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Facile Access to Mono- and Dinuclear Heteroleptic N-Heterocyclic Silylene Copper Complexes

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S *Supporting Information*

ABSTRACT: Reaction of the heteroleptic N-heterocyclic chlorosilylene L(Cl)Si: (**1**; L = PhC(NtBu)$_2$) with [Cu(tmeda)(CH$_3$CN)][OTf] (**2**; tmeda = N,N,N',N'-tetramethylethylenediamine, OTf = OSO$_2$CF$_3$ (triflate)) affords the Cu(I) complex [L(Cl)Si:→Cu(tmeda)][OTf] (**3**) in high yield as the first example of a heteroleptic N-heterocyclic silylene copper complex. Similarly, the reaction of L(OtBu)Si: (**4**; L = PhC(NtBu)$_2$) with **2** affords [L(OtBu)Si: → Cu(tmeda)][OTf] (**5**) and that of L(NMe$_2$)Si: (**6**) with **2** leads to [L(NMe$_2$)Si:→Cu(tmeda)][OTf] (**7**). Complex **3** shows a rather strong interaction in the solid state between the O atom of the triflate anion and the three-coordinate Cu(I) center with a Cu···O distance of 2.312 Å. In contrast, complex **7** features only a weak interaction (ca. 3.28 Å), while in complex **5** the cation and anion are fully separated. Strikingly, the reaction of the chelating oxo-bridged silylene :Si(L)(μ_2-O)(L)Si: (**8**) with the copper source [Cu(CH$_3$CN)$_4$][OTf] (**9**) affords the dinuclear complex salt [Cu$_2$\{η^1:η^1-LSi(μ_2-O)SiL\}$_2$][OTf]$_2$ (**10**), featuring a novel metallacyclooctane dication, selectively in a good yield. Complex **10** also exhibits a very strong interaction between the copper centers in the dication and the oxygen atoms of triflate anions in the solid state, evidenced by a Cu···O separation of only 2.141 Å. All complexes were fully characterized.
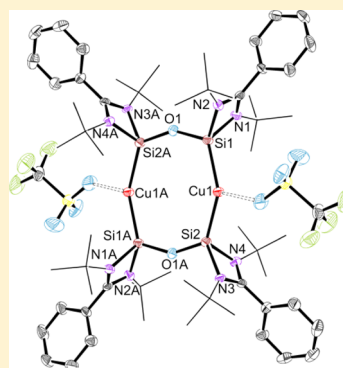
INTRODUCTION

N-heterocyclic silylene (NHSi) transition-metal complexes have emerged in the past decade as a new class of compounds which lie at the forefront of contemporary research efforts.[1] These efforts have largely been precipitated by the abundance of silicon in the earth's crust and the search for new generations of complexes capable of novel synthetic transformations, particularly in catalysis.[2] To date, they have been implicated in a relatively small number of catalytic transformations and are still comparatively scarce in comparison to their carbon homologues: that is, the N-heterocyclic carbene (NHC) metal complexes. Recent examples of their use in catalysis include that of a hydridosilylene iron NHSi complex (**I** in Chart 1) to perform ketone hydrosilylation,[3] catalytic C−C bond formation by nickel NHSi complexes (**II** and **III** in Chart 1),[4] catalytic amide reduction effected by NHSi Rh or Ir complexes, bearing the zwitterionic NHSi (**IV** in Chart 1),[5] and catalytic borylation of arenes effected by **V** (Chart 1).[6]

These examples illustrate the potential locked inside these complexes and clearly show a need for their fundamental exploration. Most of the NHSi complexes that exist to date are of transition metals of groups 5−10, with NHSi group 10 metal complexes being the most numerous.[1] In contrast, group 4 metal NHSi complexes are still rare,[7] and reports of NHSi group 11 or 12 metal complexes are also scant. In fact, other than a theoretical paper by Frenking studying the stability of NHSi Cu, Ag, and Au complexes,[8] there are only two synthetic examples, only one of which is isolable. Lappert and co-workers

Chart 1. Recent Examples of Catalytically Active N-Heterocyclic Silylene (NHSi) Complexes
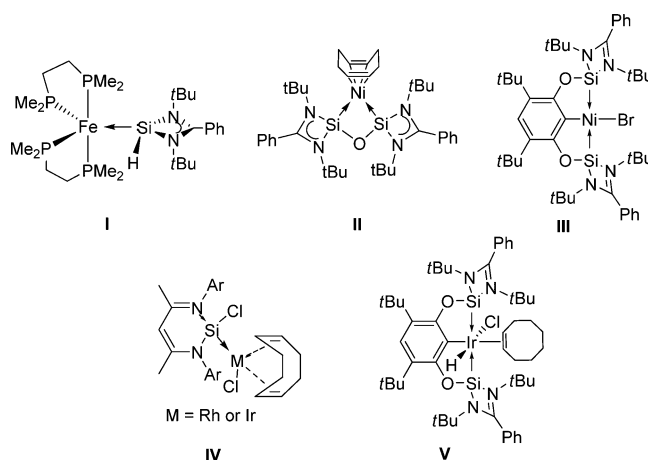

prepared an isolable tetrahedral copper-based NHSi complex by reacting a homoleptic NHSi with [CuI(PPh$_3$)$_3$], which afforded, by elimination of PPh$_3$, the tetrahedral copper NHSi complex [(PPh$_3$)$_2$Cu(←:Si\{N(CH$_2t$Bu)$_2$Ph\})I] (**VI** in Chart 2).[9] Apeloig, West, and co-workers have reported the only other example of a group 11 or 12 metal NHSi complex for Hg,

Chart 2. Reported Examples of NHSi Group 11 or 12 Metal Complexes

VI   **VII**
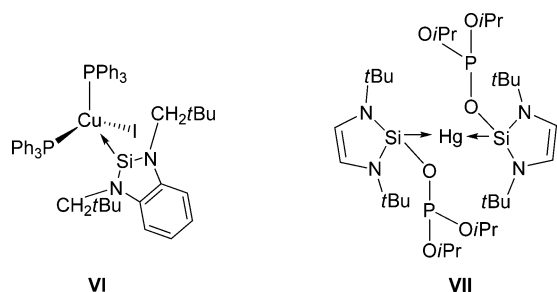
which was found to be highly reactive and could not be structurally characterized or isolated (**VII** in Chart 2).[10]

This early stage of knowledge on NHSi metal complexes turned our interest to the synthesis of new types of copper-based NHSi complexes, in an attempt to garner more structural and spectroscopic data on NHSi group 11 metal complexes, from a fundamental perspective.

Herein, we report only the second set of isolable examples of NHSi group 11 or 12 metal complexes, for copper. The facile reactions of amidinato-stabilized silylenes of the type LSiX (L = PhC(NtBu)$_2$; X = Cl, OtBu, NMe$_2$)[11] with the readily available Cu(I) precursors [Cu(tmeda)(CH$_3$CN)][OTf] afford the first examples of heteroleptic NHSi complexes of group 11 metals. Moreover, the reaction of the chelating oxo-bridged bis-silylene :SiL(μ_2-O)LSi: with the Cu(I) source [Cu(CH$_3$CN)$_4$][OTf] is also reported and affords the novel dinuclear metallacyclic complex [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$][OTf]$_2$.

■ RESULTS AND DISCUSSION

The amidinato-stabilized chlorosilylene **1**[11a] by Roesky and co-workers, L(Cl)Si: (L = PhC(NtBu)$_2$), has been shown to exhibit remarkable coordination properties to a variety of transition metals, including for example Ti,[7] V,[12] Cr, Mo, and W,[13] Mn and Re,[14] and Fe.[3,15] Inspired by the success of this ligand in its coordination ability to a range of transition metals, we decided to explore its coordination chemistry toward Cu(I), given the lack of reports in this area.

Strikingly, the reaction of **1** with [Cu(tmeda)(CH$_3$CN)]-[OTf] (**2**)[16] affords the N-heterocyclic chlorosilylene copper complex salt [L(Cl)Si:→Cu(tmeda)][OTf] (**3**), with concomitant CH$_3$CN elimination, in high yield as a colorless solid in a straightforward fashion. Complex **3** represents only the second example of a NHSi copper complex and is the first example of a heteroleptic NHSi complex for any metal in group 11 or 12 (Scheme 1).

The existence and rather facile synthetic access to other heteroleptic NHSi species based on **1** featuring substituents other than Cl at the Si(II) atom, for example: L(OtBu)Si: (**4**) and L(NMe$_2$)Si: (**6**),[11b] prompted us to explore the analogous

reactions of NHSi species **4** and **6** with the copper(I) source **2**. In both cases the reactions proceed, in analogy to the case of complex **3**, to the NHSi Cu(I) complex [L(OtBu)Si:→Cu(tmeda)][OTf] (**5**) and [L(NMe$_2$)Si:→Cu(tmeda)][OTf] (**7**), in moderate (**5**) to good (**7**) yields also as colorless solids (Scheme 2).

Complexes **3**, **5**, and **7** were all fully characterized by multinuclear NMR spectroscopy, elemental analyses, and single-crystal X-ray diffraction analyses. All three complexes feature singlet resonance signals in the ^{1}H NMR spectra corresponding to the NtBu signal of the coordinated NHSi ligand, in CD$_2$Cl$_2$ (Table 1). This suggests either a highly symmetrical rigid structure or free rotation of the coordinated NHSi on the NMR time scale in all three cases. Moreover, the expected two sets of resonance signals (NMe$_2$ and NCH$_2$CH$_2$N) for the Cu-coordinated tmeda ligands are also clearly observed in all three complexes. Complex **5** exhibits an additional singlet resonance signal at δ 1.51 ppm in the ^{1}H NMR spectrum, corresponding to the OtBu group (9 protons), while **7** has an additional resonance signal at δ 2.57 corresponding to the NMe$_2$ protons (6 protons), in accordance with expectations. A key feature in the ^{13}C{^{1}H} NMR spectra for the complexes is the somewhat deshielded chemical shift position of the amidinate NCN carbon nucleus, which seems to be rather invariant on changing the substituent on the Si atom (Table 1).

Table 1. Summary of Some Key Chemical Shifts (in ppm, Spectra Recorded in CD$_2$Cl$_2$) Observed in Complexes 3, 5, and 7

complex	^{29}Si{^{1}H}	^{1}H of tBu	^{13}C{^{1}H} of NCN
3	32.9	1.20	174.9
5	5.4	1.23	172.9
7	18.3	1.11	170.9

Most diagnostic is the presence of a sharp singlet resonance signal observed in the ^{29}Si{^{1}H} NMR spectra of the complexes (Table 1), where dramatic differences are observed among the complexes, obviously as a result of changing the substituent attached to the Si center. In previous cases, for similar NHSi complexes of Ti and Fe,[17] a negative correlation was found to exist between the chemical shift position in the ^{29}Si{^{1}H} NMR spectrum and the Hammett constant (σ_p)[18] of the substituent on the Si center (where the substituents Cl, H, and CH$_3$ were studied). In contrast, complexes **3**, **5**, and **7**, reveal no such correlation, and so these substituents do not obey this trend. However, complex **3** clearly exhibits the most deshielded Si nucleus in this series. While it is tempting to explain this by the presence of the electronegative Cl substituent in **3**, resulting from electronic withdrawal from the Si center, in a deshielded nucleus and concomitant increase in the chemical shift position,

Scheme 1. Facile Access to the Ionic Chlorosilylene Copper(I) Complex 3

1   **2**   **3**
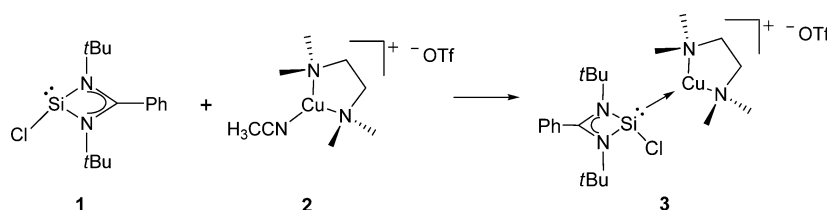
Scheme 2. Facile Access to the Heteroleptic NHSi Cu(I) Ion Pair 5 and 7, Starting from NHSi Species 4 and 6, Respectively

X = OtBu (**4**)   X = OtBu (**5**)

X = NMe₂ (**6**)   X = NMe₂ (**7**)
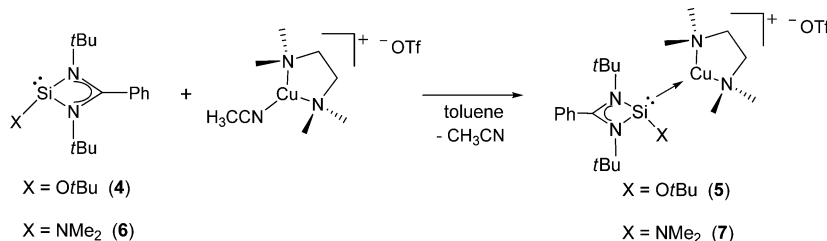
Table 2. Summary of Important Metrical Parameters in the Related Heteroleptic NHSi Complexes 3, 5, and 7[a]

complex	d(Si–Cu)	d(Si–X)	d(Cu–N3)	d(Cu–N4)	d(Cu–O)[b]	∑(Cu)
3	2.1716(12)	2.1198(15)	2.102(3)	2.136(3)	2.312	348.72
5	2.2003(6)	1.6406(14)	2.1058(16)	2.0876(17)		359.78
7	2.1982(12)	1.710(4)	2.125(4)	2.101(3)	3.277	359.84

[a]All distances are given in Å and sums of the angles in deg. [b]Contact distance to the closest O atom of the counteranion: i.e., Cu···OSO₂CF₃⁻ (OTf⁻). For complex **5** this distance is very large (>4 Å) and clearly is separated.

it is more likely that this is due to an increase in the s character of the Si–Cu bond, which is enhanced in the case of a Cl substituent on silicon. The higher s character results in a tightly bound lone pair and hence a shielding effect (vide infra).[3,20] Complexes **5** and **7** exhibit more shielded Si nuclei, and for example in complex **7**, this is an indication of electron donation capacity from the NMe₂ substituent to the Si(II) site, for which our structural studies provide additional support (vide infra), on the basis of the planarity of the N atom in the NMe₂ substituent.

Copper complexes **3**, **5**, and **7** were also characterized by single-crystal X-ray diffraction analysis,[19] where suitable crystals were obtained in all three cases from a concentrated toluene solution upon storage at −30 °C. Table 1s (Supporting Information) summarizes the relevant crystallographic parameters for these crystallographic investigations.

All three complexes feature slightly distorted tetrahedral geometries about the four-coordinate Si(II) atom, in the cation of the complex salt, as expected. The Si–Cu bond lengths are similar to each other within narrow limits: 2.1716(12)– 2.2003(6) Å (Table 2 and Figures 1−3). This metrical parameter is clearly again a reflection of the substituent on the Si center, where the shortest of the series is observed in complex **3** with a Si^II–Cl moiety. This is readily explained by the high s character in the lone pair on the silicon atom in **3**, resulting in a relatively short Si→Cu bond. A similar phenomenon was noted before in a series of iron complexes of the type [(dmpe)₂Fe←:Si(X)L] (X = Cl, H, CH₃; dmpe = 1,2-bis(dimethylphosphino)ethane) for X = Cl[3] and also for a series of aluminum and gallium complexes by Fischer, Frenking, and co-workers; the latter work also featured detailed theoretical calculations elucidating the effect of s character on bond length.[20] The high s character results in a more "compact" lone pair and concomitant bond length contraction upon coordination to a metal.

Of particular interest is the trigonal-planar geometry around the Cu(I) centers[21] in complexes **5** and **7**, evidenced by the sum of angles of Cu approximating 360°. This is notably not the case for complex **3**, which deviates from trigonal planarity at the copper center, as shown by the sum of bond angles of 348.72°. This deviation is a result of the rather short contact distance, in the solid state, between the Cu center in the cation and one of the oxygen atoms of the OTf⁻ anion at d = 2.312 Å.
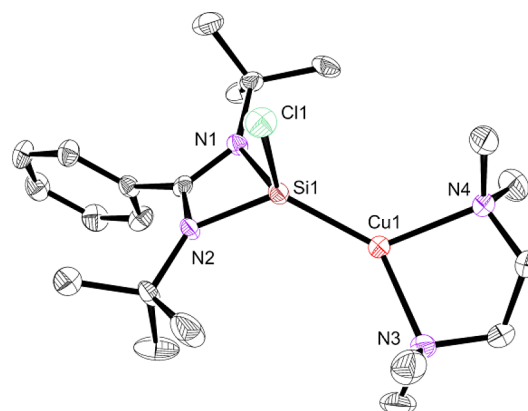

Figure 1. ORTEP representation of the cation in complex **3**. Thermal ellipsoids are set at the 50% probability level, and H atoms and the counteranion are omitted for clarity. Selected bond lengths (Å): Cl(1)−Si(1) 2.1198(15), Si(1)−N(1) 1.828(3), Si(1)−N(2) 1.839(3), Si(1)−Cu(1) 2.1716(12), Cu(1)−N(3) 2.102(3), Cu(1)− N(4) 2.136(3), Selected bond angles (deg): N(1)−Si(1)−N(2) 71.13(13), N(1)−Si(1)−Cl(1) 101.44(12), N(2)−Si(1)−Cl(1) 101.57(11), N(1)−Si(1)−Cu(1) 125.11(11), N(2)−Si(1)−Cu(1) 128.61(11), Cl(1)−Si(1)−Cu(1) 118.24(6), N(1)−Si(1)−C(7) 35.81(12), N(2)−Si(1)−C(7) 35.51(12), Cl(1)−Si(1)−C(7) 106.92(10), Cu(1)−Si(1)−C(7) 134.77(11). N(3)−Cu(1)−N(4) 85.58(12).

Hence, complex **3** in the solid state can be considered as a contact ion pair. This is particularly interesting, as it is likely a result of the increased Lewis acidity of the Cu(I) center in **3**, effected by the electronegative Cl substituent of the coordinated NHSi (Figure 4). Complex **5**, in contrast to this, exhibits a very large separation between the copper center and the O atom of the OTf⁻ anion, while in complex **7** the Cu···O distance is 3.277 Å. These results further highlight how changing the substituent at the Si center not only causes dramatic electronic changes but can also perturb the organization of the cation and anion in the solid-state structure.

Finally, in complex **7** the nitrogen atom of the NMe₂ group is trigonal planar, as the sum of angles around it approximates 360° (357.52°). The loss of pyramidalization at N suggests a substantial interaction of the lone pair on the N atom with the Si center, which also rationalizes the somewhat upfield shifted signal observed in the ²⁹Si{¹H} NMR spectrum (vide supra).
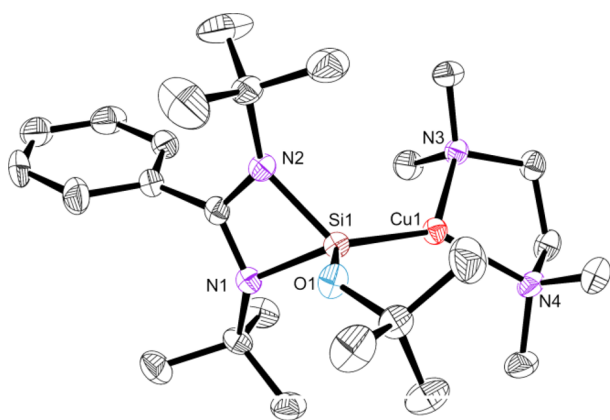
Figure 2. ORTEP representation of the cation in complex **5**. Thermal ellipsoids are set at the 50% probability level, and H atoms and the counteranion are omitted for clarity. Selected bond lengths (Å): Cu(1)−N(4) 2.0876(17), Cu(1)−N(3) 2.1058(16), Cu(1)−Si(1) 2.2003(6), N(1)−Si(1)1.8528(16),N(2)−Si(1) 1.8345(18), O(1)−Si(1) 1.6406(14). Selected bond angles (deg): N(4)−Cu(1)−N(3) 85.78(7), N(4)−Cu(1)−Si(1) 142.49(5), N(3)−Cu(1)−Si(1) 131.51(5), O(1)−Si(1)−N(2) 102.79(8), O(1)−Si(1)−N(1) 105.69(7), N(2)−Si(1)−N(1) 70.94(7), O(1)−Si(1)−Cu(1) 128.89(6), N(2)−Si(1)−Cu(1) 118.49(6), N(1)−Si(1)−Cu(1) 115.01(5).
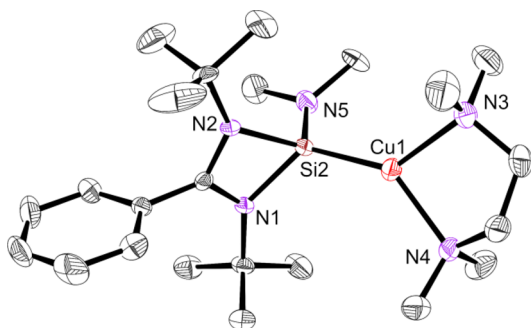

Figure 3. ORTEP representation of the cation in complex **7**. Thermal ellipsoids are set at the 50% probability level, and H atoms and the counteranion are omitted for clarity. Selected bond lengths (Å): Cu(1)−N(4) 2.101(3), Cu(1)−N(3) 2.125(4), Cu(1)−Si(2) 2.1981(12), Si(2)−N(5) 1.710(4), Si(2)−N(1) 1.854(3), Si(2)−N(2) 1.870(4). Selected bond angles (deg): N(4)−Cu(1)−N(3) 85.59(14), N(4)−Cu(1)−Si(2) 139.03(10), N(3)−Cu(1)−Si(2) 135.23(10), N(5)−Si(2)−N(1) 106.05(16), N(5)−Si(2)−N(2) 107.82(17), N(1)−Si(2)−N(2) 69.85(15), N(5)−Si(2)−Cu(1) 120.21(14), N(1)−Si(2)−Cu(1) 122.34(11), N(2)−Si(2)−Cu(1) 119.77(11).

Having isolated complexes **3**, **5**, and **7**, we became interested in exploring the reactivity of a bidentate (chelating) NHSi ligand, targeting the isolation of a chelated Cu(I) bis-NHSi complex. We employed bis-NHSi :Si(L)(μ_2-O)(L)Si: (**8**) featuring an oxo bridge between the two Si(II) centers, previously shown to be a suitable chelating ligand for Ni complexes.[22] On the basis of our observations for complexes **3**, **5**, and **7**, we envisaged that reaction of **8** with a Cu(I) source not bearing a coordinating ligand such as tmeda (for example, [Cu(CH$_3$CN)$_4$][OTf] (**9**))[23] might enable facile entry to complex salts of the type [(η^2-:Si(L)(μ_2-O)(L)Si:)Cu-(CH$_3$CN)$_n$][OTf] (n = 1, 2), bearing a η^2-coordinated bis-NHSi chelate ligand. Strikingly, the reaction of **8** with **9** affords
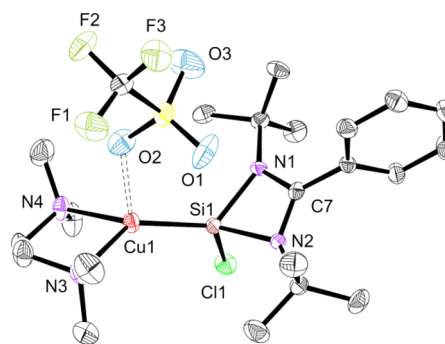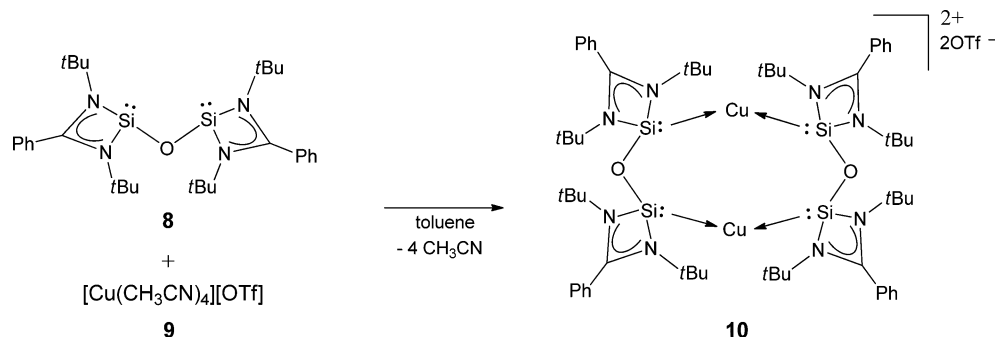

Figure 4. ORTEP representation of complex salt **3**, with both the cation and anion. Thermal ellipsoids are set at the 50% probability level, and H atoms are omitted for clarity. The contact between the O(2) atom in the triflate and the Cu(1) center is depicted by a double-dashed line. The deviation from trigonal-planar coordination at the copper center is seen clearly.

the dinuclear metallacyclooctane salt complex **10** (Scheme 3) selectively in high yield.

Crystals of complex **10** suitable for single-crystal X-ray diffraction analysis were obtained from a THF/hexane solution (2:1 v/v) upon standing at room temperature for 2 days, and the solid-state structure is depicted in Figure 5. The asymmetric unit possesses one molecule bearing a symmetry operation rendering half of it metrically invariant to the other (symmetry element C_s). The compound bears a unique dicationic metallacyclooctane ring[24] with the elements copper, silicon, and oxygen. This rather unique architecture observed in the cation of **10** is reminiscent of some copper complexes reported recently[25] and a globular 56-membered copper(I) siloxane.[26] The two OTf$^-$ counteranions are strongly associated with the copper centers, evidenced by a rather short Cu−O (O atom of SO$_3$) bond length of 2.141 Å, rendering **10** a contact ion pair, akin to what was observed in complex **3** (vide supra: d(Cu−O) = 2.312 Å).

The multinuclear NMR spectra of complex **10**, at ambient temperature in CD$_2$Cl$_2$, suggest fluxional solution behavior of the triflate counteranions in addition to a discrete charge-separated dication coexisting in solution. In the ^{1}H NMR spectrum, two signals (one broad and one sharp) correspond-ing to the tBu groups of the amidinato ligand are observed, with an integral ratio of approximately 1:0.63. The ^{29}Si{^{1}H} NMR spectrum exhibits two resonance signals, with one sharp (δ 3.26) and one broad (δ 7.73 ppm). Both of these signals are shifted downfield from the "free" bis-NHSi ligand, which features a resonance signal at δ −16.1 ppm, clearly signifying coordination to the metal. Moreover, two signal sets are also observed in the ^{13}C{^{1}H} NMR spectrum, exemplified inter alia by the NCN signals, which appear at δ 172.8 and 174.9 ppm, respectively, the latter also being somewhat broadened. Collectively, these data clearly show that two species are present in solution. The sharp signals correspond most likely to the discrete charge-separated ion pair [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$, which in itself is highly symmetrical and should yield only a single resonance signal in the ^{29}Si{^{1}H} spectrum and one set of signals in the ^{1}H and ^{13}C spectra, respectively. The broad components in the spectra are hence attributable to a dynamic coordination/decoordination of the OTf$^-$ to the dication ([Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$···(OTf)^-_n), n = 1, 2), which is in accord with the structural analysis, where a rather strong interaction was seen. These findings are akin to those for

Scheme 3. Synthesis of Complex Salt 10[a]

[a]Here **10** is represented as a charge-separated salt, although OTf⁻ does interact with the Cu centers both in the solid state and in solution.
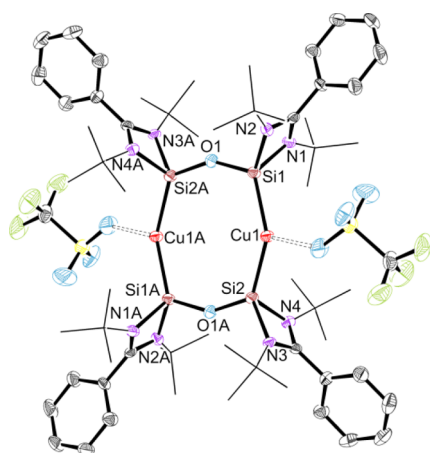

Figure 5. ORTEP representation of complex salt **10** in the solid state. Thermal ellipsoids are set at the 50% probability, and H atoms are omitted for clarity. Symmetry operation: $-x + 1$, $-y$, $-z + 1$. Selected bond lengths (Å): Cu(1)–O(2) 2.141(4), Cu(1)–Si(1) 2.2719(13), Cu(1)–Si(2) 2.2853(14), Si(1)–O(1) 1.642(3), Si(1)–N(2) 1.845(4), Si(1)–N(1) 1.859(4), Si(2)–O(1) 1.639(3), Si(2)–N(3) 1.846(4), Si(2)–N(4) 1.863(4). Selected bond angles (deg): O(2)–Cu(1)–Si(1) 115.39(12), O(2)–Cu(1)–Si(2) 99.85(12), Si(1)–Cu(1)–Si(2) 143.90(5), O(1)–Si(1)–N(2) 103.16(17), O(1)–Si(1)–N(1) 104.91(17), N(2)–Si(1)–N(1) 70.58(17), O(1)–Si(1)–Cu(1) 119.02(13), N(2)–Si(1)–Cu(1) 127.73(13), N(1)–Si(1)–Cu(1) 120.78(13).

recently reported Cu(I) complexes bearing chelating pyrazole ligands, which also feature similar dynamic behavior of a coordinating iodide anion.[27]

■ SUMMARY AND CONCLUSIONS

A series of the first heteroleptic N-heterocyclic silylene (NHSi) Cu(I) complexes for any coinage metals has been prepared. Moreover, these complexes represent only the second set of isolable examples of any NHSi Cu(I) complexes. The complexes are readily accessible upon straightforward reactions of the heteroleptic silylenes L(X)Si: (X = Cl, OtBu, NMe₂) with [Cu(tmeda)(CH₃CN)][OTf], affording complex salts of the general formula [L(X)Si:→Cu(tmeda)][OTf]. Reactions of the chelating oxo-bridged bis-NHSi species :Si(L)(μ₂-O)(L)Si: with [Cu(CH₃CN)₄][OTf] affords the unusual complex salt [Cu₂{η¹:η¹-LSi(μ₂-O)SiL}₂][OTf]₂, featuring a metallacyclic dication. The solid-state structure of the latter reveals a strong interaction of the triflate anion oxygen atom with the Cu(I) sites. These complexes reveal the potentially rich coordination

chemistry of heteroleptic NHSi ligands with coinage metals for the first time and potentially open up new vistas in group 11 metal NHSi coordination chemistry.

■ EXPERIMENTAL SECTION

General Considerations. All experiments and manipulations were carried out under a dry and oxygen-free atmosphere of nitrogen or argon using standard Schlenk techniques or in an MBraun inert-atmosphere drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and stored over activated molecular sieves (4 Å). Prior to use all solvents were degassed at least once via a freeze–pump–thaw cycle. CD₂Cl₂ was dried by refluxing with CaH₂ for 48 h, distilled, and stored over activated molecular sieves (4 Å) for use. The NMR spectra were recorded on a Bruker AV 200 or 400 spectrometer. Concentrated solutions of samples in CD₂Cl₂ were sealed off in a Young-type NMR tube for measurements. The ¹H and ¹³C{¹H} spectra were referenced to the residual solvent signals as internal standards (δ_H 5.32; δ_c 53.84 ppm for CD₂Cl₂). The ²⁹Si{¹H} NMR spectra were referenced to TMS (tetramethylsilane) as an external standard. Abbreviations: s, singlet; m, multiplet; br, broad; quint, quintet. Unambiguous signal assignments were made by employing a combination of DEPT-45 and 2D NMR H,C-COSY (HMQC) experiments. For the single-crystal X-ray structure determinations, crystals were mounted on glass capillaries in perfluorinated oil and measured under a cold N₂ flow. The data were collected on an Agilent Technologies Xcalibur S Sapphire at 150 K (Mo Kα radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. N-heterocyclic silylenes **1**, **4**, **6**[11] and the copper precursors [Cu(tmeda)(CH₃CN)][OTf][16] and [Cu(CH₃CN)₄][OTf][21] were prepared according to the reported procedures.

Synthesis of [L(Cl)Si:→Cu(tmeda)][OTf] (3). L(Cl)Si (0.147 g, 0.5 mmol) and [Cu(tmeda)(CH₃CN)][OTf] (0.185 g, 0.5 mmol) were placed in a Schlenk flask (100 mL) in the glovebox, and toluene (30 mL) was transferred to the flask via cannula with stirring at −78 °C. Then the mixture was warmed to room temperature with constant stirring. After it was stirred for 12 h at room temperature, the obtained clear colorless solution was concentrated to ca. 5 mL and filtered. The filtrate was left at 0 °C for 24 h to afford a colorless crystalline product of **3**. The product was collected by decantation of the supernatant, and the obtained solid was dried in vacuo for several hours. Yield: 0.26 g, 0.4 mmol (80%). ¹H NMR (200.1 MHz, CD₂Cl₂, 298 K, ppm): δ 1.20 (s, 18 H, tBu-H), 2.61 (br, 12 H, N(CH₃)₂), 2.65 (br, 4 H, NCH₂CH₂N), 7.12–7.25 (m, 1 H, Ph-H), 7.40–7.67 (m, 4 H, Ph-H). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K, ppm): δ 31.2 (tBu-CH₃), 48.4 (N(CH₃)₂), 55.0 (tBu-C), 58.3 (NCH₂CH₂N), 122.9 (CF₃, $^1J_{C-F}$ = 321 Hz) 128.5, 128.8, 129.31, 130.8, 129.9 (Ph-CH), 131.4 (Ph-C), 174.9 (NCN). ¹⁹F{¹H} NMR (188.3 MHz, CD₂Cl₂, 298 K, ppm): δ −78.7. ²⁹Si{¹H} NMR (79 MHz, CD₂Cl₂, 298 K, ppm): δ 32.9. Anal. Calcd for C₂₉H₃₉ClCuF₃N₄O₃SSi·¹/₃(toluene) (determined from ¹H

NMR spectroscopy): C, 44.66; H, 6.42; N, 8.56; S, 4.90. Found: C, 43.96; H, 6.49; N, 8.91; S, 4.57.

Synthesis of [L(O*t*Bu)Si:→Cu(tmeda)][OTf] (5). This compound was synthesized by a procedure similar to that for compound **3**. Yield: 0.24 g, 0.36 mmol (72%). ^{1}H NMR (200.1 MHz, CD$_2$Cl$_2$, 298 K, ppm): δ 1.23 (s, 18 H, N*t*Bu-*H*), 1.51 (s, 9 H, O*t*Bu-*H*), 2.67 (br, 12 H, N(CH$_3$)$_2$), 2.73 (br, 4 H, NCH$_2$CH$_2$N), 7.32−7.36 (m, 1 H, Ph-*H*), 7.49−7.66 (m, 4 H, Ph-*H*). ^{13}C{^{1}H} NMR (50.3 MHz, CD$_2$Cl$_2$, 298 K, ppm): δ 31.3 (N*t*Bu-*CH$_3$*), 32.2 (O*t*Bu-*CH$_3$*), 48.1 (N(CH$_3$)$_2$) 53.8 (N*t*Bu-*C*), 57.9 (NCH$_2$CH$_2$N), 74.5 (O*t*Bu-*C*), 124.3 (CF$_3$, $^1J_{C-F}$ = 321 Hz), 127.2, 128.3, 128.4, 128.7, 130.8 (Ph−*C*H), 131.0 (Ph-*C*), 172.9 (N*C*N). ^{19}F{^{1}H} NMR (188.3 MHz, CD$_2$Cl$_2$, 298 K, ppm): δ −78.8. ^{29}Si{^{1}H} NMR (79 MHz, CD$_2$Cl$_2$, 298 K, ppm): δ 5.4. Anal. Calcd for [C$_{26}$H$_{48}$CuF$_3$N$_4$O$_4$SSi]: C, 47.22; H, 7.32; N, 8.47; S, 4.85. Found: C, 47.25; H, 7.22; N, 8.33; S, 4.40.

Synthesis of [L(NMe$_2$)Si:→Cu(tmeda)][OTf] (7). This compound was synthesized by a procedure similar to that for compound **3**. Yield: 0.21 g, 0.33 mmol (66%). ^{1}H NMR (200.1 MHz, CD$_2$Cl$_2$, 298 K, ppm): δ 1.11 (s, 18 H, *t*Bu-*H*), 2.57 (br, 12 H, N(CH$_3$)$_2$), 2.62 (br, 6 H, NMe$_2$-*H*), 2.64 (br, 4 H, NCH$_2$CH$_2$N), 7.23−7.30 (m, 1 H, Ph-*H*), 7.38−7.56 (m, 4 H, Ph-*H*). ^{13}C{^{1}H} NMR (50.3 MHz, CD$_2$Cl$_2$, 298 K, ppm): δ 31.0 (*t*Bu-*CH$_3$*), 47.8 (N(CH$_3$)$_2$), 53.3 (NMe$_2$-*C*), 57.8 (NCH$_2$CH$_2$N), 124.2 (CF$_3$), 127.0, 128.4, 128.5, 129.1, 130.7 (Ph-*C*H), 131.2 (Ph-*C*), 170.9 (N*C*N). ^{19}F{^{1}H} NMR (188.3 MHz, CD$_2$Cl$_2$, 298 K, ppm): δ −78.8. ^{29}Si{^{1}H} NMR (79 MHz, CD$_2$Cl$_2$, 298 K, ppm): δ 18.3. Anal. Calcd for [C$_{24}$H$_{45}$CuF$_3$N$_5$O$_3$SSi]: C, 45.59; H, 7.17; N, 11.08; S, 5.07. Found: C, 45.79; H, 6.95; N, 10.49; S, 4.81.

Synthesis of [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$][OTf]$_2$ (10). :Si(L)(μ_2-O)(L)Si: (0.267 g, 0.5 mmol) and [Cu(CH$_3$CN)$_4$][OTf] (0.188 g, 0.5 mmol) were placed in a Schlenk flask in the glovebox (100 mL). Toluene (40 mL) was transferred to the flask via cannula with stirring at −78 °C. The mixture was warmed to room temperature gradually and stirred for another 12 h. Then the solution was filtered, and the filtrate was concentrated to ca. 5 mL and left at −20 °C for 3 days to afford a colorless crystalline product of **10**. The product was collected by decantation, and the obtained solid was dried in vacuo for several hours. Crystals of **10** suitable for X-ray single-crystal diffraction analysis were obtained by recrystallization in THF and *n*-hexane (2/1 v/v) at room temperature. Yield: 0.39 g, 0.26 mmol (52%). ^{1}H NMR (200.1 MHz, CD$_2$Cl$_2$, 298 K, ppm): δ 1.24 (s, 36 H, *t*Bu-*H*, [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$···(OTf)$_n$), 1.27 (s, 36 H, *t*Bu-*H*, [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$), 7.39−7.69 (m, 20 H, Ph-*H*). ^{13}C{^{1}H} NMR (50.3 MHz, CD$_2$Cl$_2$, 298 K, ppm): δ 31.7 (br s, *t*Bu-*CH$_3$*, [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$···(OTf)$_n$), 32.0 (s, *t*Bu-*CH$_3$*, [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$), 54.2 (N(CH$_3$)$_3$, [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$···(OTf)$_n$ + [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$), 125.6, 127.0, 128.5, 128.7, 128.8, 128.9, 129.1, 129.3, 129.5, 130.0, 131.3, 131.5 (all s, Ph-*C*, [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$···(OTf)$_n$ + [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$) 172.8 (N*C*N, [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$), 174.9 (br, N*C*N, [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$···(OTf)$_n$). The carbon signal for CF$_3$ is not observed in the ^{13}C NMR spectrum. ^{19}F{^{1}H} NMR (188.3 MHz, CD$_2$Cl$_2$, 298 K, ppm): δ −77.1. ^{29}Si{^{1}H} NMR (79 MHz, CD$_2$Cl$_2$, 298 K, ppm): δ 3.26 (s, [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$), 7.73 (br, [Cu$_2${η^1:η^1-LSi(μ_2-O)SiL}$_2$]$^{2+}$···(OTf)$_n$). Anal. Calcd for [C$_{62}$H$_{92}$Cu$_2$F$_6$N$_8$O$_8$S$_2$Si$_4$]: C, 49.81; H, 6.20; N, 7.50; S, 4.29. Found: C, 50.11; H, 6.49; N, 7.43; S, 3.97.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF files giving NMR spectra of complex **10** as well as details on X-ray crystal structure analyses and crystallographic data for **3**, **5**, **7** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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