



 Cite this: *New J. Chem.*, 2025, 49, 6554

 Received 1st October 2024,
 Accepted 13th March 2025

DOI: 10.1039/d4nj04276j

rsc.li/njc

Bis(N-heterocyclic carbene)s incorporating silicon in the ligand backbone†

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A straightforward, modular, and high yielding synthetic protocol for accessing bis(N-heterocyclic carbene)s incorporating alkyl and aryl *N*-substituents with varied steric profiles, as well as flexible dimethylsilane and dimethylsiloxane linkers is presented. This provides a more direct entry to both new and reported chelating bis(carbene) ligands. The incorporation of dimethylsilicon fragments rather than linear alkyl chains in the linker is expected to enhance the chelating properties of the ligand by means of the Thorpe–Ingold effect.

Introduction

The first bis(N-heterocyclic carbene)s, bis(NHC)s, was reported only five years after Arduengo's seminal communication of the first stable N-heterocyclic carbene, NHC, in 1991.¹ Since then, bidentate bis(NHC)s have established themselves as exceptional ancillary ligands in homogeneous catalysis and small molecule activation, acting as excellent σ -donors and moderate π -acceptors with easily tunable steric profiles. Their transition metal complexes have been employed in a variety of applications,^{2–4} including cross-coupling reactions, methane oxidation,⁵ hydrogenation⁶ and transfer hydrogenation, water oxidation,⁷ photocatalysis, assembly of supramolecular architectures,^{8,9} deoxygenative arylation,¹⁰ and others.¹¹ Amongst the ample palette of known bis(NHC) ligands, an overwhelming majority are tethered by linear alkyl chains ranging between one to four carbons long. Chelation (A) is typically enforced by rigid, strictly *cis*-binding methylene-bridged bis(NHC)s (Chart 1), whereas ligands incorporating longer linkers frequently coordinate in a ditopic fashion, yielding bimetallic complexes (B). Equilibria between chelating and bridging structures have been observed,¹² and this issue is compounded by the potential formation of open-chain, bridging, double-bridging, and oligomeric species, which in turn can make product purification and isolation difficult. Several bis(NHC)s incorporating long alkyl chains ($n > 4$, Chart 1) have also been reported, and they usually formed

bridging bimetallic complexes of type B.^{2,3} NHCs connected by long alkyl chains have been incorporated into macrocyclic ligand systems.¹³ However, exceedingly few examples of chelating bis(NHC)s incorporating alkyl linkers longer than four atoms are known,^{12,14} and they always incorporate *N*-alkyl substituents, or “wingtips”. The presence of donor atoms such as nitrogen,¹⁵ oxygen,¹⁶ or heavier chalcogens¹⁷ in the linker appears to promote chelation, even if these atoms are not directly involved in bonding to the metal.

Notwithstanding the widespread use and proven applicability as ancillary ligands in catalysis of monodentate, *N*-aryl-substituted NHCs incorporating mesityl (IMes and SIMes) and 2,6-diisopropylphenyl (IPr and SIPr) substituents, the number of chelating, *N*-aryl-substituted bis(NHC)s featuring longer alkyl linkers remains small.³ Only a handful of such complexes A with $n > 1$ have been crystallographically characterized, including: $n = 2, 3$, and 4, R = Mes and Dipp, $ML_n = \text{Re}(\text{CO})_3\text{Br}$ and $\text{Re}(\text{CO})_3(\text{MeCN})^+$;¹⁸ $n = 2$ and 3, R = Ph and Mes, $ML_n = \text{Rh}(\text{cod})^+$;¹⁹ $n = 2, 3$, and 4, R = Mes, $ML_n = \text{Ni}(\text{CO})_3$;²⁰ $n = 2$, R = Mes, $ML_n = \text{FeBr}_2$;²¹ $n = 2$, R = 2,6-Me₂C₆H₃ and 4-(EtOOC)C₆H₄, $ML_n = \text{PdBr}_2$;²² $n = 2$, R = Mes and

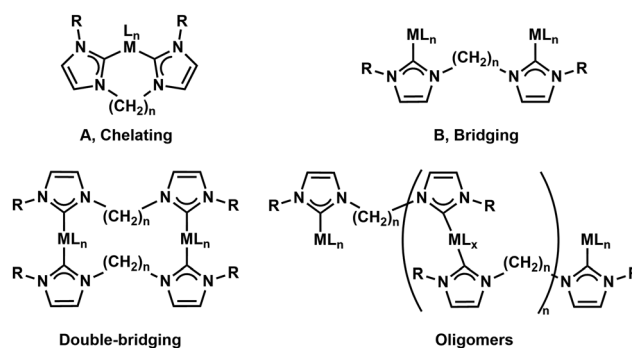


Chart 1 Binding modes of bidentate NHCs.

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 † Electronic supplementary information (ESI) available: Experimental details for the synthesis of organosilanes and *N*-substituted imidazole reagents, as well as NMR spectra for all compounds and crystallographic details **2b**, **2e** and **2i**. CCDC 2279641–2279643. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4nj04276j>

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2,4-Me₂C₆H₃, ML_n = PdBr₂;²³ n = 2, R = 1,2-cyclohexylene, ML_n = PdCl₂.²⁴

A logical yet underexplored avenue to enhance the chelating ability *vs.* ditopic coordination of bis(NHC)s involves the incorporation of substituted (branched) alkyl linkers. Known as the Thorpe–Ingold effect or *gem*-dimethyl effect, it was originally coined in 1915 to rationalize the increased rates of intramolecular cyclization reactions in response to increased steric hindrance.²⁵ Shaw extrapolated the concept to metallacycles by developing chelate complexes of diphosphine ligands with ten-carbon-long linkers.²⁶ The large steric requirements of the phosphine fragments resulted in hindered intramolecular conformational changes, and thus a negligible entropy loss upon metalation.

Several studies have heuristically simplified the coordination behavior of bidentate bis(NHC) ligands (chelation *vs.* bridging) in square-planar late-transition-metal to two factors: steric bulk of the imidazolyl R-groups, and length of the linker.² Shorter linkers coerce the imidazolyl R groups to lie in the NHC–M–NHC plane, while longer, more flexible linkers cause the imidazolyl R groups to bend out of metal plane to alleviate strain. With other words, chelation is favored by small R groups and long linkers, or large R groups and short linkers.²⁷ We recently synthesized ligand variants that defy the above postulates to stabilize electron-rich, chelate complexes of nickel featuring unusual reactivity.²⁸ By exploiting the Thorpe–Ingold effect using branched organosilyl backbone linkers, chelation was enforced with ligands incorporating large R groups (2,6-diisopropylphenyl or Dipp) and long linkers consisting of 3- or 5-atom chains. Although the ligands were accessible in few synthetic steps, the reactions have often been plagued by low yields and long reaction times.

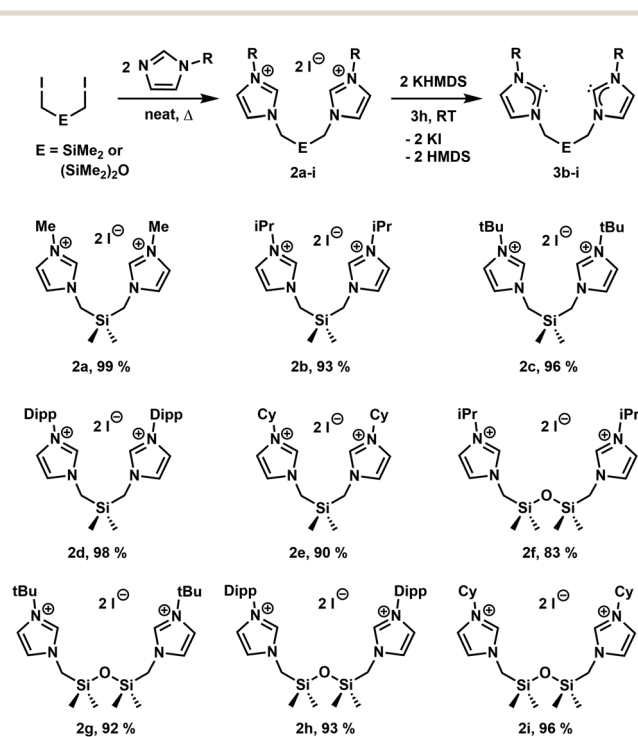
We present herein a straightforward synthetic protocol for the generation of bis(imidazolium) salts linked by organosilyl groups. These main-group fragments allow for expedient assembly of bis(imidazolium) salts with sterically bulky linkers *via* nucleophilic substitution. Subsequent deprotonation generates the carbene ligands, which are stable and can be handled at room-temperature under anhydrous, anaerobic conditions.

Results and discussion

The traditional method for generating multitopic imidazolium salts involves the reaction of an *N*-substituted imidazole with an appropriate alkyl halide in a standard nucleophilic substitution. Capitalizing on this methodology, a wide array of *N*-aryl bis(imidazolium) salts incorporating linear alkyl linkers between two and ten-carbons long were synthesized under solvent-free conditions.²⁹ Unfortunately, this methodology cannot be used to incorporate substituted alkane linkers: Steric hindrance inhibits the backside attack of incoming nucleophiles on the electrophilic halomethyl-carbon.³⁰ Organosilane analogues will, however, undergo nucleophilic substitution at a carbon alpha to the silicon^{31,32} and thus, this appeared as a suitable synthetic strategy for the generation of bis(NHC) ligands incorporating substituted linkers. The isostructural relationship between silicon and carbon allows for the replacement of carbon for

synthetic convenience at the expense of some thermodynamic stability. An ancillary bis(*N*-methylbenzimidazole) ligand featuring a (–CH₂)₂SiMe₂ linker, which proved effective in the nickel-catalyzed Kumada Coupling, is the only bis(NHC) ligand incorporating silicon in the linker reported to date.³² In addition, an NHC–Si–NHC pincer ligand was template-built in the coordination sphere of cobalt,³³ and bis(methylimidazolium) diiodides incorporating dimethylsiloxane-containing linkers have been reported.³⁴

In a typical procedure, the organosilyl diiodide and an excess of *N*-Dipp imidazole were combined in a closed flask with magnetic stirring. Heating the mixtures up to the melting point of the imidazole for one hour saw the formation of a precipitate, with complete solidification of the reaction mixtures upon cooling back to room temperature. Compounds **2d** and **2h** were obtained in high yields upon washing the solids and drying *in vacuo* (Scheme 1). On the other hand, reactions involving liquid alkyl-imidazoles (R = Me, *i*Pr, *t*Bu) required lower reaction temperatures (*ca.* 80–100 °C for 1–2 hours, see Experimental section). Dissolution of the product mixtures in dichloromethane or acetonitrile and addition of an anti-solvent (hexanes, diethyl ether, or ethyl acetate) caused re-precipitation of the products, which were isolated by vacuum filtration as air-stable, off-white solids. Compound purity was confirmed by satisfactory elemental analysis, and molecular connectivity confirmed by ¹H and ¹³C one-dimensional NMR techniques, as well as two-dimensional heteronuclear single quantum coherence (HSQC) and heteronuclear multiple-bond correlation (HMBC) pulse sequences. In all cases, a diagnostic, strongly-desielded signal was observed between 9–10 ppm in the ¹H spectra, attributed to the imidazolium C2



Scheme 1 Synthesis of bis(imidazolium) diiodides **2a–i** and the corresponding free bis(NHC)s **3b–i**.



proton. *N*-Methylene protons on the linker were identified as singlets around 3–4 ppm, and diagnostic dimethylsilyl protons were located in the shielded, 0–1 ppm spectral range.

With the exception of **2a**, the imidazolium salts could be deprotonated with potassium hexamethyldisilazide in either anhydrous benzene or tetrahydrofuran under an argon atmosphere at room temperature (Scheme 1). The mixtures were stirred for *ca.* three hours and subsequently filtered to remove insoluble byproducts. Solvent removal *in vacuo* yielded the free carbenes as off-white solids or brown oils, depending on substituent R: **3d** and **3h** were solids, as previously described,²⁸ while **3b**, **3c**, **3f**, **3g**, and **3i** were oils and thus were stored in their crude form. ¹H NMR showed the disappearance of the strongly deshielded signal at 9–10 ppm and all other resonances were located at their expected chemical shifts. Similarly, ¹³C signals attributed to the carbene carbons were observed around 212–216 ppm. Under an inert atmosphere, the free carbenes could be stored for at least three months at –35 °C and could be handled at room temperature in solution and the solid state. Attempts to isolate free carbene **3a** were not successful.

Conclusions

We report a high-yielding synthetic protocol with general applicability for the expedient generation of bis(imidazolium) salts linked by organosilyl groups. Furthermore, we outline deprotonation procedures for the synthesis of the corresponding free bis(carbene) ligands, which can be handled at room-temperature under anhydrous and air-free conditions. This straightforward protocol allows for the systematic assembly of bidentate carbene ligands incorporating long, branched organosilane linkers, as well as alkyl and aryl *N*-substituents with varied steric profile. According to the Thorpe–Ingold effect, the steric bulk of the backbone improves the chelating ability of these ligands, as confirmed by our previous studies.²⁸ Besides providing a more facile access to ligands we previously reported, this work also introduces new derivatives with smaller steric profiles, with potential use in catalytic applications.

Experimental

General considerations

Imidazolium salts **2a–i** were synthesized in air using commercially supplied solvents (Millipore-Sigma, Fischer Scientific) that were used as received. Free ligands **3b–i** were generated with careful exclusion of air and moisture in an argon atmosphere, using a double-manifold vacuum line and an MBRAUN glovebox operating with argon (Air Liquide, 99.999% purity). Solvents were dried over 4 Å molecular sieves or sodium/benzophenone and degassed prior to use. All NMR spectra were acquired on Bruker Avance and Avance III 400 MHz spectrometers at 298 K. ¹H and ¹³C NMR chemical shifts were referenced to residual solvent peaks and naturally abundant ¹³C resonances for all deuterated solvents: δ CH₂Cl₂-*d*₁ (5.32 ppm, ¹H) and CH₂Cl₂-*d*₂ (54.00 ppm, ¹³C); THF-*d*₇ (3.58 ppm, ¹H) and THF-*d*₈ (67.57 ppm, ¹³C); toluene-*d*₇ (2.09 ppm, ¹H)

and toluene-*d*₈ (20.4 ppm, ¹³C). All ¹³C spectra were broad-band proton-decoupled.

X-ray crystallographic data were collected on a Bruker SMART APEX II CCD diffractometer using suitable single crystals coated in Paratone 8277 oil (Exxon) and mounted on glass-fiber loops. Measurements were processed with the Apex III software suite. Structures were solved using the SHELXT³⁵ structure solution program with intrinsic phasing and refined using the SHELXL³⁶ refinement package with least squares minimization, all under the Olex2 platform.³⁷ Full crystallographic details can be found in each independently uploaded crystallographic information file (cif).

Elemental analyses were obtained on a PerkinElmer Model 2400 Series II analyzer. The Table of Contents graphic was generated with the aid of ChatGPT 4.0.³⁸

Synthetic methods

General synthesis of bis(imidazolium) salts, 2. In a 20 mL scintillation vial, bis(iodomethyl)dimethylsilane or bis(iodomethyl)-1,1,3,3-tetramethyldisiloxane was combined neat with a 50% excess of *N*-substituted imidazole. The vial was closed and the mixture was heated for 1–2 hours. Upon cooling, *ca.* 5 mL of DCM or acetonitrile was added to dissolve the solid, and the product was reprecipitated upon addition of *ca.* 40 mL of an anti-solvent (hexanes, diethyl ether, or ethyl acetate). The resulting salts were isolated *via* vacuum filtration as white or off-white solids.

Synthesis of 2a. *N*-Methylimidazole (2.00 g, 24.4 mmol) and bis(iodomethyl)dimethylsilane (2.77 g, 8.16 mmol) were heated neat to 100 °C for two hours. Upon cooling, 5 mL of acetonitrile was added to dissolve the solid, and the product was reprecipitated upon addition of *ca.* 40 mL of ethyl acetate. After thorough sonication, **2a** was isolated *via* vacuum filtration as a white solid (4.06 g, 8.04 mmol, 99%). Spectral data matched literature.³² Anal. for C₁₂H₂₂N₄I₂Si (%): calcd C 28.58; H 4.40; N 11.11. Found C 28.42; H 4.73; N 11.18.

Synthesis of 2b. *N*-iso-propylimidazole (1.00 g, 9.08 mmol) and bis(iodomethyl)dimethylsilane (1.03 g, 3.03 mmol) were heated neat to 100 °C for two hours. Upon cooling, *ca.* 5 mL of DCM was added to dissolve the solid, and the product was reprecipitated upon addition of *ca.* 40 mL of diethyl ether. **2b** was isolated *via* vacuum filtration as a white solid (1.574 g, 2.81 mmol, 93%). ¹H NMR (400 MHz, CD₃CN) δ 9.29 (s, 1H, N₂CH), 7.54 (s, 1H, ImH), 7.53 (s, 1H, ImH), 4.68 (hept, *J* = 6.7 Hz, 1H, CH(CH₃)₂), 4.26 (s, 2H, CH₂), 1.54 (d, *J* = 8.0 Hz, 6H, CH(CH₃)₂), 0.26 (s, 3H, Si(CH₃)₂). ¹³C{¹H} NMR (101 MHz, CD₃CN) δ 135.13 (s, N₂C), 124.28 (s, C₂N₂C), 121.51 (s, C₂N₂C), 53.99 (s, CH(CH₃)₂), 39.52 (s, CH₂), 22.95 (s, CH(CH₃)₂), –5.15 (s, Si(CH₃)₂). ²⁹Si{¹H} (119 MHz, CD₃CN) δ 3.62. Anal. for C₁₆H₃₀N₄I₂Si (%): calcd C 34.30; H 5.40; N 10.00. Found C 34.21; H 5.58; N 9.97.

Synthesis of 2c. *N*-tert-Butylimidazole (1.00 g, 8.05 mmol) and bis(iodomethyl)dimethylsilane (0.913 g, 2.69 mmol) were heated neat to 100 °C for two hours. Upon cooling, *ca.* 5 mL of DCM was added to dissolve the solid, and the product was reprecipitated upon addition of *ca.* 40 mL of ethyl acetate. **2c** was isolated *via* vacuum filtration as a white solid (1.52 g, 2.58 mmol, 96%). ¹H NMR (400 MHz, DMSO-*d*₆)



δ 9.25 (s, 1H, N₂CH), 8.05 (s, 1H, ImH), 7.76 (s, 1H, ImH), 4.11 (s, 2H, CH₂), 1.60 (s, 9H, C(CH₃)₃), 0.14 (s, 3H, Si(CH₃)₂). ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 133.88 (s, N₂C), 123.27 (s, C₂N₂C), 120.51 (s, C₂N₂C), 59.52 (s, C(CH₃)₃), 38.27 (s, CH₂), 29.04 (s, C(CH₃)₃), -5.83 (s, Si(CH₃)₂). ²⁹Si{¹H} (79 MHz, DMSO-*d*₆) δ 3.31. Anal. for C₁₈H₃₄N₄I₂Si (%): calcd C 36.74; H 5.82; N 9.52. Found C 36.58; H 5.95; N 9.57.

Synthesis of 2d. *N*-(2,6-Diisopropylphenyl)imidazole (3.17 g, 13.9 mmol) and bis(iodomethyl)dimethylsilane (1.45 g, 4.25 mmol) were heated neat to 130 °C for one hour. Upon cooling, *ca.* 5 mL of DCM was then added to dissolve the solid, and the product was reprecipitated upon addition of *ca.* 40 mL of diethyl ether. **2d** was isolated *via* vacuum filtration as a white solid (3.30 g, 4.14 mmol, 98%). Spectral data matched literature.^{28b}

Synthesis of 2e. *N*-Cyclohexylimidazole (1.55 g, 10.3 mmol) and bis(iodomethyl)dimethylsilane (1.14 g, 3.35 mmol) were heated neat to 100 °C for two hours. Upon cooling, *ca.* 5 mL of acetonitrile was added to dissolve the solid, and the product was reprecipitated upon addition of *ca.* 40 mL of ethyl acetate. After thorough sonication, **2e** was isolated *via* vacuum filtration as a white solid (1.936 g, 3.02 mmol, 90%). ¹H NMR (400 MHz, CDCl₃) δ 9.82 (s, 1H, N₂CH), 7.81 (s, 1H, ImH), 7.48 (s, 1H, ImH), 4.55 (s, 2H, CH₂), 4.39–4.31 (m, 1H, Cy-CH), 2.18 (m, ²J_{HH} = 12.3 Hz, 2H, Cy-CH₂), 1.83 (m, ²J_{HH} = 13.8 Hz, 2H, Cy-CH₂), 1.74–1.63 (m, 3H, Cy-CH₂), 1.45–1.34 (m, 2H, Cy-CH₂), 1.27–1.16 (m, 1H, Cy-CH₂), 0.34 (s, 3H, Si(CH₃)₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 134.0 (s, N₂C), 123.7 (s, C₂N₂C), 120.6 (s, C₂N₂C), 59.9 (s, Cy-CH), 39.1 (s, CH₂), 33.4 (s, Cy-CH₂), 24.8 (s, Cy-CH₂), 24.4 (s, Cy-CH₂), -4.51 (s, Si(CH₃)₂). ²⁹Si{¹H} (79 MHz, CDCl₃) δ 3.00. Anal. for C₂₂H₃₈N₄I₂Si (%): calcd C 41.26; H 5.98; N 8.75. Found C 41.16; H 6.15; N 8.75.

Synthesis of 2f. *N*-iso-Propylimidazole (1.01 g, 9.17 mmol) and 1,3-bis(iodomethyl)-1,1,3,3-tetramethyldisiloxane (1.26 g, 3.04 mmol) were heated neat to 100 °C for two hours. Upon cooling, *ca.* 5 mL of DCM was added to dissolve the solid, and the product was reprecipitated upon addition of *ca.* 40 mL of diethyl ether. **2f** was isolated *via* vacuum filtration as a yellow solid (1.60 g, 2.52 mmol, 82.9%). ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.22 (s, 1H, N₂CH), 7.96 (s, 1H, ImH), 7.66 (s, 1H, ImH), 4.70 (hept, *J* = 6.6 Hz, 1H, CH(CH₃)₂), 3.94 (s, 2H, CH₂), 1.47 (d, *J* = 8.0 Hz, 6H, CH(CH₃)₂), 0.14 (s, 6H, Si(CH₃)₂). ¹³C{¹H} NMR (151 MHz, DMSO-*d*₆) δ 133.99 (s, N₂C), 123.31 (s, C₂N₂C), 120.65 (s, C₂N₂C), 52.13 (s, CH(CH₃)₂), 41.01 (s, CH₂), 22.44 (s, CH(CH₃)₂), -1.12 (s, Si(CH₃)₂). ²⁹Si{¹H} (79 MHz, DMSO-*d*₆) δ 5.64. Anal. for C₁₈H₃₆N₄I₂Si₂O (%): calcd C 34.07; H 5.72; N 8.83. Found C 33.74; H 5.88; N 8.71.

Synthesis of 2g. *N*-tert-Butylimidazole (1.00 g, 8.05 mmol) and 1,3-bis(iodomethyl)-1,1,3,3-tetramethyldisiloxane (1.11 g, 2.68 mmol) were heated to 100 °C for two hours. Upon cooling, *ca.* 5 mL of DCM was then added to dissolve the solid, and the product was reprecipitated upon addition of *ca.* 40 mL of ethyl acetate. **2g** was isolated *via* vacuum filtration as a white solid (1.64 g, 2.48 mmol, 92.4%). ¹H NMR (400 MHz, CDCl₃) δ 10.12 (s, 1H, N₂CH), 7.71 (s, 1H, ImH), 7.60 (s, 1H, ImH), 4.33 (s, 2H, CH₂), 1.69 (s, 9H, C(CH₃)₃), 0.23 (s, 6H, Si(CH₃)₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 134.40 (s, N₂C), 123.86 (s, C₂N₂C), 119.91

(s, C₂N₂C), 60.56 (s, C(CH₃)₃), 41.92 (s, CH₂), 30.46 (s, C(CH₃)₃), -0.30 (s, Si(CH₃)₂). ²⁹Si{¹H} (79 MHz, CDCl₃) δ 5.76. Anal. for C₂₀H₄₀N₄I₂Si₂O (%): calcd C 36.26; H 6.09; N 8.46. Found C 36.25; H 6.29; N 8.45.

Synthesis of 2h. *N*-(2,6-Diisopropylphenyl)imidazole (1.00 g, 4.38 mmol) and 1,3-bis(iodomethyl)-1,1,3,3-tetramethyldisiloxane (0.609 g, 1.47 mmol) were heated to 130 °C for one hour. Upon cooling, *ca.* 5 mL of DCM was then added to dissolve the solid, and the product was reprecipitated upon addition of *ca.* 40 mL of diethyl ether. **2h** was isolated *via* vacuum filtration as an off-white solid (1.191 g, 1.37 mmol, 93.0%). Spectral data matched literature.^{28a}

Synthesis of 2i. *N*-Cyclohexylimidazole (1.58 g, 10.5 mmol) and 1,3-bis(iodomethyl)-1,1,3,3-tetramethyldisiloxane (1.46 g, 3.53 mmol) were heated to 100 °C for two hours. Upon cooling, *ca.* 5 mL of acetonitrile was then added to dissolve the solid, and the product was reprecipitated upon addition of *ca.* 40 mL of ethyl acetate. After thorough sonication, **2i** was isolated *via* vacuum filtration as a white solid (2.423 g, 3.39 mmol, 96.2%). ¹H NMR (400 MHz, CDCl₃) δ 9.93 (s, 1H, N₂CH), 7.64 (s, 1H, ImH), 7.56 (s, 1H, ImH), 4.40–4.32 (m, 1H, Cy-CH), 4.23 (s, 2H, CH₂), 2.12 (d, ²J_{HH} = 11.5 Hz, 2H, Cy-CH₂), 1.82 (d, ²J_{HH} = 13.8 Hz, 2H, Cy-CH₂), 1.75–1.61 (m, 3H, Cy-CH₂), 1.45–1.34 (m, 2H, Cy-CH₂), 1.27–1.14 (m, 1H, Cy-CH₂), 0.17 (s, 3H, Si(CH₃)₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 134.1 (s, N₂C), 123.5 (s, C₂N₂C), 120.6 (s, C₂N₂C), 59.8 (s, Cy-CH), 41.8 (s, CH₂), 33.5 (s, Cy-CH₂), 24.8 (s, Cy-CH₂), 24.4 (s, Cy-CH₂), -0.50 (s, Si(CH₃)₂). ²⁹Si{¹H} (79 MHz, CDCl₃) δ 5.80. Anal. for C₂₄H₄₄N₄I₂Si₂O (%): calcd C 40.34; H 6.21; N 7.84. Found C 40.41; H 6.40; N 7.85.

General synthesis of bis(carbene) ligands, 3. In a swivel frit, the bis(imidazolium salt) **2** was combined with KHMDS, and *ca.* 50 mL of benzene or THF were condensed *via* vacuum distillation. The apparatus was filled with argon and the mixture was stirred for 3 hours at room temperature. The insoluble solids were removed by filtration and the filtrate was concentrated *in vacuo*. The solvent was removed *in vacuo*, and **3** was obtained as a brown oil or subsequently washed with pentane to furnish the products as off-white solids.

Synthesis of 3b. **2b** (1.40 g, 2.50 mmol) and KHMDS (0.997 g, 5.00 mmol) were stirred for three hours in benzene. Insoluble solids were filtered off and the filtrate was concentrated *in vacuo* to yield **3b** as a brown oil. (0.534 g, 1.75 mmol, 70.2% yield). ¹H NMR (400 MHz, C₆D₆) δ 6.61 (s, 1H, ImH), 6.47 (s, 1H, ImH), 4.35 (hept, *J* = 6.7 Hz, 1H, CH(CH₃)₂), 3.73 (s, 2H, CH₂), 1.24 (d, *J* = 8.0 Hz, 6H, CH(CH₃)₂), 0.38 (s, 3H, Si(CH₃)₂). ¹³C{¹H} NMR (101 MHz, C₆D₆) δ 212.4 (s, N₂C), 120.40 (s, C₂N₂C), 115.11 (s, C₂N₂C), 51.65 (s, CH(CH₃)₂), 40.75 (s, CH₂), 24.06 (s, CH(CH₃)₂), -3.42 (s, Si(CH₃)₂).

Synthesis of 3c. **2c** (1.20 g, 2.04 mmol) and KHMDS (0.814 g, 4.08 mmol) were stirred for three hours in THF. Insoluble solids were filtered off and the filtrate was concentrated *in vacuo* to yield **3c** as a brown oil. (0.502 g, 1.51 mmol, 74.0% yield). ¹H NMR (400 MHz, C₆D₆) δ 6.67 (s, 1H, ImH), 6.63 (s, 1H, ImH), 3.73 (s, 2H, CH₂), 1.46 (s, 9H, C(CH₃)₃), 0.37 (s, 3H, Si(CH₃)₂). ¹³C{¹H} NMR (101 MHz, C₆D₆) δ 213.1 (s, N₂C), 120.2



(s, C₂N₂C), 115.0 (s, C₂N₂C), 55.5 (s, C(CH₃)₃), 41.2 (s, CH₂), 31.4 (s, C(CH₃)₃), -3.11 (s, Si(CH₃)₂).

Synthesis of 3d. 2d (1.30 g, 1.64 mmol) and KHMDS (0.655 g, 3.28 mmol) were stirred for three hours in benzene. Insoluble solids were filtered off and the filtrate was concentrated *in vacuo*. The residue was washed with pentane and dried under vacuum to yield **3d** as an off-white solid. (0.402 g, 0.743 mmol, 45.6% yield). Spectral data matched literature.

Synthesis of 3e. 2e (1.00 g, 1.56 mmol) and KHMDS (0.623 g, 3.12 mmol) were stirred for three hours in benzene. Insoluble solids were filtered off and the filtrate was concentrated *in vacuo*. The residue was subjected to six rounds of pentane addition, sonication, and solvent removal *in vacuo* to speed up the removal of all volatiles. The solid was subsequently washed with 10 mL of pentane and dried under vacuum to yield **3e** as an off-white solid. (0.384 g, 0.998 mmol, 63.9% yield). ¹H NMR (600 MHz, C₆D₆) δ 6.63 (d, ³J_{HH} = 1.5 Hz, 1H, ImH), 6.52 (d, ³J_{HH} = 1.5 Hz, 1H, ImH), 4.04 (m, 1H, Cy-CH), 3.75 (s, 2H, CH₂), 2.07–1.92 (m, 2H, Cy-CH₂), 1.64–1.52 (m, 4H, Cy-CH₂), 1.47–1.41 (m, 1H, Cy-CH₂), 1.21–1.08 (m, 2H, Cy-CH₂), 1.02–0.95 (m, 1H, Cy-CH₂), 0.39 (s, 3H, Si(CH₃)₂). ¹³C{¹H} NMR (151 MHz, C₆D₆) δ 212.1 (s, N₂C), 120.5 (s, C₂N₂C), 115.9 (s, C₂N₂C), 59.7 (s, Cy-CH), 40.9 (s, CH₂), 35.3 (s, Cy-CH₂), 26.0 (s, Cy-CH₂), 25.8 (s, Cy-CH₂), -3.25 (s, Si(CH₃)₂).

Synthesis of 3f. 2f (1.20 g, 1.89 mmol) and KHMDS (0.755 g, 3.78 mmol) were stirred for three hours in benzene. Insoluble solids were filtered off and the filtrate was concentrated *in vacuo* to yield **3f** as a brown oil. (0.457 g, 1.21 mmol, 63.8% yield). ¹H NMR (400 MHz, C₆D₆) δ 6.58 (s, 1H, ImH), 6.48 (s, 1H, ImH), 4.37 (hept, J = 6.7 Hz, 2H, CH(CH₃)₂), 3.53 (s, 2H, CH₂), 1.24 (d, J = 8.0 Hz, 6H, CH(CH₃)₂), 0.37 (s, 6H, Si(CH₃)₂). ¹³C{¹H} NMR (101 MHz, C₆D₆) δ 213.1 (s, N₂C), 120.7 (s, C₂N₂C), 115.7 (s, C₂N₂C), 52.2 (s, CH₂), 43.3 (s, CH(CH₃)₂), 24.5 (s, CH(CH₃)₂), 1.00 (s, Si(CH₃)₂).

Synthesis of 3g. 2g (1.70 g, 2.57 mmol) and KHMDS (1.03 g, 5.14 mmol) were stirred for three hours in THF. Insoluble solids were filtered off and the filtrate was concentrated *in vacuo* to yield **3g** as a brown oil. (0.429 g, 1.06 mmol, 41.1% yield). ¹H NMR (400 MHz, C₆D₆) δ 6.72 (s, 1H, ImH), 6.60 (s, 1H, ImH), 3.52 (s, 2H, CH₂), 1.45 (s, 9H, C(CH₃)₃), 0.33 (s, 6H, Si(CH₃)₂). ¹³C{¹H} NMR (101 MHz, C₆D₆) δ 213.3 (s, N₂C), 120.0 (s, C₂N₂C), 115.2 (s, C₂N₂C), 55.5 (s, C(CH₃)₃), 43.2 (s, CH₂), 31.5 (s, C(CH₃)₃), 0.82 (s, Si(CH₃)₂).

Synthesis of 3h. 2h (1.26 g, 1.45 mmol) and KHMDS (0.593 g, 2.97 mmol) were stirred for three hours in benzene. Insoluble solids were filtered off and the filtrate was concentrated *in vacuo*. The residue was washed with pentane and dried under vacuum to yield **3h** as a white solid. (0.600 g, 0.976 mmol, 67.4% yield). Spectral data matched literature.

Synthesis of 3i. 2i (1.26 g, 1.77 mmol) and KHMDS (0.705 g, 3.53 mmol) were stirred for three hours in benzene. Insoluble solids were filtered off and the filtrate was concentrated *in vacuo* to yield **3i** as an orange oil. (0.490 g, 1.07 mmol, 60.6% yield). ¹H NMR (600 MHz, C₆D₆) δ 6.63 (s, 1H, ImH), 6.60 (s, 1H, ImH), 4.03–3.95 (m, 1H, Cy-CH), 3.51 (s, 2H, SiCH₂), 1.97 (d, ²J_{HH} = 9.0 Hz, 2H, Cy-CH₂), 1.63–1.56 (m, 4H, Cy-CH₂), 1.44 (d, ²J_{HH} = 12.6 Hz, 1H, Cy-CH₂), 1.16–1.08 (m, 2H, Cy-CH₂), 1.03–0.95 (m, 1H, Cy-CH₂), 0.34 (s, 6H, Si(CH₃)₂). ¹³C{¹H} NMR

(151 MHz, C₆D₆) δ 212.8 (s, N₂C), 120.2 (s, C₂N₂C), 116.2 (s, C₂N₂C), 59.6 (s, Cy-CH), 43.0 (s, CH₂), 35.2 (s, Cy-CH₂), 26.0 (s, Cy-CH₂), 25.8 (s, Cy-CH₂), 0.86 (s, Si(CH₃)₂).

Author contributions

The experimental work was carried out jointly by B. M. P. L. and K. A. M., following a synthesis design developed by B. M. P. L. The synthesis of starting materials was aided by A. H., D. S. L., J. E., and K. B. Structure data collection and refinement was performed by B. M. P. L. The manuscript was written jointly by B. M. P. L., K. A. M., and R. R., who managed the project.

Data availability

The data supporting this article have been included in the Experimental section of the manuscript and in the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support was provided by the University of Calgary and the Natural Sciences and Engineering Research Council of Canada (NSERC) in the form of Discovery Grant #2019-07195 to R. R.

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