryl}}$), 135.6 ($CH_{m\text{-aryl}}$), 133.1 ($CH_{p\text{-aryl}}$), 131.3 ($CH_{p\text{-aryl}}$), 130.1 ($C_{ipso\text{-aryl}}$), 129.8 ($C_{ipso\text{-aryl}}$), 129.4 ($C_{o\text{-aryl}}$), 124.9 ($C_{o\text{-aryl}}$), 53.4 (NCH_2), 51.1 (NCH_2), 49.5 (NCH_2), 49.4 (NCH_2), 45.6 (NCH_2CH_2), 45.5 (NCH_2CH_2), 28.8 (Me_2CH), 25.2 [$(CH_3)_2CH$], 25.1 ($CH_2CH_2CH_2$), 24.2 [$(CH_3)_2CH$], 18.4 (*o*-ArCH_3).

MS (ESI+): *m/z* (%) = 525.36 (30, [M – Br]$^+$), 223.17 (100, [M – 2 Br]$^{2+}$).

Crystal Data and Structure Refinement for 6[20]

Empirical formula $C_{30.50}H_{43.50}Br_2Cl_{4.50}N_4$; crystal system: triclinic; space group: $P\bar{1}$, $Z = 4$; unit cell dimensions: $a = 13.918$ Å, $\alpha = 105.722°$, $b = 16.3375$ Å, $\beta = 93.205°$, $c = 16.8897(19)$ Å, $\gamma = 90.619°$; goodness-of-fit on F^2: 1.06; final R indices $[I > 2\sigma(I)]$: $R1 = 0.074$, $wR2 = 0.143$; largest difference peak and hole 0.81 and –0.70 eÅ^{-3}.

1-Methyl-4,5-dihydro-1*H*-imidazole (7)

This synthesis was carried out according to the method of Cetinkaya et al.[18] In a round-bottomed flask equipped with a 15 cm Vigreux column and distillation bridge *N*-methylethylenediamine (2.83 g, 38.1 mmol) was stirred with *N*,*N*-dimethylformamide dimethyl acetal (5.1 g, 41 mmol) at 90 °C. The mixture was heated to 110 °C for 1 h and then distilled to yield the product (178–180 °C/1 bar) as a colorless oil; yield: 2.6 g (81%, 31 mmol). The product fraction contained up to 15% of DMF and MeOH (determined by ^{1}H NMR spectroscopy) and was used without further purification.

^{1}H NMR (250.134 MHz, $CDCl_3$): δ = 6.70 (s, 1 H, NCHN), 3.79 (t, $^3J_{H,H}$ = 9.6 Hz, 2 H, NCH_2), 3.14 (t, $^3J_{H,H}$ = 9.6 Hz, 2 H, NCH_2), 2.80 (s, 3 H, NCH_3).

^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ = 158.6 (NCHN), 55.4 (NCH_2), 50.9 (CH_3NCH_2), 34.3 (NCH_3).

MS (ESI+): *m/z* (%) = 410.40 (60, $[M_4 + DMF + H]^+$), 326.35 (100, $[M_3 + DMF + H]^+$), 242.31 (70, $[M_2 + DMF + H]^+$), 85.21 (100, $[M + H]^+$).

1,3-Propanediyl-1-[3-(2,4,6-trimethylphenyl)imidazolium]-1-[3-(2,6-diisopropylphenyl)-4,5-dihydro-1*H*-imidazolium] Bromide Chloride (8)

A mixture of **5b** (0.35 g, 0.90 mmol) and *N*-mesitylimidazole (0.19 g, 1.0 mmol) was heated at 100 °C for 3 h, when the reagents first melted and then formed a light orange glass.[10] After cooling to r.t., the glass was dissolved in EtOH (10 mL) and precipitated by the addition of Et_2O, decanted, and dried in vacuo. The resulting light yellow foam was stirred for 24 h in a mixture of EtOAc (15 mL) and a few drops of CH_2Cl_2 to afford the product as colorless solid; yield: 0.36 mg (80%, 0.63 mmol). Crystals for X-ray structure determination were collected from a CH_2Cl_2–Et_2O solution at r.t.; mp 266 °C.

^{1}H NMR (300.131 MHz, $CDCl_3$): δ = 10.22 [s, 1 H, NCHN (imidazole)], 9.51 (s, 1 H, NCHN), 8.49 [pseudo s, 1 H, NC*H*CHN (imidazole)], 7.39 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, $CH_{p\text{-aryl}}$), 7.19 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, $CH_{m\text{-aryl}}$), 7.05 [pseudo s, 1 H, NCHC*H*N (imidazole)], 6.97 [s, 2 H, $CH_{m\text{-aryl}}$ (mesityl)], 5.12 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, imidazole-CH_2), 4.72 (t, $^3J_{H,H}$ = 12.0 Hz, 2 H, NCH_2), 4.33 (t, $^3J_{H,H}$ = 6.0 Hz, 2 H, imidazoline-CH_2), 4.26 (t, $^3J_{H,H}$ = 12.0 Hz, 2 H, NCH_2), 2.99 (pseudo sept, $^3J_{H,H}$ = 7.0 Hz, 2 H, 2 × Me_2CH), 2.72 (pseudo quint, 2 H, $CH_2CH_2CH_2$), 2.31 (s, 3 H, *p*-ArylCH_3), 2.03 (s, 6 H, *o*-ArCH_3), 1.26 [d, $^3J_{H,H}$ = 7.0 Hz, 6 H, 2 × $(CH_3)_2$CH], 1.23 [d, $^3J_{H,H}$ = 7.0 Hz, 6 H, 2 × $(CH_3)_2$CH].

^{13}C{^{1}H} NMR (75.467 MHz, $CDCl_3$): δ = 158.7 [NCHN (imidazoline)], 146.6 ($C_{o\text{-aryl}}$ (imidazoline)], 141.3 [($C_{p\text{-aryl}}$ (mesityl)], 137.5 [NCHN (imidazole)], 134.2 [$C_{o\text{-aryl}}$ (mesityl)], 131.1 [$CH_{p\text{-aryl}}$ (imidazoline)], 130.7 [$C_{ipso\text{-aryl}}$ (mesityl)], 130.0 [$CH_{m\text{-aryl}}$ (mesityl)], 129.8 ($C_{ipso\text{-aryl}}$ (imidazoline)], 124.9 [$CH_{m\text{-aryl}}$ (imidazoline)], 124.4 (NCHCHN), 122.7 (NCHCHN), 53.6 (NCH_2), 49.7 (NCH_2), 47.2 [(imidazole) NCH_2CH_2], 45.6 [(imidazoline) NCH_2CH_2], 28.9 ($CH_2CH_2CH_2$), 28.8 (Me_2CH), 25.3 [$(CH_3)_2$CH], 25.2 [$(CH_3)_2$CH], 21.1 (*p*-ArCH_3), 17.6 (*o*-ArCH_3).

MS (ESI+): *m/z* (%) = 539.4 (100, $[M – Cl]^+$), 493.4 (20, $[M – Br]^+$).

Crystal Data and Structure Refinement for 8[20]

Empirical formula $C_{30}H_{42}Br_{1.75}Cl_{0.25}N_4$; crystal system: monoclinic; space group: $P2_1/n$; $Z = 4$; unit cell dimensions: $a = 18.5166(14)$ Å, $\alpha = 90°$, $b = 6.5178$ Å, $\beta = 90.159°$, $c = 25.6265(19)$ Å, $\gamma = 90°$; goodness-of-fit on F^2: 1.02; final R indices $[I > 2\sigma(I)]$: $R1 = 0.034$, $wR2 = 0.075$; largest difference peak and hole 0.39 and –0.20 eÅ^{-3}.

1,3-Propanediyl-1-[3-methyl-4,5-dihydro-1*H*-imidazolium]-1-[3-(2,6-diisopropylphenyl)-4,5-dihydro-1*H*-imidazolium] Bromide Chloride (9)

A stirred mixture of **5b** (1.5 g, 3.9 mmol) and **7** (0.45 g, 5.9 mmol) was heated at 90 °C for 3 h, when the reagents first melted and then formed a light orange glass. Once cooled to r.t., the crude product was dissolved in EtOH (20 mL) and precipitated by the addition of Et_2O, decanted, and dried in vacuo. The resulting light yellow foam was stirred for 24 h in a mixture of EtOAc (15 mL) and a few drops of CH_2Cl_2 to afford the product as a colorless solid; yield: 1.2 g (68%, 2.6 mmol); mp 141 °C.

^{1}H NMR (300.130 MHz, $CDCl_3$): δ = 9.74 (s, 1 H, NC*H*NAryl), 9.60 (s, 1 H, NC*H*NCH_3), 7.35 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, $CH_{p\text{-aryl}}$), 7.15 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, $CH_{m\text{-aryl}}$), 4.53 (t, $^3J_{H,H}$ = 10.5 Hz, 2 H, NCH_2CH_2NAryl), 4.25–4.11 (m, 6 H, NCH_2), 4.03–3.92 (m, 4 H, $NCH_2CH_2NCH_3$), 3.28 (s, 3 H, NCH_3), 2.90 (sept, $^3J_{H,H}$ = 6.6 Hz, 2 H, 2 × Me_2CH), 2.28 (m, 2 H, $CH_2CH_2CH_2$), 1.20 [d, $^3J_{H,H}$ = 6.6 Hz, 12 H, 2 × $(CH_3)_2$CH].

^{13}C{^{1}H} NMR (75.467 MHz, $CDCl_3$): δ = 159.8 (NCHNAryl), 158.9 (NCHNCH_3), 146.9 ($C_{o\text{-aryl}}$), 131.4 ($CH_{p\text{-aryl}}$), 130.3 ($C_{ipso\text{-aryl}}$), 125.2 ($CH_{m\text{-aryl}}$), 54.0 (NCH_2CH_2NAryl), 51.3 (CH_2N), 49.7 (NCH_2), 49.7 (NCH_2), 45.8 (AlkylNCH_2CH_2N), 45.4 (AlkylNCH_2CH_2N), 35.5 (NCH_3), 29.1 (Me_2CH), 25.5 [$(CH_3)_2$CH], 24.5 [$(CH_3)_2$CH].

MS (ESI+): *m/z* (%) = 435.39 (50, $[M – Cl]^+$), 391.47 (20, $[M – Br]^+$), 178.47 (100, $[M – Br – Cl]^{2+}$).

Dicopper(I) Complex 10 Based on Ligand Precursor 3a

In an argon-filled Schlenk flask, **3a** (0.20 g, 0.30 mmol) and NaHMDS (0.11 g, 0.60 mmol) were dissolved in anhyd toluene (5 mL) and stirred at r.t. for 1 h. $(CuBrSMe_2)_2$ (0.13 g, 0.31 mmol) was added under argon to the light orange solution. The obtained yellowish suspension was stirred for additional 24 h at r. t. During this time, the mixture might change to a more gray color. It is recommended to let the mixture react until the suspension had an orange color, which might last up to 48 h. The solvent was removed in vacuo and the slightly orange residue was stirred in anhyd CH_2Cl_2 (5 mL). The suspension was filtered through a plug of Celite. Dropwise addition of anhyd Et_2O to the filtrate under vigorous stirring under argon precipitated the product as an off-white solid. Recrystallization from CH_2Cl_2 and Et_2O gave **10** as air-sensitive white or off-white solid; yield: 0.11 g (50%, 0.14 mmol). Crystals for X-ray structure determination were collected from a CH_2Cl_2–Et_2O solution at –50 °C; mp 204 °C.

^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 6.87 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, $CH_{p\text{-aryl}}$), 6.71 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, $CH_{m\text{-aryl}}$), 3.49 (t, $^3J_{H,H}$ = 6.0 Hz, 4 H, NCH_2), 3.41 (t, $^3J_{H,H}$ = 6.0 Hz, 4 H, NCH_2), 3.35 (t, $^3J_{H,H}$ = 4.5 Hz, 4 H, NCH_2), 2.49 (pseudo sept, $^3J_{H,H}$ = 6.9 Hz, 4 H, 2 × Me_2CH), 1.74 (quint, $^3J_{H,H}$ = 4.5 Hz, 2 H, $CH_2CH_2CH_2$), 0.79 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, 2 × $(CH_3)_2$CH], 0.74 (d, $^3J_{H,H}$ = 6.9 Hz, 12 H, 2 × $(CH_3)_2$CH].

^{13}C{^{1}H} NMR (75.468 MHz, $CDCl_3$–DMSO-d_6): δ = 200.2 (C–Cu), 145.8 ($C_{o\text{-aryl}}$), 133.6 ($C_{ipso\text{-aryl}}$), 128.3 ($CH_{p\text{-aryl}}$), 123.3 ($CH_{m\text{-aryl}}$), 52.7 (ArylNCH_2), 48.1 (AlkylNCH_2), 46.5 ($NCH_2CH_2CH_2$), 27.1 (Me_2CH), 26.2 ($CH_2CH_2CH_2$), 24.2 [$(CH_3)_2$CH], 22.9 [$(CH_3)_2$CH].

MS (ESI+): *m/z* (%) = 645.29 (100, $[M – 2 Br + OH]^+$).

Anal. Calcd for $C_{33}H_{48}Br_2Cu_2N_4$ (784.08): C, 50.32; H, 6.14; N, 7.11. Found: C, 49.92; H, 6.25; N, 6.92.

Crystal Data and Structure Refinement for 10[20]

Empirical formula $C_{33}H_{48}Br_2Cu_2N_4$; crystal system: monoclinic; space group: $P2_1/c$; $Z = 4$; unit cell dimensions: $a = 13.4293$ Å, $\alpha = 90°$, $b = 13.1184$ Å, $\beta = 103.461°$, $c = 21.2313(19)$ Å, $\gamma = 90°$; goodness-of-fit on F^2: 1.10; final R indices $[I > 2\sigma(I)]$: $R_1 = 0.044$, $wR_2 = 0.082$; largest difference peak and hole 0.42 and –0.43 eÅ^{-3}.

Dicopper(I) Complex 11 Based on Ligand Precursor 3b

In an argon-filled Schlenk flask, **3b** (0.20 g, 0.35 mmol) and Ag_2O (0.10 g, 0.43 mmol) were suspended in anhyd CH_2Cl_2 (5 mL). The reaction mixture was stirred at r.t. for 24 h in the absence of light. Then, $(CuBrSMe_2)_2$ (0.15 g, 0.36 mmol) was added under argon and the mixture was stirred for 24 h at r.t. Then, the mixture was filtered via Schlenk technique through a plug of Celite. After 1 h, some more silver precipitated, which was removed by a second filtration. Dropwise addition of anhyd Et_2O to the slightly green filtrate precipitated the crude product as an air-sensitive greenish solid. Recrystallization from CH_2Cl_2 and Et_2O gave the product as a white solid; yield: 0.10 g (43%, 0.15 mmol). Crystals for X-ray structure determination were collected from a THF–Et_2O solution at r.t.; mp 153 °C.

^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 6.88 (s, 4 H, $CH_{m\text{-aryl}}$), 3.86 (pseudo s, 8 H, NCH_2), 3.79 (t, $^3J_{H,H}$ = 7.8 Hz, 4 H, NCH_2CH_2), 2.25 (s, 6 H, 2 × *p*-ArCH_3), 2.21(s, 12 H, 4 × *o*-ArCH_3), 2.15 (quint, $^3J_{H,H}$ = 7.8 Hz, 2 H, $CH_2CH_2CH_2$).

^{13}C{^{1}H} NMR (75.467 MHz, $CDCl_3$): δ = 201.8 (C–Cu), 138.5 ($C_{p\text{-aryl}}$), 135.6 ($CH_{m\text{-aryl}}$), 135.0 ($C_{ipso\text{-aryl}}$), 129.6 ($C_{o\text{-aryl}}$), 51.2 (ArylNCH_2), 49.1 (AlkylNCH_2), 47.7 ($NCH_2CH_2CH_2$), 27.5 ($CH_2CH_2CH_2$), 21.0 (*p*-ArCH_3), 18.3 (*o*-ArCH_3).

MS (ESI+): *m/z* (%) = 561.25 (100, $[M - 2\ Br + OH]^+$).

Anal. Calcd for $C_{27}H_{36}Br_2Cu_2N_4$ (703.50): C, 46.10; H, 5.16; N, 7.96. Found: C, 46.19; H, 5.25; N, 7.76.

Crystal Data and Structure Refinement for 11

Empirical formula $C_{27}H_{36}Br_2Cu_2N_4$; crystal system: monoclinic; space group: $P2_1/n$; $Z = 9$; unit cell dimensions: $a = 13.1062$ Å, $\alpha = 90°$, $b = 33.1870$ Å, $\beta = 91.518°$, $c = 13.4956(19)$ Å, $\gamma = 90°$; goodness-of-fit on F^2: 1.76; final R indices $[I > 2\sigma(I)]$: $R_1 = 0.154$, $wR_2 = 0.351$; largest difference peak and hole 2.42 and –1.34 eÅ^{-3}.

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(20) CCDC 768548–768552 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033, E-mail: deposit@ccdc.cam.ac.uk].