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ARTICLE TYPE

# Synthesis, Structural Characterization and Thermal Properties of Copper and Silver Silyl Complexes<sup>†</sup>

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The synthesis of copper and silver silyl complexes containing either *N*-heterocyclic carbenes or nitrogen donors is described. Alterations made to both the neutral donor ligands as well as the silyl group provided access to a number of different compounds. Many of the complexes synthesized were studied in the solid state and the effect of the donor ligand on the final structure of the complexes was examined. The thermal properties of the complexes were explored using thermogravimetric analysis, differential scanning calorimetry and sublimations. Some of the complexes synthesized were demonstrated to be promising volatile metal precursors.

## Introduction

The field of transition metal-silyl chemistry has received considerable attention<sup>1, 2</sup> as metal-silyl complexes are implicated as intermediates in a number of catalytic processes.<sup>3-8</sup> In addition, there is a fundamental interest in these complexes since the isolation of metal-silyl species allows for comparisons of the reactivity between M-C and M-Si linkages.<sup>9, 10</sup> Perhaps more interesting, complexes containing metal-silicon bonds have also been examined for the development of new materials.<sup>11</sup>

Group 11 metal-silyls, specifically those of copper and silver, are a particularly interesting class of reagents. Early work on these complexes focused on the synthesis of metal-silyl species supported by phosphine ligands, but little reactivity was explored.<sup>12-16</sup> These species have also received attention due to the importance of Cu-Si bonds in organic synthesis, for example in the silylation of  $\alpha,\beta$ -unsaturated ketones, alkynes and arenes.<sup>17, 18</sup> More recently, new routes to make group 11 silicon bonds have been explored<sup>19</sup> and the metal-silyl complexes have found use as catalysts for a number of processes including the silylation of aldehydes<sup>20</sup> and the reduction of CO<sub>2</sub>.<sup>21</sup>

While the preparation of Cu, Ag and Au films has received significant attention due to their applications in microelectronics,<sup>22-25</sup> the use of group 11 silyls as metal precursors for this process has remained unexplored. Reagents employing a M-Si bond would be desirable since metal oxide formation can be avoided if the appropriate, oxygen free co-ligands are selected. This would make the complexes less susceptible to oxygen inclusion in the metal films generated.<sup>24</sup>

In this context, we aimed to explore the synthesis of copper and silver silyl complexes to serve as volatile metal precursors. Reasonable thermal stability is a prerequisite for the development of precursors used in metal deposition chemistry,<sup>23</sup> so we sought ligands that would stabilize complexes containing M-Si bonds. To this end, *N*-heterocyclic carbenes (NHCs) were chosen as a

starting point as they have been shown to be effective for the stabilization of reactive species.<sup>19, 26-28</sup> Furthermore, as a number of NHC copper and silver complexes are known, there is a substantial library of reagents that may serve as starting materials in the synthesis of the corresponding silyl complexes.<sup>29, 30</sup> Herein, the synthesis and solid state characterization of NHC supported copper and silver silyl species is described. The effects of modifying the carbene ligands as well as the silyl groups on the geometry and coordination number of the complexes are examined and the impact of these changes on volatility is explored. A second class of ligands, namely nitrogen-based donors, were also explored to support these silyl complexes and their structures and properties are reported and compared with the NHC ligated derivatives.

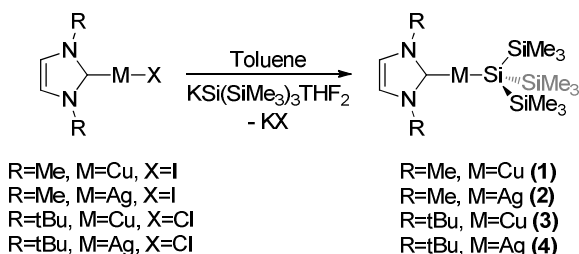
## Results and Discussion

### Synthesis of *N*-heterocyclic carbene metal-silyl complexes

Employing salt metathesis reactions, the combination of KSi(SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> with the NHC metal halides (Ime)MI or ItBuMCl (M = Cu or Ag, Ime = 1,3-*bis*(methyl)imidazol-2-ylidene, ItBu = 1,3-*bis*(tert-butyl)imidazol-2-ylidene) yielded the complexes (Ime)CuSi(SiMe<sub>3</sub>)<sub>3</sub> (**1**), (Ime)AgSi(SiMe<sub>3</sub>)<sub>3</sub> (**2**), (ItBu)CuSi(SiMe<sub>3</sub>)<sub>3</sub> (**3**) and (ItBu)AgSi(SiMe<sub>3</sub>)<sub>3</sub> (**4**) in yields ranging from 63 to 76% (Scheme 1). While the copper complexes are similar to those previously reported,<sup>19, 21</sup> to the best of our knowledge, complexes **2** and **4** are the first examples of NHC silver-silyl complexes. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **1-4** are similar and unremarkable, with the most interesting feature being the chemical shift for the carbene carbon in the <sup>13</sup>C{<sup>1</sup>H} spectra. This signal appears as a singlet in **1**, **2** and **3** at 189.6, 189.8 and 179.4 ppm, respectively, but as a doublet of doublets centered at 188.1 ppm in **4**. Though the singlet nature of the carbene signal is not surprising for **1** and **3**, as there are no NMR active nuclei in proximity to the carbene carbon, the fact that

coupling to  $^{107/109}\text{Ag}$  is observed for **4** but not **2** is surprising. The difference between **2** and **4** may be due to an exchange process as it has previously been demonstrated that silver-halide complexes of carbenes can exist in two forms, a neutral NHC-Ag-X form and an ionic  $[\text{NHC}_2\text{Ag}]^+[\text{AgX}_2]^-$  form.<sup>31-33</sup> In addition, many NHC silver complexes have been shown to have a singlet for the carbene carbon in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum,<sup>30</sup> similar to that observed for **2**. The singlet nature of the chemical shift is believed to signify a weaker C-Ag bond that results in the exchange process.<sup>30, 32</sup> For complex **2**, this suggests a possible NHC/silyl group exchange to generate  $[\text{IMe}_2\text{Ag}]^+[\text{Ag}(\text{Si}(\text{SiMe}_3)_2)_2]^-$ . In complex **4** however, strong coupling is seen between the carbene carbon and the two silver isotopes ( $^{107}\text{Ag}$ ;  $J_{\text{SiAg}} 179$  Hz and  $^{109}\text{Ag}$ ;  $J_{\text{SiAg}} 213$  Hz) indicating an exchange is likely not occurring. Likely, the bulkier NHC ligand in **4** discourages the formation of the ionic species.

To gain further insight into the possibility of an exchange process in **2**, the  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra for each compound were also obtained. In all cases, the signals for the  $\text{SiMe}_3$  groups appear as singlets ranging from -5.5 ppm (**1**) to -6.8 ppm (**3**). While it was expected that the signal for the metal bound Si atom would provide the most evidence of possible differences in exchange behavior between complexes **2** and **4**, the signal could only be directly observed for compound **4**, which contained a doublet of doublets at -140.2 ppm. In the cases of complexes **1**, **2** and **3**, the signal was located using a  $^{29}\text{Si}-^1\text{H}$  HMBC experiment and thus only the peak position could be determined for **2**.



Scheme 1. Synthesis of complexes **1-4**.

Complexes **1-4** crystallize readily from alkane solvents such as pentane and hexane, allowing for determination of the solid state structures (Figures 1-4). For each metal, both the M-C and M-Si bonds are shorter in the IMe complexes (**1** and **2**) than they are in the ItBu complexes (**3** and **4**) (Table 1). However, **1** and **2** also deviate more from linearity with C-M-Si bond angles of  $171.91(11)^\circ$  and  $171.6(2)^\circ$ , for **1** (M=Cu) and **2** (M=Ag) respectively, than do **3** ( $178.60(5)^\circ$ ) and **4** ( $178.77(5)^\circ$ ). These differences may be due, in part, to the larger size of the ItBu

Table 1: Selected bond lengths and angles for **1-4**.

	Bond Lengths (Å) and Angles ( $^\circ$ )		
	C(1)-M	Si(1)-M	C(1)-M-Si(1)
<b>1</b>	1.915(3)	2.2553(10)	171.91(11)
<b>2</b>	2.110(7)	2.383(2)	171.6(2)
<b>3</b>	1.9366(16)	2.2636(5)	178.60(5)
<b>4</b>	2.1512(18)	2.3936(5)	178.77(5)

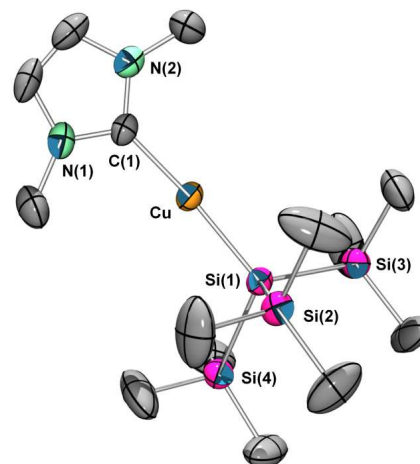


Figure 1. POV-Ray rendered ORTEP plot of the molecular structure of **1** (50% thermal ellipsoids). C; gray, N; aquamarine, Si: deep pink, Cu: copper. H-atoms omitted for clarity.

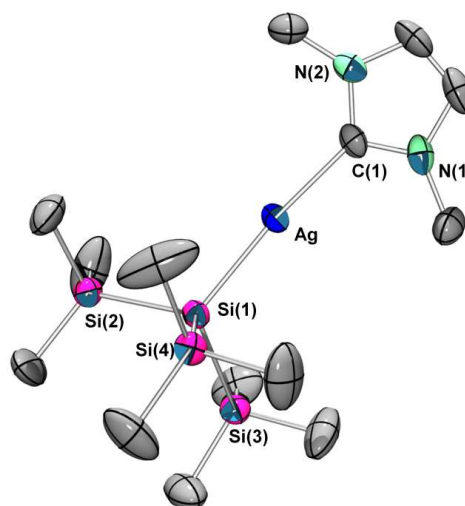


Figure 2. POV-Ray rendered ORTEP plot of the molecular structure of **2** (50% thermal ellipsoids). C; gray, N; aquamarine, Si: deep pink, Ag: slate blue. H-atoms omitted for clarity.

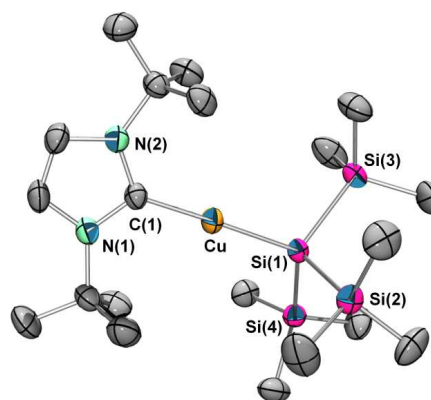
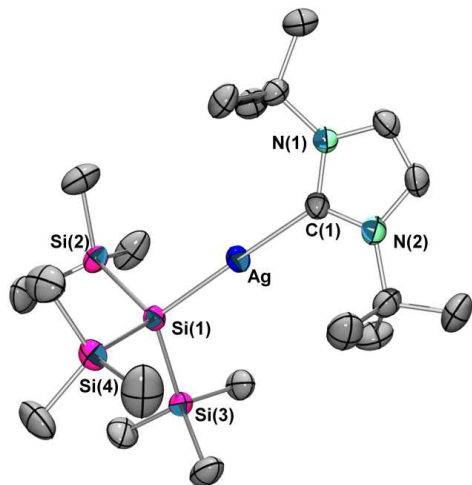


Figure 3. POV-Ray rendered ORTEP plot of the molecular structure of **3** (50% thermal ellipsoids). C; gray, N; aquamarine, Si: deep pink, Cu: copper. H-atoms omitted for clarity.



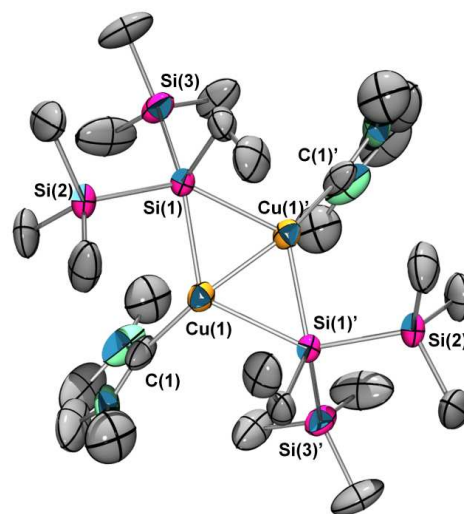
**Figure 4.** POV-Ray rendered ORTEP plot of the molecular structure of **4** (50% thermal ellipsoids). C; gray, N; aquamarine, Si: deep pink, Ag: slate blue. H-atoms omitted for clarity.

ligand which leads to increased crowding around the metal center increasing the bond distances and pushing the ligands as far apart as possible in **3** and **4**.

Based on previous work by Coyle *et al.* where complexes analogous to **1** and **3**, but with  $N(\text{SiMe}_3)_2$  rather than  $\text{Si}(\text{SiMe}_3)_3$  groups, were used as reagents in atomic layer deposition,<sup>24, 34</sup> we performed sublimations of complexes **1-4** to explore their volatility. Complexes **1** and **3** sublimed at 95 and 105 °C, respectively, at 0.02 torr. In the cases of the silver complexes, **2** and **4**, sublimation is observed at 90 and 95 °C respectively, but silver mirrors are also observed to form during the sublimation process. To gain a more in depth understanding of the thermal properties of complexes **1-4**, they were subjected to testing using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (See supporting information: Figures S1-S4 (DSC), Figures S5-S8 (TGA)). Using DSC, it was found that all of the complexes decompose below 250 °C and have a narrow melting point range from 136 to 144 °C (**1**: 136 °C, **2**: 144 °C, **3**: 140 °C, **4**: 143 °C). The TGA data provided more valuable information in terms of the volatility of the complexes. When run at 760 torr, IMe complexes **1** and **2** show only 60-70% mass loss with onset temperatures calculated to be 210 °C and 176 °C, respectively. Performing the TGA at 0.2 torr, however, gave significantly better results with greater than 95% mass loss observed with onset temperatures of 106 °C (**1**) and 111 °C (**2**). Complexes **3** and **4** demonstrated better thermal stability compared to **1** and **2** at 760 torr, with 80-90% mass loss observed, as well as at 0.2 torr where >99% mass loss was observed for each (onset temperatures: 155-159 °C (**3**), 158 °C (**4**)).

The combined results from sublimations and TGA data demonstrated that complexes of the form  $\text{NHC-M-Si}(\text{SiMe}_3)_3$  have promising thermal behavior. In an attempt to uncover complexes with more promising thermal properties, modifications to the silyl group were examined. We have previously explored the use of the silyl group  $\text{SiEt}(\text{SiMe}_3)_2$  in the synthesis of yttrium and gadolinium silyl complexes.<sup>35</sup> Using analogous salt metathesis protocols as described above for the synthesis of **1**, the combination of  $(\text{IME})\text{CuI}$  with  $\text{SiEt}(\text{SiMe}_3)_2(\text{THF})_{0.5}$  generates **5** in 60% yield (Scheme 2). The

$^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **5** indicate a 1:1 NHC:silyl group ratio suggesting a similar formulation as that seen for complexes **1** and **3**. There are three signals in the  $^1\text{H}$  NMR spectrum for the modified silyl ligand at 1.61, 1.34 and 0.63 ppm integrating to 3, 2 and 18 protons and representing the methyl, methylene and  $\text{SiMe}_3$  groups respectively. The most diagnostic feature in the  $^{13}\text{C}\{^1\text{H}\}$  spectrum is the singlet resonance at 182.0 ppm for the carbene carbon of the coordinated IMe. This signal is upfield by 10 ppm from that observed for complex **1**. In the  $^{29}\text{Si}$  NMR spectrum, two signals with chemical shifts at -9.75 and -77.65 ppm for the  $\text{SiMe}_3$  groups and metal bound Si, respectively, could be observed using a  $^{29}\text{Si}\{^1\text{H}\}$  experiment. Complex **5** could be crystallized from concentrated solutions of hexanes and the solid state structure was determined (Figure 5).

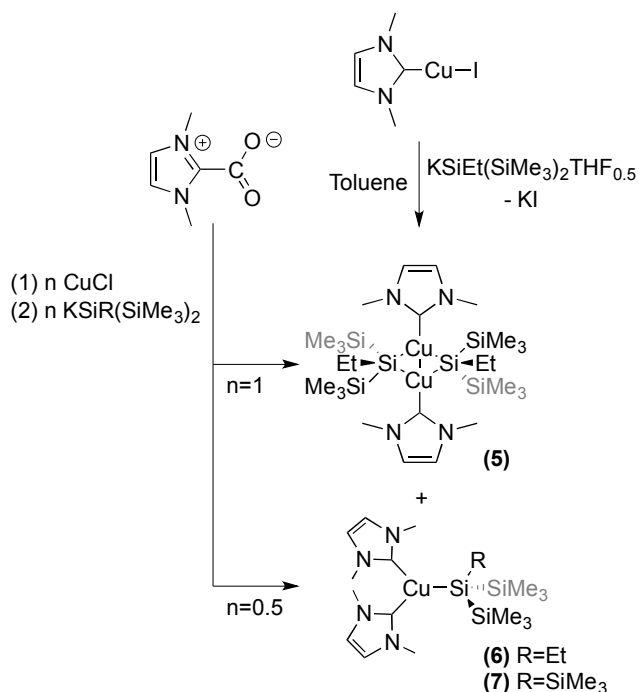


**Figure 5.** POV-Ray rendered ORTEP plot of the molecular structure of **5** (30% thermal ellipsoids). C; gray, N; aquamarine, Si: deep pink, Cu: copper. H-atoms omitted for clarity. Selected bond distances (Å) and angles (°): Cu(1)-Si(1) 2.4232(9), Cu(1)-Si(1') 2.5922(8), Cu-C(1) 1.949(4), Cu(1)-Cu(1') 2.2854(9), C(1)-Cu(1)-Si(1) 123.79(10), C(1)-Cu(1)-Si(1') 115.21(10), Si(1)-Cu(1)-Si(1') 120.93(3), Cu(1)-Si(1)-Cu(1') 54.09(2).

Unlike complexes **1-4**, **5** crystallizes as a dimer with  $\text{SiEt}(\text{SiMe}_3)_2$  groups bridging two copper centers that are each coordinated by one NHC. The Cu-C(1) bond distance in **5** is 1.949(4) Å, longer than that observed for **1** but similar to that observed in **3**. The Cu-Si bond distances of 2.4232(9) and 2.5922(8) Å in **5** are significantly elongated relative to **1** and **3**, likely due to the bridging nature in the present example. The C-Cu-Si bond angles are 123.79(10)° and 115.21(10)°, much smaller than those observed in **1** and **3**, but this is expected due to the trigonal planar nature of **5**. The Si-Cu-Si bond angle in **5** is 120.93(3)°, and there is a Cu-Cu distance of 2.2854(9) Å, in line with other copper-copper bonds, suggesting a copper-copper interaction.<sup>36</sup>

The dimeric complex, **5**, was further examined using DSC and TGA to determine whether it had similar properties to the monometallic species. The DSC data showed **5** melts at 97 °C and decomposes around 150 °C. Both of these temperatures are lower than those observed for the  $\text{Si}(\text{SiMe}_3)_3$  analogue (**1**). The TGA results showed much less volatility, as 40% and 60% mass loss was observed at 760 and 0.2 torr, respectively. Similarly, when sublimations were attempted on **5** at 0.02 torr, sublimation

of the complex was observed at 80 °C but it was accompanied by significant decomposition. Furthermore, if the sublimation was allowed to proceed for longer than 8 hours, the sublimed product began to decompose from a yellow solid to a red solid. These results are all consistent with the dimeric species being significantly less stable than the monomeric complexes.



Scheme 2. Synthesis of complexes 5-7.

While attempting to increase the yields of **5** by harvesting a second crop of crystals from the mother liquor, a product with a different unit cell (**6**), was observed. A single crystal X-ray diffraction study of **6** revealed that it was the *bis*-NHC-Cu-silyl complex IMe<sub>2</sub>CuSiEt(SiMe<sub>3</sub>)<sub>2</sub> (Figure 6). The fact that both a mono- and *bis*-NHC silyl complex can be isolated is reminiscent of previously explored copper and silver silyl chemistry that showed one to three equivalents of a phosphine ligand could coordinate to the metal center along with a silyl group.<sup>12-14</sup> It is likely that **6** formed through decomposition of a small amount of **5** followed by carbene transfer to another equivalent of **5**, generating **6**. Complex **6** could be prepared independently by reacting two equivalents of 1,3-dimethylimidazolium-2-carboxylate (IMeCO<sub>2</sub>) with one equivalent of CuCl followed by the addition of one equivalent of KSiEt(SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>0.5</sub> (Scheme 2). Following work-up, **6** was isolated in 49% yield. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **6** are similar to those in complex **5**, with the most notable difference in the proton spectrum being the 2:1 ratio of signals for the NHC:silyl groups. The chemical shifts for the carbene carbons shifts significantly downfield, relative to **5**, to 195.7 ppm. The <sup>29</sup>Si{<sup>1</sup>H} signals of -10.3 and -86.7 ppm are similar to those in **5**, with the major difference being the copper bound Si shifted slightly upfield.

The Cu-C bond distances of 1.937(4) and 1.932(5) Å are similar to those observed in **5**, but the Cu-Si bond distance of 2.3306(12) Å is shorter by approximately 0.10-0.15 Å. While a decrease in Cu-Si bond distance is observed on going from **5** to **6**, the distance in **6** is still longer than those observed in the mono-

NHC complexes **1** and **3**, due to the steric constraints imposed by the coordination of an additional donor ligand. The C-Cu-Si bond angles are similar, at 115.05(12)° and 114.47(13)°, and the C-Cu-C bond angle is slightly larger than expected (130.47(17)°) for a

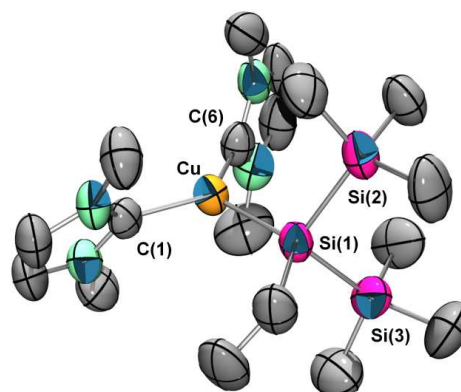


Figure 6. POV-Ray rendered ORTEP plot of the molecular structure of **6** (50% thermal ellipsoids). C; gray, N; aquamarine, Si; deep pink, Cu; copper. H-atoms omitted for clarity. Selected bond distances (Å) and angles (°): Cu-Si(1) 2.3306(12), Cu-C(1) 1.937(4), Cu-C(6) 1.932(5), C(1)-Cu-Si(1) 115.05(12), C(6)-Cu-Si(1) 114.47(13), C(1)-Cu-C(6) 130.47(17).

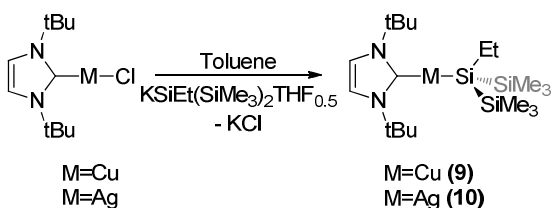
trigonal planar molecule.

It is interesting to note that a complex analogous to **6** was not observed in the synthesis of **1**, with one possible explanation being the difference in the size of the silyl ligand employed. To examine whether an Si(SiMe<sub>3</sub>)<sub>3</sub> analogue of **6** could be synthesized, two equivalents of IMeCO<sub>2</sub>, one equivalent of CuCl, and one equivalent of KSi(SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> were combined generating **7** in 35% yield. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra (See supporting information: Figures S11-S12) are similar to those of **1**, however, the signals for the olefinic and Me groups respectively, while the signal for the SiMe<sub>3</sub> groups is shifted upfield to 0.48 ppm in the <sup>1</sup>H spectrum (Figure S13). Furthermore, as was observed for the conversion of **5** to **6**, there is a downfield shift observed for the carbene carbon to 195.1 ppm in the <sup>13</sup>C{<sup>1</sup>H} spectrum. The preparation of **7** was lower yielding than that of **6** due to difficulties in separating **1**, which also formed in the reaction, from **7** (Figure S13 shows a stack of the <sup>1</sup>H NMR of **1** and **7**), suggesting that **1** may be an intermediate en route to **7**. Following a combination of **1** and IMeCO<sub>2</sub> by NMR confirmed that **7** is formed, but the reaction is slow due to the poor solubility of the IMeCO<sub>2</sub> precursor. Separation of **7** and **1** was non-trivial as they have similar solubility's in alkane solvents and sublime together at 95 °C and 0.02 torr. The sublimation behavior does however suggest that the coordination of a second carbene does not significantly alter the volatility properties.

To further examine the impact of changing the silyl group from Si(SiMe<sub>3</sub>)<sub>3</sub> to SiEt(SiMe<sub>3</sub>)<sub>2</sub>, salt metathesis reactions with (IMe)AgI, (ItBu)CuCl and (ItBu)AgCl were completed. The combination of (IMe)AgI and KSiEt(SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>0.5</sub> leads to a single product, **8**, as a yellow oil after work-up. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra are similar to those obtained for **5**, showing a 1:1 NHC:silyl group ratio (Figures S14-S15). The carbene carbon for **8** appears as a singlet in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum at 191.9 ppm, similar to that observed for **2**. Complex **8**

is pyrophoric and ignites upon exposure to air. Due to the oily nature of the product, **8** could not be characterized in the solid state. Furthermore, despite repeated attempts, we could not distill **8** so it could not be completely purified.

Reactions of (ItBu)CuCl and (ItBu)AgCl with  $\text{KSiEt}(\text{SiMe}_3)_2(\text{THF})_{0.5}$  generate the corresponding silyl products, **9** and **10**, in 66% and 64% yield, respectively (Scheme 3). The  $^1\text{H}$  NMR spectra of both complexes show signals for the ItBu and  $\text{SiEt}(\text{SiMe}_3)_2$  ligands in a 1:1 ratio. The signals for the carbene carbon atoms appear at 180.0 and 189.1 ppm for **9** and **10**, respectively, in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum. Similar to complexes **3** and **4**, the carbene carbon signals are a singlet for **9**, but overlapping doublets, due to coupling to the two spin  $\frac{1}{2}$  isotopes of Ag, for **10**. The observed multiplicity in **10** suggests strong coupling to the Ag center and likely a stronger metal-carbon bond than that observed for **2** or **8** where IMe was employed.



Scheme 3. Synthesis of complexes **9** and **10**.

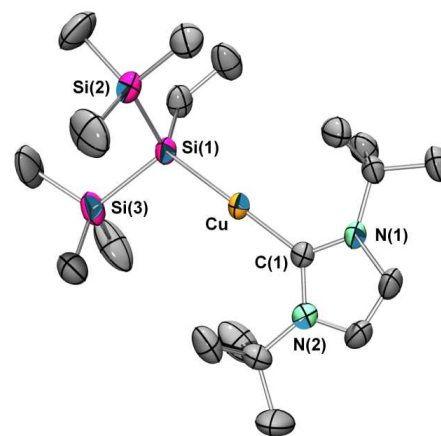
Single crystals of **9** and **10** were obtained from concentrated pentane solutions of the complexes and X-ray diffraction analysis performed on each (Figures 7 and 8). Unlike in the case of **5**, but similar to **3** and **4**, both **9** and **10** crystallized as mono-metallic, linear complexes. This is likely because the greater size of ItBu relative to IMe prevents the formation of the bimetallic species. The M-C (**9**: 1.9481(16) Å, **10**: 2.165(2) Å) and M-Si (**9**: 1.9481(16) Å, **10**: 2.165(2) Å) bonds of **9** and **10** are slightly longer than those in **1-4**. In the case of **9**, while the M-C bond length is similar to that in **5** and **6**, the Cu-Si bond is significantly shorter. Despite the decrease in the size of the silyl group, the C-M-Si bond angles of 178.29(5) and 177.98(6)° for **9** and **10**, respectively, are much closer to **3** and **4** than they are to **1** and **2**.

Table 2: Selected bond lengths and angles for **9** and **10**.

	Bond Lengths (Å) and Angles (°)		
	C(1)-M	Si(1)-M	C(1)-M-Si(1)
<b>9</b>	1.9481(16)	2.2754(5)	178.29(5)
<b>10</b>	2.165(2)	2.4006(6)	177.98(6)

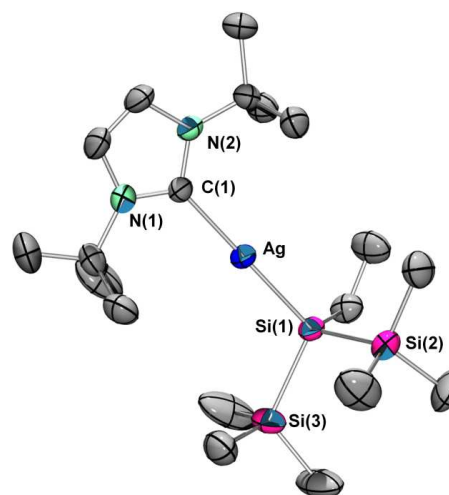
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Neither **9** nor **10** coordinate a second ItBu ligand, remaining mono NHC derivatives even in the presence of excess free carbene. In terms of volatility, **9** and **10** both sublime readily at 90 °C at 0.02 torr, lower in temperature than the  $\text{Si}(\text{SiMe}_3)_3$  analogues **3** and **4**. While the lower sublimation temperature is desirable, **9** also appears to be more thermally sensitive than **3**, as increasing the temperature to 95 °C leads to considerable decomposition. Furthermore, if **9** is left under sublimation conditions for longer than 24 h, the sublimed product begins to



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Figure 7. POV-Ray rendered ORTEP plot of the molecular structure of **9** (50% thermal ellipsoids). C; gray, N; aquamarine, Si; deep pink, Cu; copper. H-atoms omitted for clarity.



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Figure 8. POV-Ray rendered ORTEP plot of the molecular structure of **10** (50% thermal ellipsoids). C; gray, N; aquamarine, Si; deep pink, Ag; slate blue. H-atoms omitted for clarity.

decompose. The narrow temperature range between sublimation and decomposition, as well as the propensity of the sublimed product to decompose, are similar to that observed for **5**, and suggests the exchange of a silyl group for an ethyl group, while increasing volatility also decreases stability.

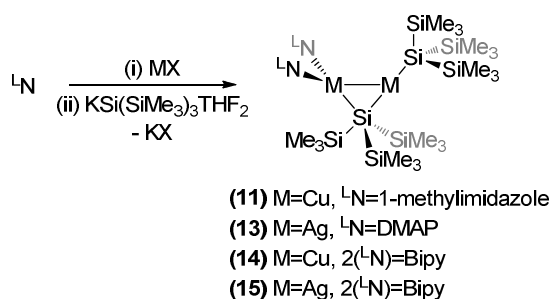
The study of NHC-metal-silyl complexes suggested that subtle modifications to the silyl group the NHC could lead to significant differences in the nature of the complexes formed. This allowed for the isolation of mono- and bis-NHC complexes, as well as monomeric and dimeric copper species. These modifications and structural differences also manifested themselves in different volatilities and stabilities of the complexes formed. To further examine the effect of ligand modifications, N-donor ligands were explored as substitutes for the carbene donors.

### Synthesis of metal-silyl complexes containing N-donors

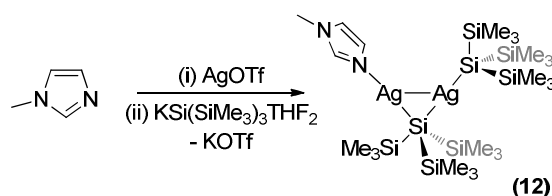
Given the success of NHCs as ligands in supporting copper and silver silyl complexes, we were also interested in whether simple, more easily accessible, nitrogen donor ligands could be used in a similar manner. As a starting point, 1-methylimidazole was chosen due to its structural similarity to IMe (it is a precursor in the synthesis of IMe). The combination of equimolar amounts

of 1-methylimidazole, CuCl or AgOTf and  $\text{KSi}(\text{SiMe}_3)_3(\text{THF})_2$  generated the dinuclear compounds **11** and **12** in low yields of 30% and 15% yield, respectively (Schemes 4 and 5). During these reactions a considerable amount of  $\text{M}(0)$  is observed. This may be due in part to the deprotonation of the 2-position of the imidazole ring by the strongly basic  $\text{KSi}(\text{SiMe}_3)_3(\text{THF})_2$  reagent.<sup>37</sup> The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of each new compound show only a single resonance for the  $\text{SiMe}_3$  groups at 0.58 ppm for both in the  $^1\text{H}$  spectra and 5.78 (**11**) and 6.16 (**12**) ppm in the  $^{13}\text{C}\{^1\text{H}\}$  spectra. The expected signals for the 1-methylimidazole ligands are also present but closer examination of the  $^1\text{H}$  NMR spectrum of each shows that the complexes formed have different formulations since the ratio of the 1-methylimidazole ligand to the silyl group is 1:1 in **11** but 1:2 in **12**.

X-ray quality crystals of **11** and **12** were obtained and diffraction studies were completed on each (Figures S16 and S17). Both structures show bimetallic, silyl bridged species with the 1-methylimidazole ligand(s) coordinated to one metal center and the other coordinated by two silyl groups. In addition, both complexes also contain a M-M contact. Related structures have been observed for Cu,<sup>15, 36</sup> but Ag compounds of this formulation are unknown.



Scheme 4. Synthesis of complexes **11** and **13-15**.



Scheme 5. Synthesis of complex **12**.

The low yielding nature of the syntheses of **11** and **12** made a better route to related species desirable. To avoid the potential issues with acidic sites on the N-donor ligand, 4-dimethylaminopyridine (DMAP) was used instead of 1-methylimidazole. When a reaction similar to that employed in the synthesis of **11** was carried out with DMAP and CuCl, only mixtures were obtained. While we were able to obtain crystallographic evidence for the formation of a species analogous to **11**, with DMAP as the neutral ligands (Figure S18), we could never isolate this species in a pure form. When the reaction was completed with AgOTf, however, a clean product (**13**) could be isolated, albeit again in low (22%) yield (Scheme 6).

As for **12**, a single resonance was observed for the  $\text{SiMe}_3$

groups in both the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **13** at 0.61 and 6.10 ppm, respectively. However, the ratio of DMAP ligand to silyl group in the  $^1\text{H}$  spectrum of **13** was found to be 1:1 rather than the 1:2 as was observed for **12**. A single crystal X-ray diffraction study performed on crystals of **13** confirmed that the formulation was similar to that observed for **11**, with a trigonal planar silver atom coordinated to two DMAP ligands and a bridging silyl in contact with a linear silver center bound to two silyl groups (Figure S19).

The differences in the structures of **12** and **13** as well as the difficulty associated with isolating the Cu analogue of **13** suggest one reason for the low yield of these complexes may be ligand lability. In an attempt to overcome this issue and isolate related species in higher yields, the monodentate N-donor ligands were replaced with the bidentate 2,2'-bipyridine (bipy). The reaction of one equivalent of bipy with two equivalents of CuBr or AgOTf and two equivalents of  $\text{KSi}(\text{SiMe}_3)_3(\text{THF})_2$  gave **14** and **15** in better yields of 60 and 58%, respectively (Scheme 7). Again, single resonances for the  $\text{Si}(\text{SiMe}_3)_3$  groups in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were observed. To further confirm that **14** and **15** were analogous to the complexes synthesized containing monodentate N-donor ligands, single crystals were grown and subjected to X-ray diffraction studies (Figures 9 and 10).

Since the  $^1\text{H}$  NMR spectra of complexes **11-15** all demonstrated singlet resonances for the  $\text{Si}(\text{SiMe}_3)_3$  groups, despite the fact that the crystallography suggested inequivalence, variable temperature NMR studies were completed on **14** and **15** to examine their behavior in solution. Upon cooling a toluene- $d_8$  solution of **14** the signal at 0.40 ppm (298 K) undergoes coalescence at 236 K, and two sharp singlets are observed at 0.69 and 0.42 ppm at 191 K. A similar result is observed for **15** with a somewhat higher coalescence temperature of 270 K. The fluxional process responsible for this behavior is likely a rocking of the  $\text{M}(\text{Si}(\text{SiMe}_3)_3)_2$  group back and forth along the M-M bond, with the data suggesting barriers of 11.0(3) and 12.7(3) kcal/mol for **14** and **15** respectively.

Based on the similar solid state structures obtained, all of the N-donor complexes (**11-15**) may be viewed as a cation-anion

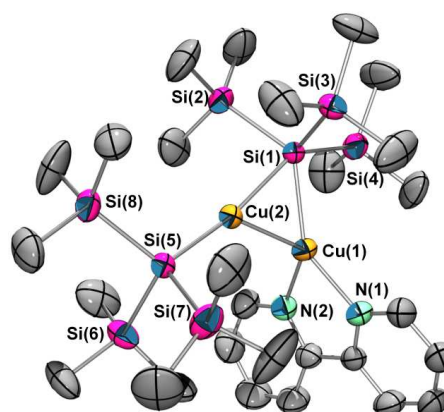


Figure 9. POV-Ray rendered ORTEP plot of the molecular structure of **14** (50% thermal ellipsoids). C; gray, N; aquamarine, Si: deep pink, Cu: copper. H-atoms omitted for clarity.

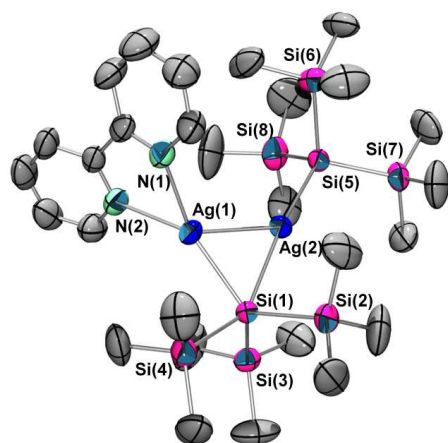
Cite this: DOI: 10.1039/c0xx00000x

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## ARTICLE TYPE

Table 3: Selected bond lengths and angles for **11-15**.

	Selected bond distances (Å) and angles (°)					
	M(1)-Si(1)	M(2)-Si(1)	M(2)-Si(5)	M(1)-M(5)	M(1)-N	Si(1)-M(2)-Si(5)
<b>11</b> , M=Cu	2.3369(5)	2.4003(5)	2.2907(5)	2.4328(4)	2.0185(17) 2.0382(17)	168.514(19)
<b>12</b> , M=Ag	2.438(2)	2.6413(19)	2.412(2)	2.6815(8)	2.154(6)	168.12(7)
<b>13</b> , M=Ag	2.4577(15)	2.5949(14)	2.4195(14)	2.6913(6)	2.295(5) 2.297(5)	167.45(5)
<b>14</b> , M=Cu	2.3187(6)	2.3903(6)	2.2744(7)	2.4002(5)	2.067(2) 2.076(2)	169.02(2)
<b>15</b> , M=Ag	2.4711(6)	2.6024(6)	2.4102(6)	2.6753(3)	2.347(2) 2.346(2)	171.65(2)



**Figure 10.** POV-Ray rendered ORTEP plot of the molecular structure of **15** (50% thermal ellipsoids). C; gray, N; aquamarine, Si: deep pink, Ag: slate blue. H-atoms omitted for clarity.

pair of the form  $[L_nM]^+[M(Si(SiMe_3)_3)_2]^-$  ( $M = Cu, Ag, n = 1, 2$ ), where the anionic metal center interacts with the cationic center *via* the M-M contact. This view is supported by the observation that in complexes such as  $[K][Cu(Si(SiMe_3)_3)_2]$ , an interaction between the Cu and K centers is observed.<sup>16</sup> Additionally, this formulation is similar to that proposed in many NHC-M-halide species  $[(NHC_2M)(X_2M)^-]$  and these structures may be related to the intermediates proposed for the ligand exchange that was suggested for complex **2** (*vide supra*).

The solid state characterization of **11-15** allowed for comparisons to be made on the effect of ligand choice on some of the metric parameters (Table 3). For the copper complexes, the average Cu-N bond distance is shorter for complex **11** (2.0284(17) Å) than it is for **14** (2.072(2) Å), while the Cu-Cu distance in **11** (2.4328(4) Å) is longer than it is in **14** (2.4002(5) Å). For the silver complexes, **15** has the longest M-N contacts (2.347(2) Å) followed by **13** (2.296(5) Å) and **12** (2.1546) Å). This trend is not completely reflected in the Ag-Ag contact however, as while **15** has the shortest Ag-Ag distance

(2.6753(3) Å), the same distance in **13** (2.6913(6) Å) is longer than it is in **12** (2.6815(8) Å). In terms of the M-Si contacts, the M(2)-Si(5) distances remain similar for each the copper and silver complexes, while for silver at least, it appears that a lengthening of the M(1)-Si(1) bond distance leads to a shortening of the M(2)-Si(1) distance.

As **14** and **15** could be isolated in reasonable yields, the volatility of these complexes was of interest. However, attempted sublimations of these species lead to decomposition rather than sublimation. This suggests that the bimetallic nature found in the N-donor supported compounds limits their volatility probably due to the higher molecular weights.

## Conclusions

Herein we have reported the syntheses of a number of copper and silver silyl complexes supported by C- and N-donor ligands. The use of different NHC as well as silyl ligands provided a diverse array of structures in the complexes synthesized with formulations of NHC-M-Silyl, NHC<sub>2</sub>-M-Silyl and a dimeric silyl bridged  $[NHC-M-Silyl]_2$  species observed. The thermal properties of the complexes were examined and the complexes of the form NHC-M-Si(SiMe<sub>3</sub>)<sub>3</sub> were shown to be promising volatile metal precursors. It was noted during the investigation of the NHC ligands that although modifying the NHC had little effect on the volatility of the complexes, reducing the symmetry in the silyl group produced significantly more sensitive complexes. In the synthesis of the N-donor complexes, bimetallic species were obtained regardless of the ligand chosen. The most notable result obtained was that using a bidentate ligand allowed for the isolation of the desired species in higher yields than when monodentate ligands were employed, likely due to ligand lability. We are currently exploring these complexes further and examining whether they are suitable precursors for the deposition of metal films.

## Experimental section



### General Considerations

All preparations were performed under an atmosphere of dry, O<sub>2</sub>-free Ar employing both vacuum line techniques and inert atmosphere glove boxes. Residual oxygen and moisture were removed from the argon stream by passage through an OxisorBW scrubber from Matheson Gas Products. Toluene, tetrahydrofuran, and hexanes solvents were dried and purified using the Grubbs/Dow purification system and stored in evacuated 500 mL thick walled glass vessels over sodium-tetraglyme/benzophenone ketyl. Pentane was dried, distilled, and stored in an evacuated 500 mL vessel over sodium-tetraglyme/benzophenone ketyl. All solvents were distilled prior to use. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra were acquired on Bruker Avance 400 and 600 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C NMR were internally referenced to deuterated C<sub>6</sub>D<sub>6</sub> (δ = 7.16 ppm (<sup>1</sup>H), 128.06 ppm (<sup>13</sup>C)) relative to Me<sub>4</sub>Si. <sup>29</sup>Si resonances were referenced externally to Me<sub>4</sub>Si. NMR samples were prepared in the glove box, capped and sealed with parafilm. The chemical shift values of <sup>29</sup>Si NMR signals were determined using a 1-dimensional <sup>29</sup>Si{<sup>1</sup>H} NMR experiment, a 2-dimensional <sup>1</sup>H-<sup>29</sup>Si HMBC experiment or a combination of the two as noted. Coupling constants (*J*) are reported as absolute values. All glassware was dried overnight at 120 °C and evacuated for 1 hour prior to use. Combustion analyses were performed in-house employing a Perkin Elmer 2400 Series II CHNS Analyzer. C<sub>6</sub>D<sub>6</sub> was purchased from the Cambridge Isotope Laboratories and was dried over sodium, distilled, degassed and stored under Ar in a glove box. (Ime)CuI,<sup>37</sup> (Ime)AgI,<sup>38</sup> (ItBu)CuCl,<sup>29</sup> KSi(SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub>, EtSi(SiMe<sub>3</sub>)<sub>3</sub> and KSi(SiMe<sub>3</sub>)<sub>2</sub>Et(THF)<sub>0.5</sub><sup>39</sup> and IMeCO<sub>2</sub><sup>40</sup> were prepared according to previously reported procedures. (ItBu)AgCl was prepared using a similar strategy to those previously described for the synthesis of NHC-silver halides.<sup>30</sup> (Me<sub>3</sub>Si)<sub>4</sub>Si was obtained from Alfa Aesar. AgOTf, CuX (X = Cl, Br, I), 1-methylimidazole, 2,2'-bipyridine and 4-dimethylaminopyridine were obtained from Aldrich Chemical Co. All chemicals were used as received.

**Synthesis of ItBuAgCl.** ItBuHCl (1 g, 4.614 mmol) and silver (I) oxide (668 mg, 2.884 mmol) were combined in a 50 mL round bottom flask and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added via a cannula. The reaction mixture was wrapped in Al-foil and allowed to stir at room temperature. After 18 h, the solution was filtered through a plug of celite on a fine porosity frit and the solvent was removed in vacuo. The off-white solid was redissolved in minimal CH<sub>2</sub>Cl<sub>2</sub> and pentane was added to precipitate a white solid. The supernatant was decanted and the white solid dried. The product was obtained as a white solid in 79% yield (1.18 g, 3.645 mmol). The compound can be recrystallized by slow diffusion of pentane into CH<sub>2</sub>Cl<sub>2</sub> at -35 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ ppm) 7.16 (s, 2H, CH), 1.74 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ ppm) 176.29 (bs, carbene-C ItBu), 117.27 (s, CH ItBu), 58.07 (s, C(CH<sub>3</sub>)<sub>3</sub>), 32.13 (s, C(CH<sub>3</sub>)<sub>3</sub> ItBu). Elemental Analysis for C<sub>11</sub>H<sub>20</sub>N<sub>2</sub>AgCl (323.60) Calculated: C, 40.83; H, 6.23; N, 8.65; Actual: C, 41.46; H, 6.39; N, 8.71.

### Synthesis of (Ime)CuSi(SiMe<sub>3</sub>)<sub>3</sub> (1) and (ItBu)CuSi(SiMe<sub>3</sub>)<sub>3</sub>

(3). These compounds were prepared in a similar fashion and thus only one preparation is detailed. (1): A solution of KSi(SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> in toluene (376 mg, 0.872 mmol; 5 mL) was added drop wise to stirring gray suspension of (Ime)CuI in toluene (250 mg, 0.872 mmol; 5 mL) at -35 °C. The cloudy gray suspension was stirred for 18 h before being filtered through a plug of celite to a clear pale yellow solution. The solvent was removed and the off-white solid was extracted with pentane. The mixture was cooled to -35 °C and after 24 hours yielded the product as a crop of off-white crystals. A second crop could be obtained by re-cooling the supernatant giving the product in 63% yield (223 mg; 0.549 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 5.67 (s, 2H, CH), 2.91 (s, 6H, CH<sub>3</sub>), 0.62 (s, 27H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 189.56 (s, carbene-C Ime), 120.58 (s, CH Ime), 37.02 (s, CH<sub>3</sub> Ime), 5.83 (s, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>1</sup>H-<sup>29</sup>Si HMBC NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -5.5 (Si(SiMe<sub>3</sub>)<sub>3</sub>), -136.8 (Si(SiMe<sub>3</sub>)<sub>3</sub>). Elemental Analysis for C<sub>14</sub>H<sub>35</sub>N<sub>2</sub>Si<sub>4</sub>Cu (406.73) Calculated: C, 41.30; H, 8.67; N, 6.89; Actual: C, 41.41; H, 9.13; N, 6.87.

(3): Starting with KSi(SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (431 mg, 1.000 mmol) and (ItBu)CuCl (280 mg, 1.000 mmol), the product was obtained as white crystals in 74% yield (363 mg; 0.740 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 6.27 (s, 2H, CH), 1.45 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.61 (s, 27H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 179.38 (s, carbene-C ItBu), 115.23 (s, CH ItBu), 57.77 (s, C(CH<sub>3</sub>)<sub>3</sub>), 32.38 (s, C(CH<sub>3</sub>)<sub>3</sub> ItBu), 5.46 (s, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -6.73 (s, Si(SiMe<sub>3</sub>)<sub>3</sub>). <sup>1</sup>H-<sup>29</sup>Si HMBC NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -6.79 (Si(SiMe<sub>3</sub>)<sub>3</sub>), -147.70 (Si(SiMe<sub>3</sub>)<sub>3</sub>). Elemental Analysis for C<sub>20</sub>H<sub>47</sub>N<sub>2</sub>Si<sub>4</sub>Cu (491.05) Calculated: C, 48.92; H, 9.65; N, 5.70; Actual: C, 48.90; H, 9.89; N, 5.58.

### Synthesis of (Ime)AgSi(SiMe<sub>3</sub>)<sub>3</sub> (2) and (ItBu)AgSi(SiMe<sub>3</sub>)<sub>3</sub>

(4). These compounds were prepared in a similar fashion and thus only one preparation is detailed. (2): A solution of KSi(SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> in toluene (456 mg, 1.057 mmol; 5 mL) was added drop wise to stirring gray suspension of (Ime)AgI in toluene (350 mg, 1.057 mmol; 5 mL) at -35 °C. The cloudy gray suspension was stirred for 18 h before being filtered through a plug of celite to a clear pale yellow solution. The solvent was removed and the off-white solid was extracted with pentane. The mixture was cooled to -35 °C and after 24 hours yielded the product as a crop of off-white crystals. A second crop could be obtained by re-cooling the supernatant giving the product in 76% yield (362 mg; 0.803 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 5.61 (s, 2H, CH), 2.90 (s, 6H, CH<sub>3</sub>), 0.64 (s, 27H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 189.76 (s, carbene-C Ime), 120.50 (s, CH Ime), 37.00 (s, CH<sub>3</sub> Ime), 5.81 (s, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -5.56 (s, Si(SiMe<sub>3</sub>)<sub>3</sub>). <sup>1</sup>H-<sup>29</sup>Si HMBC NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -5.45 (Si(SiMe<sub>3</sub>)<sub>3</sub>), -136.87 (Si(SiMe<sub>3</sub>)<sub>3</sub>). Elemental Analysis for C<sub>14</sub>H<sub>35</sub>N<sub>2</sub>Si<sub>4</sub>Ag (451.05) Calculated: C, 37.25; H, 7.82; N, 6.21; Actual: C, 37.13; H, 8.00; N, 6.12.

(4): Starting with KSi(SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (431 mg, 1.000 mmol) and (ItBu)AgCl (324 mg, 1.000 mmol), the product was obtained as a crop of white crystals in 71% yield (380 mg; 0.710 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 6.33 (s, 2H, CH), 1.41 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.62 (s, 27H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR

(C<sub>6</sub>D<sub>6</sub>, δ ppm) 188.10 (apparent dof, <sup>1</sup>J<sub>CAg109</sub> 131 Hz, <sup>1</sup>J<sub>CAg107</sub> 113 Hz, *carbene-C* *ItBu*), 115.57 (s, CH *ItBu*), 57.77 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.98 (s, C(CH<sub>3</sub>)<sub>3</sub> *ItBu*), 5.46 (d, <sup>3</sup>J<sub>CAg</sub> 4 Hz, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -5.95 (s, Si(SiMe<sub>3</sub>)<sub>3</sub>), -140.21 (dof, <sup>1</sup>J<sub>SiAg109</sub> 213 Hz, <sup>1</sup>J<sub>SiAg107</sub> 179 Hz, Si(SiMe<sub>3</sub>)<sub>3</sub>). <sup>1</sup>H-<sup>29</sup>Si HMBC NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -5.84 (Si(SiMe<sub>3</sub>)<sub>3</sub>), -140.82 (Si(SiMe<sub>3</sub>)<sub>3</sub>). Elemental Analysis for C<sub>20</sub>H<sub>47</sub>N<sub>2</sub>Si<sub>4</sub>Ag (535.37) Calculated: C, 44.87; H, 8.85; N, 5.23; Actual: C, 44.50; H, 8.53; N, 4.95.

**Synthesis of (IME)CuSiEt(SiMe<sub>3</sub>)<sub>2</sub> (5).** A solution of KSiEt(SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>0.5</sub> in toluene (279 mg, 1.000 mmol; 5 mL) was added drop wise to stirring gray suspension of (IME)CuI in toluene (287 mg, 1.000 mmol; 5 mL) at -35 °C. The cloudy suspension was stirred for 18 h before being filtered through a plug of celite to a clear yellow solution. The solvent was removed and the yellow solid was combined with pentane and cooled to -35 °C. After 24 hours the supernatant was removed and the product was obtained as a crystalline yellow solid in 60% yield (218 mg; 0.600 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 5.60 (s, 2H, CH), 3.00 (s, 6H, NCH<sub>3</sub>), 1.61 (t, 3H, <sup>3</sup>J<sub>HH</sub> 7.8 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 1.34 (quart, 2H, <sup>3</sup>J<sub>HH</sub> 7.8 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 0.63 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 182.01 (s, *carbene-C* IMe), 120.20 (s, CH IMe), 36.74 (s, CH<sub>3</sub> IMe), 17.79 (s, SiCH<sub>2</sub>CH<sub>3</sub>), 3.72 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 2.78 (s, SiCH<sub>2</sub>CH<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -9.75 (s, SiEt(SiMe<sub>3</sub>)<sub>2</sub>), -77.65 (s, SiEt(SiMe<sub>3</sub>)<sub>2</sub>). Elemental Analysis for C<sub>13</sub>H<sub>31</sub>N<sub>2</sub>Si<sub>3</sub>Cu (362.87) Calculated: C, 43.03; H, 8.61; N, 7.72; Actual: C, 42.83; H, 8.28; N, 7.72.

**Synthesis of (IME)<sub>2</sub>CuSiEt(SiMe<sub>3</sub>)<sub>2</sub> (6) and (IME)<sub>2</sub>CuSi(SiMe<sub>3</sub>)<sub>3</sub> (7).** These compounds were prepared in a similar fashion and thus only one preparation is detailed. (6): Solid IMeCO<sub>2</sub> (140 mg, 1.000 mmol) was added to solid CuCl (50 mg, 0.500 mmol) and 10 mL of THF was added. The mixture was stirred for 1h giving a cloudy off-white suspension. The mixture was cooled to -35 °C and a solution of KSiEt(SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>0.5</sub> in THF (140 mg, 0.500 mmol; 5 mL) was added drop wise. An immediate change to a deep red mixture is observed. The cloudy suspension was stirred for 18 h before being filtered through a plug of celite to a clear orange-yellow solution. The solvent was removed and the yellow solid was combined with toluene and filtered through a plug of celite before the solvent was removed. The solid was then combined with pentane and cooled to -35 °C. After 24 hours the supernatant was removed and the product was obtained as a crystalline yellow solid in 49% yield (112 mg; 0.244 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 6.06 (s, 4H, CH), 3.28 (s, 12H, NCH<sub>3</sub>), 1.31 (t, 3H, <sup>3</sup>J<sub>HH</sub> 7.7 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 1.18 (quart, 2H, <sup>3</sup>J<sub>HH</sub> 7.7 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 0.47 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 195.74 (s, *carbene-C* IMe), 119.68 (s, CH IMe), 36.69 (s, CH<sub>3</sub> IMe), 16.29 (s, SiCH<sub>2</sub>CH<sub>3</sub>), 4.62 (s, SiCH<sub>2</sub>CH<sub>3</sub>), 3.69 (s, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -9.96 (s, SiEt(SiMe<sub>3</sub>)<sub>2</sub>), -86.25 (s, SiEt(SiMe<sub>3</sub>)<sub>2</sub>). <sup>1</sup>H-<sup>29</sup>Si HMBC NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -10.11 (SiEt(SiMe<sub>3</sub>)<sub>2</sub>), -86.49 (SiEt(SiMe<sub>3</sub>)<sub>2</sub>). Elemental Analysis for C<sub>18</sub>H<sub>39</sub>N<sub>4</sub>Si<sub>3</sub>Cu (458.99) Calculated: C, 47.10; H, 8.56; N, 12.20; Actual: C, 46.85; H, 8.76; N, 12.63.

(7): Starting with IMeCO<sub>2</sub> (140 mg, 1.000 mmol), CuCl (50 mg, 0.500 mmol) and KSi(SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (216 mg, 0.500 mmol) the product was obtained as an orange-yellow solid in 35% yield (88 mg; 0.175 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 6.05 (s, 4H, CH), 3.27 (s, 12H, NCH<sub>3</sub>), 0.48 (s, 27H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 195.11 (s, *carbene-C* IMe), 119.89 (s, CH IMe), 36.88 (s, CH<sub>3</sub> IMe), 5.90 (s, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>1</sup>H-<sup>29</sup>Si HMBC NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -6.65 (Si(SiMe<sub>3</sub>)<sub>3</sub>), -160.83 (Si(SiMe<sub>3</sub>)<sub>3</sub>). Elemental Analysis for C<sub>19</sub>H<sub>43</sub>N<sub>4</sub>Si<sub>4</sub>Cu (503.01) Calculated: C, 45.37; H, 8.62; N, 11.14; Actual: (1) C, 44.71; H, 8.82; N, 11.16, (2) C, 44.60; H, 8.47; N, 11.11, (3) C, 44.46; H, 8.70; N, 11.11. Elemental analysis for this complex consistently returned low carbon possibly due to carbide formation.

**Synthesis of (IME)AgSiEt(SiMe<sub>3</sub>)<sub>2</sub> (8).** A solution of KSiEt(SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>0.5</sub> in toluene (279 mg, 1.000 mmol; 5 mL) was added drop wise to stirring gray suspension of (IME)AgI in toluene (331 mg, 1.000 mmol; 5 mL) at -35 °C. The cloudy gray suspension was stirred for 18 h before being filtered through a plug of celite to a clear pale yellow solution. The solvent was removed and a colorless oily residue was extracted with pentane, filtered and re-dried giving the crude product as a viscous oil in 64% yield (262 mg; 0.643 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 5.82 (s, 2H, CH), 3.00 (s, 6H, NCH<sub>3</sub>), 1.55 (t, 3H, <sup>3</sup>J<sub>HH</sub> 7.7 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 1.28 (quart, 2H, <sup>3</sup>J<sub>HH</sub> 7.7 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 0.54 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 191.90 (s, *carbene-C* IMe), 120.63 (s, CH IMe), 37.07 (s, CH<sub>3</sub> IMe), 18.00 (s, SiCH<sub>2</sub>CH<sub>3</sub>), 3.63 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 3.36 (s, SiCH<sub>2</sub>CH<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -9.03 (s, SiEt(SiMe<sub>3</sub>)<sub>2</sub>), -66.60 (s, SiEt(SiMe<sub>3</sub>)<sub>2</sub>). <sup>1</sup>H-<sup>29</sup>Si HMBC NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -9.01 (SiEt(SiMe<sub>3</sub>)<sub>2</sub>), -66.83 (SiEt(SiMe<sub>3</sub>)<sub>2</sub>).

**Synthesis of (ItBu)CuSiEt(SiMe<sub>3</sub>)<sub>2</sub> (9).** A solution of KSiEt(SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>0.5</sub> in toluene (279 mg, 1.000 mmol; 5 mL) was added drop wise to stirring white suspension of (ItBu)CuCl in toluene (280 mg, 1.000 mmol; 5 mL) at -35 °C. The cloudy suspension was stirred for 18 h before being filtered through a plug of celite to a clear pale red solution. The solvent was removed and the off-white solid was combined with hexane and filtered. The clear colorless solution was cooled to -35 °C, and after 2 hours the supernatant was removed and the product was obtained as colorless needles in 66% yield (294 mg; 0.657 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 6.33 (s, 2H, CH), 1.57 (t, 3H, <sup>3</sup>J<sub>HH</sub> 7.7 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 1.47 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.28 (quart of d, 2H, <sup>3</sup>J<sub>HH</sub> 7.7 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 0.56 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 179.99 (s, *carbene-C* *ItBu*), 115.31 (s, CH *ItBu*), 57.76 (s, C(CH<sub>3</sub>)<sub>3</sub>), 32.33 (s, C(CH<sub>3</sub>)<sub>3</sub> *ItBu*), 17.39 (s, SiCH<sub>2</sub>CH<sub>3</sub>), 3.31 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 2.54 (s, SiCH<sub>2</sub>CH<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -10.01 (s, Si(SiMe<sub>3</sub>)<sub>2</sub>Et), -79.02 (s, Si(SiMe<sub>3</sub>)<sub>2</sub>Et). Elemental Analysis for C<sub>19</sub>H<sub>43</sub>N<sub>2</sub>Si<sub>3</sub>Cu (447.03) Calculated: C, 51.05; H, 9.69; N, 6.26; Actual: C, 51.07; H, 9.98; N, 6.31.

**Synthesis of (ItBu)AgSiEt(SiMe<sub>3</sub>)<sub>2</sub> (10).** A solution of KSiEt(SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>0.5</sub> in toluene (279 mg, 1.000 mmol; 5 mL) was added drop wise to stirring gray suspension of (ItBu)AgCl in toluene (324 mg, 1.000 mmol; 5 mL) at -35 °C. The cloudy

gray suspension was stirred for 18 h before being filtered through a plug of celite to a clear almost colorless solution. The solvent was removed and the white solid was extracted with hexane, filtered and stored at -35 °C for 2 hours producing the product as white needles in 64% yield (314 mg; 0.639 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 6.38 (s, 2H, CH), 1.58 (t, 3H, <sup>3</sup>J<sub>HH</sub> 7.9 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 1.44 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.31 (quart of d, 2H, <sup>3</sup>J<sub>HH</sub> 7.9 Hz, <sup>3</sup>J<sub>HAg</sub> 1.6 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 0.57 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 189.11 (apparent dofd, <sup>1</sup>J<sub>CAg109</sub> 119 Hz, <sup>1</sup>J<sub>CAg107</sub> 103 Hz, carbene-C *l*tBu), 115.66 (d, <sup>3</sup>J<sub>CAg</sub> 3 Hz, CH *l*tBu), 57.76 (s, C(CH<sub>3</sub>)<sub>3</sub>), 32.03 (s, C(CH<sub>3</sub>)<sub>3</sub> *l*tBu), 17.90 (d, <sup>3</sup>J<sub>CAg</sub> 6 Hz, SiCH<sub>2</sub>CH<sub>3</sub>), 3.22 (d, <sup>3</sup>J<sub>CAg</sub> 3 Hz, Si(CH<sub>3</sub>)<sub>3</sub>), 3.05 (d, <sup>2</sup>J<sub>CAg</sub> 2 Hz, SiCH<sub>2</sub>CH<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -9.40 (d, <sup>2</sup>J<sub>SiAg</sub> 4 Hz, *SiEt*(SiMe<sub>3</sub>)<sub>2</sub>), -69.38 (dofd, <sup>1</sup>J<sub>SiAg109</sub> 239 Hz, <sup>1</sup>J<sub>SiAg107</sub> 207 Hz, *SiEt*(SiMe<sub>3</sub>)<sub>2</sub>). Elemental Analysis for C<sub>19</sub>H<sub>43</sub>N<sub>2</sub>Si<sub>3</sub>Ag (491.35) Calculated: C, 46.45; H, 8.82; N, 5.70; Actual: C, 46.50; H, 8.47; N, 5.69.

**Synthesis of (Imidazole)<sub>2</sub>[CuSi(SiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub> (11).** Neat *N*-methylimidazole (80 μL, 1.000 mmol) was added to a stirring off-white suspension of CuCl in THF (99 mg, 1.000 mmol; 4 mL) giving a cloudy white mixture. The reaction mixture was stirred for 2 h before cooling to -35 °C. A -35 °C solution of KSi(SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> in THF (431 mg, 1.000 mmol; 5 mL) was added drop wise to the stirring suspension of methylimidazoleCuCl giving a gray-brown mixture. The mixture was stirred for a further 18 h before being filtered through a plug of celite to a clear brown-orange solution. The solvent was removed and the brown-orange solid was extracted with hexane and filtered through a plug of celite. The pale brown-orange solution was cooled to -35 °C and after 24 hours yielded the product as a crop of off-white crystals in 30% yield (118 mg; 0.150 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 6.97 (s, 2H, CH), 6.77 (s, 2H, CH), 5.89 (s, 2H, CH), 2.34 (s, 6H, N-CH<sub>3</sub>), 0.58 (s, 54H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 138.42 (s, CH), 128.49 (s, CH), 120.26 (s, CH), 32.59 (s, CH<sub>3</sub>), 5.78 (s, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>1</sup>H-<sup>29</sup>Si HMBC NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -7.40 (Si(SiMe<sub>3</sub>)<sub>3</sub>), -145.51 (Si(SiMe<sub>3</sub>)<sub>3</sub>). Elemental Analysis for C<sub>26</sub>H<sub>66</sub>N<sub>4</sub>Si<sub>8</sub>Cu<sub>2</sub> (785.72) Calculated: C, 39.75; H, 8.47; N, 7.13; Actual: C, 39.87; H, 8.45; N, 7.08.

**Synthesis of (Imidazole)[Ag<sub>2</sub>[Si(SiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub>] (12).** Neat *N*-methylimidazole (80 μL, 1.000 mmol) was added to a stirring white suspension of AgOTf in THF (257 mg, 1.000 mmol; 4 mL) giving a mostly clear, colorless solution. The reaction mixture was stirred for 2 h before cooling to -35 °C. A -35 °C solution of KSi(SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> in THF (431 mg, 1.000 mmol; 5 mL) was added drop wise to the stirring solution of methylimidazole and AgOTf quickly giving a dark red-brown solution. The mixture was stirred for a further 18 h before being filtered through a plug of celite to a clear red-brown solution. The solvent was removed and the brown solid was extracted with hexane and filtered through a plug of celite. The pale brown solution was cooled to -35 °C and after 24 hours yielded the product as a crop of off-white crystals in 15% yield (60 mg; 0.075 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 6.61 (s, 2H, 2*x*CH), 5.78 (s, 2H, CH), 2.17 (s, 3H, N-CH<sub>3</sub>), 0.58 (s, 54H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 138.17 (bs, CH),

128.81 (bs, CH), 120.54 (bs, CH), 32.65 (s, CH<sub>3</sub>), 6.16 (s, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -5.39 (s, Si(SiMe<sub>3</sub>)<sub>3</sub>), signal for Si(SiMe<sub>3</sub>)<sub>3</sub> could not be located. Elemental Analysis for C<sub>22</sub>H<sub>60</sub>N<sub>2</sub>Si<sub>8</sub>Ag<sub>2</sub> (792.27) Calculated: C, 33.35; H, 7.63; N, 3.53; Actual: C, 32.87; H, 7.29; N, 3.63.

**Synthesis of (DMAP)<sub>2</sub>[AgSi(SiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub> (13).** A solution of DMAP in THF (122 mg, 1.000 mmol; 2 mL) was added to a stirring white suspension of AgOTf in THF (257 mg, 1.000 mmol; 4 mL) giving a cloudy white mixture. The reaction mixture was stirred for 2 h before cooling to -35 °C. A -35 °C solution of KSi(SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> in THF (431 mg, 1.000 mmol; 5 mL) was added drop wise to the stirring suspension of DMAP and AgOTf quickly giving a dark red-brown solution. The mixture was stirred for a further 18 h before being filtered through a plug of celite to a clear red-brown solution. The solvent was removed and the brown solid was extracted with hexane and filtered through a plug of celite. The pale brown solution was cooled to -35 °C and after 24 hours yielded the product as a crop of off-white crystals in 22% yield (102 mg; 0.110 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 8.06 (d, 4H, <sup>3</sup>J<sub>HH</sub> 4.8 Hz, Ar-H), 5.90 (d, 4H, <sup>3</sup>J<sub>HH</sub> 4.8 Hz, Ar-H), 2.09 (s, 12H, CH<sub>3</sub>), 0.61 (s, 54H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 154.42 (s, C-NMe<sub>2</sub> DMAP), 150.19 (s, Ar-CH), 106.96 (s, Ar-CH), 38.22 (s, CH<sub>3</sub>), 6.10 (s, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -5.26 (s, Si(SiMe<sub>3</sub>)<sub>3</sub>), -136.60 (s, Si(SiMe<sub>3</sub>)<sub>3</sub>). <sup>1</sup>H-<sup>29</sup>Si HMBC NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -5.41 (Si(SiMe<sub>3</sub>)<sub>3</sub>), could not locate Si(SiMe<sub>3</sub>)<sub>3</sub> signal. Elemental Analysis for C<sub>30</sub>H<sub>74</sub>N<sub>4</sub>Si<sub>8</sub>Ag<sub>2</sub> (930.48) Calculated: C, 38.73; H, 8.01; N, 6.02; Actual: C, 38.75; H, 8.25; N, 5.60.

**Synthesis of (Bipy)[CuSi(SiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub> (14).** A solution of Bipy in toluene (78 mg, 0.500 mmol; 2 mL) was added to a stirring white suspension of CuBr in toluene (143 mg, 1.000 mmol; 4 mL) giving a cloudy red-brown suspension. The reaction mixture was stirred for 2 h before cooling to -35 °C. A -35 °C solution of KSi(SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> in toluene (431 mg, 1.000 mmol; 5 mL) was added drop wise to the stirring suspension of Bipy and CuBr quickly giving a cloudy purple solution. The mixture was stirred for a further 18 h before being filtered through a plug of celite to a clear red-purple solution. The solvent was removed and the brown-purple solid was extracted with hexane and filtered through a plug of celite. The deep purple solution was cooled to -35 °C and after 24 hours yielded the product as a crop of purple crystals (212 mg). A second crop could be obtained by concentrating the supernatant and cooling it to -35 °C (20 mg). The product was obtained in 60% yield (232 mg; 0.298 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 8.80 (d, 2H, <sup>3</sup>J<sub>HH</sub> 5.0 Hz, Ar-CH), 6.98 (d, 2H, <sup>3</sup>J<sub>HH</sub> 7.7 Hz, Ar-CH), 6.90 (dofd, 2H, <sup>3</sup>J<sub>HH</sub> 7.7 Hz, <sup>3</sup>J<sub>HH</sub> 1.5 Hz, Ar-CH), 6.61 (vt, 2H, <sup>3</sup>J<sub>HH</sub> 5.9 Hz, Ar-CH), 0.46 (s, 54H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 151.71 (s, carbene-C), 150.79 (s, Ar-CH), 138.56 (s, Ar-CH), 126.17 (s, Ar-CH), 120.93 (s, Ar-CH), 5.78 (s, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -7.98 (s, Si(SiMe<sub>3</sub>)<sub>3</sub>). <sup>1</sup>H-<sup>29</sup>Si HMBC NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -7.90 (Si(SiMe<sub>3</sub>)<sub>3</sub>). Could not locate Si(SiMe<sub>3</sub>)<sub>3</sub> signal. Elemental Analysis for C<sub>28</sub>H<sub>64</sub>N<sub>2</sub>Si<sub>8</sub>Cu<sub>2</sub> (779.72) Calculated: C, 43.13; H, 8.27; N, 3.59; Actual: C, 43.59; H, 8.62; N, 3.53.

**Synthesis of (Bipy)[AgSi(SiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub> (15).** A solution of Bipy in toluene (78 mg, 0.500 mmol; 2 mL) was added to a stirring white suspension of AgOTf in toluene (257 mg, 1.000 mmol; 4 mL) giving a clear colorless solution. The reaction mixture was stirred for 2 h before cooling to -35 °C. A -35 °C solution of KSi(SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> in toluene (431 mg, 1.000 mmol; 5 mL) was added drop wise to the stirring suspension of Bipy and AgOTf quickly giving a cloudy red-brown solution. The mixture was stirred for a further 18 h before being filtered through a plug of celite to a clear red-brown solution. The solvent was removed and the brown solid was extracted with hexane and filtered through a plug of celite. The deep red solution was cooled to -35 °C and after 24 hours yielded the product as a crop of red crystals in 58% yield (250 mg; 0.288 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 8.61 (bs, 2H, Ar-CH), 7.07 (bs, 2H, Ar-CH), 6.97 (bs, 2H, Ar-CH), 6.63 (bs, 2H, Ar-CH), 0.49 (s, 54H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) 152.02 (b, carbene-C), 150.97 (s, Ar-CH), 138.34 (s, Ar-CH), 125.25 (s, Ar-CH), 121.61 (s, Ar-CH), 6.07 (s, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ ppm) -5.44 (s, Si (SiMe<sub>3</sub>)<sub>3</sub>). Could not locate Si(SiMe<sub>3</sub>)<sub>3</sub> signal. Elemental Analysis for C<sub>28</sub>H<sub>64</sub>N<sub>2</sub>Si<sub>8</sub>Ag<sub>2</sub> (868.36) Calculated: C, 38.73; H, 7.43; N, 3.23; Actual: C, 38.46; H, 7.16; N, 3.19.

**Crystal structure analysis.** X-ray crystallographic analyses were performed on suitable crystals coated in Paratone 8277 oil (Exxon) and mounted on a glass fibre. Measurements were collected on either a Nonius KappaCCD (Mo Kα) or a Bruker APEX II CCD diffractometer (Cu Kα); full details can be found in the independently deposited crystallographic information files (CCDC 1037722-1037735). X-ray figures were rendered using POV-Ray software.<sup>42</sup>

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## Notes and references

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† Electronic Supplementary Information (ESI) available: TGA and DSC data for **1-5**, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **7** and **8**, POV-ray depictions of **11-13** and (DMAP)<sub>2</sub>[Cu(Si(SiMe<sub>3</sub>)<sub>3</sub>)<sub>2</sub>], tables of crystallographic data, and crystallographic data in CIF format. See DOI: 10.1039/b000000x/. See DOI: 10.1039/b000000x/

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## Graphical Abstract

A series of copper and silver-silyl complexes containing N-heterocyclic carbene or N-donor ligands were synthesized and characterized in the solid state. A number of different structural forms were observed and many compounds were shown to be volatile.

