Inorganic Chemistry

[(NHC)Cu¹–ER₃] Complexes (ER₃ = SiMe₂Ph, SiPh₃, SnMe₃): From Linear, Mononuclear Complexes to Polynuclear Complexes with Ultrashort Cu¹···Cu¹ Distances

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S Supporting Information

ABSTRACT: A series of complexes of the type $[(NHC)Cu-ER_3]$ (NHC = IDipp, IMes, ItBu, Me₂IMe, and ER₃ = SiMe₂Ph, SiPh₃, SnMe₃) and [(NHC)Cu-R'] (NHC = IDipp, Me₂IMe and R' = Ph, C \equiv CPh) was synthesized in good yields by the reaction of the corresponding [(NHC)Cu-OtBu] complex with the respective silylborane pinB-ER₃ (pin = OCMe₂CMe₂O; ER₃ = SiMe₂Ph, SiPh₃), the stannylborane $((C_2H_4)(iPrN)_2)B$ -SnMe₃, or a boronic acid ester pinB-R' (R' = Ph, C \equiv CPh). Solid structures of all complexes were systematically studied by X-ray diffraction analysis. The solid state structures of the complexes $[(NHC)Cu-ER_3]$ show a dependence of the structural motif from the steric properties of the NHC ligand. The sterically demanding NHC ligands



(IDipp, IMes, IfBu) lead to monomeric, linear complexes [(NHC)Cu–ER₃], while with the less demanding Me₂IMe ligand, polynuclear, μ -ER₃-bridged complexes with ultrashort Cu…Cu distances are observed. For the related complexes [(NHC)Cu–R'] no analogous complexes with bridging anionic ligands are realized. Instead, irrespective of the NHC ligand, linear coordinated copper complexes of different types are formed. ²⁹Si heteronuclear solution NMR spectroscopic data on [(NHC)Cu¹–SiR₃] exhibit distinctly different chemical shifts for the (in the solid state) monomeric and dimeric complexes suggesting different structure types also in solution. This agrees well with the observation of a trinuclear complex [(Me₂IMe)Cu–SnMe₃]₃ both in the solid state and in solution. Initial catalytic studies suggest that [(NHC)Cu–OtBu] complexes (NHC = ItBu, Me₂IMe) are, in addition to the established [(IDipp)Cu–OtBu] complex, efficient precatalysts for the silylation of aldehydes and α,β -unsaturated ketones with pinB–SiMe₂Ph.

■ INTRODUCTION

NHC-Cu^I complexes are widely used as (pre)catalysts in a plethora of catalytic transformations, such as conjugate addition, allylic substitution, and boration reactions of unsaturated substrates but also in C-H bond activation/ functionalization reactions and the functionalization of carbonheteroatom bonds.¹ NHC-Cu^I complexes as (pre)catalysts in silvlation reactions of imines, aldehydes, and α_{β} -unsaturated carbonyl/carboxyl compounds employing silylboranes have lately been a particularly active field of research.² Complexes of this type have also been studied in detail as models of reactive intermediates for silylation, borylation, and hydrogenation/ reduction processes.^{3,4a-c,5,6} The sterically demanding IDipp ligand has been especially successfully employed in order to stabilize reactive intermediates such as $[(IDipp)Cu-ER_3](SiR_3)$ = SiMe₂Ph (1a), SiPh₃ (1b)), $[(IDipp)Cu-H]_2$ (Figure 1), and $[(IDipp)Cu-Bpin] (IDipp = 1,3-bis(2,6-di-isopropylphenyl)-imidazol-2-ylidene, pin = pinacolato = OCMe_2CMe_2O).^{4a,5a,6a,7}$ Concerning NHC-Cu^I silyl complexes in particular besides 1a,b also the complexes [(IMe)Cu-Si(TMS)₃], [(IMe)Cu- $SiEt(TMS)_2$ (Figure 1), [(ItBu)Cu-Si(TMS)_3], and [(ItBu)-



Figure 1. Selected structurally characterized (NHC)Cu^I complexes (dipp =2,6-di-isopropylphenyl).^{4a,6a,7,8}

 $Cu-SiEt(TMS)_2$] (IMe = 1,3-bis(methyl)imidazol-2-ylidene, ItBu = 1,3-bis(tert-butyl)imidazol-2-ylidene) have been reported.⁸ However, the latter complexes have not been studied in the context of silylation reactions and bear silyl groups not commonly employed in those reactions. Nonetheless, the structures and reactivity of NHC-Cu¹ silyl complexes have not



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been systematically studied in dependence of the respective NHC and silyl ligand.

For the mentioned NHC–Cu^I complexes, generally an approximately linear two-coordinated Cu^I ion may be expected. However, aggregation with the anionic ligand as bridging ligands may also be expected. In fact, the combination of the small hydrido ligand even with a sterically demanding NHC ligand or of a sterically demanding silyl group but a little demanding NHC ligand leads to dimeric μ -hydrido/silyl bridged structures (Figure 1).^{6a,8} The resulting complexes [(IDipp)Cu–H]₂ and [(IMe)Cu–SiEt(TMS)₂]₂ exhibit, at least in the solid state, extraordinarily short Cu···Cu distances of 2.3 and 2.2854(9) Å, respectivly.^{6a,8} Although Cu···Cu interactions shorter than the sum of the van der Waals radii (2.8 Å) are well-established as *cuprophilic interactions*, this is well below the Cu···Cu distances typically found in such cases (≥ 2.35 Å).^{9,10}

While a bridging coordination mode of the anionic ligands is not surprising and is well-documented for copper(I) silyl and related copper(I) boryl, alkynyl, and arenyl complexes, to the best of our knowledge only the above mentioned complexes bear NHCs as ancillary ligands.^{3b,c,11-13} Considering this and the relevance of (NHC)Cu^I fragments for silvlation reactions, a deeper insight into the structural chemistry of (NHC)Cu^I silvl complexes, particularly with respect to the influence of the NHC ligands, appears highly desirable. While sterically little demanding NHC ligands are frequently used in computational studies for economic reasons, they have not been widely used experimentally nor has the impact of the NHC ligand on the properties of NHC-Cu silvl complexes been studied systematically.^{4a,14,15} Beyond the fundamental relevance of these questions, they are inclined to have a direct impact on understanding and, hence, the further rational development of NHC-Cu catalyzed silvlation reactions. Furthermore, considering the relevance of NHC-Cu^I complexes as catalysts in general a deeper structural understanding appears even more crucial.

In the present work systematically a number of complexes of the type $[(NHC)Cu-ER_3]$ (NHC = IDipp, IMes (1,3bis(2,4,6-trimethyl-phenyl)imidazol-2-ylidene), ItBu, Me₂IMe = 1,3,4,5-tetra(methyl)imidazol-2-ylidene; ER₃ = SiMe₂Ph, SiPh₃, SnMe₃) are studied regarding their solid state structures' dependence on the NHC and the silyl ligand. Moreover, we also included other related ligands of the 14th group with a known ability to act as bridging ligands in Cu^I complexes such as trimethylstannyl but also phenyl and alkynyl.^{11,12}

EXPERIMENTAL SECTION

General Considerations. pinB–SiMe₂Ph,^{16a,b} pinB–SiPh₃,^{16a,b} pinB–C=C–Ph,^{16a,c} ((C₂H₄)(*i*PrN)₂)B-SnMe₃,^{16d} ItBu,^{16e} Me₂IMe,^{16f} CuOt-Bu,^{16g} [(IDipp)CuOtBu],^{16h,i} [(IMes)CuOtBu],^{16h,j} and [(IDipp)Cu–SiMe₂Ph] (1a)^{4a} were prepared according to literature procedures. All other compounds were commercially available and were used as received; their purity and identity were checked by appropriate methods. All solvents were dried using MBraun solvent purification systems, deoxygenated using the freeze–pump–thaw method and stored under purified nitrogen. All manipulations were performed using standard Schlenk techniques under an atmosphere of purified nitrogen or in a nitrogen filled glovebox (MBraun). NMR spectra were recorded on Bruker DPX 200, Avance 400, or Avance 600 spectrometers. For air sensitive samples NMR tubes equipped with screw caps (WILMAD) were used, and the solvents were dried over potassium/benzophenone and degassed. Chemical shifts (δ) are given in ppm, using the (residual) resonance

signal of the solvents (C₆D₆ ¹H NMR, 7.16 ppm; ¹³C NMR, 128.06 ppm; CDCl₃ ¹H NMR, 7.26 ppm all obtained from Eurisotop with 99.5% deuteration).¹⁷ ³¹P, ²⁹Si, and ¹¹⁹Sn chemical shifts are reported relative to external 85% H₃PO₄, Me₄Si, and Me₄Sn, respectively. ¹³C, ³¹P, ²⁹Si, and ¹¹⁹Sn NMR spectra were recorded employing (²⁹Si, ¹¹⁹Sn: inverse-gated) composite pulse ¹H decoupling. If necessary, 2D NMR techniques were employed to assign the individual signals (¹H-¹H NOESY (1 s mixing time), ¹H-¹H COSY, ¹H-¹³C HSQC, and ¹H-¹³C HMBC). Simulations were conducted with the DAISY/ TOPSPIN program package (Bruker). GC/MS measurements were performed using a Shimadzu GCMS-QP2010SE instrument operating in positive EI mode (70 eV). Melting points were determined in flamesealed capillaries under nitrogen and are not corrected. Elemental analyses were performed at the Institut für Anorganische and Analytische Chemie of the Technische Universität Carolo-Wilhelmina zu Braunschweig.

 $[(IDipp)Cu-SiMe_2Ph]$ (1a).^{4a 29}Si{¹H} NMR (79.5 MHz, C₆D₆, rt): δ -14.1.

[(IDipp)Cu–SiPh₃] (**1b**). In a nitrogen filled glovebox [(IDipp)Cu–OfBu] (100 mg, 0.19 mmol, 1.0 equiv) and pinB–SiPh₃ (74 mg, 0.19 mmol, 1.0 equiv) were combined in dry toluene (3 mL). After 10 min the turbid mixture was cooled to -40 °C. After a few days, crystals had separated, and the supernatant solution was decanted. The colorless crystals (suitable for X-ray diffraction) were washed with *n*-pentane (2 × 3 mL) and dried in vacuo to give a colorless powder (88 mg, 0.12 mmol, 65%). ¹H NMR (400 MHz, C₆D₆, rt): δ 7.50–7.47 (m 6 H, SiPh₃), 7.24 (t, ³J_{HH} = 7.8 Hz, 2 H, 4-CH_{dipp}), 7.19–7.13 (m, 9 H, SiPh₃), 7.06 (d, ³J_{HH} = 7.8 Hz, 4 H, 3,5-CH_{dipp}), 6.21 (s, 2 H, CH_{NHC}), 2.54 (sept, ³J_{HH} = 6.9 Hz, 4 H, CH(CH₃)₂), 1.26 (d, ³J_{HH} = 7.0 Hz, 12 H, CH(CH₃)₂), 1.05 (d, ³J_{HH} = 6.9 Hz, 12 H, CH(CH₃)₂). ¹³C{¹H} NMR (100 MHz, C₆D₆, rt): 184.7 (C_{NHC}), 147.4 (C_{Ph}), 145.9 (2,6-C_{dipp}), 137.3 (CH_{Ph}), 134.9 (1-C_{dipp}), 130.6 (4-CH_{dipp}), 127.2 (CH_{Ph}), 126.5 (CH_{Ph}), 124.2 (3,5-CH_{dipp}), 122.1 (CH_{NHC}), 29.0 (CH(CH₃)₂), 25.3 (CH(CH₃)₂), 23.6 (CH(CH₃)₂). ²⁹Si{¹H} NMR (79.5 MHz, C₆D₆, rt): δ –0.4. Mp: 202–206 °C. Anal. Calcd for C₄₅H₅₁CuN₂Si: C, 75.96; H, 7.22; N, 3.94. Found: C, 76.04; H, 7.23; N, 3.86.

[(IDipp)Cu-SnMe₃] (1c). In a nitrogen filled glovebox [(IDipp)-Cu-OtBu] (100 mg, 0.19 mmol, 1.0 equiv) and $((C_2H_4)(iPrN)_2)B-$ SnMe₃ (60 mg, 0.19 mmol, 1.0 equiv) were combined in dry toluene (4 mL). After 1 h the solvent was evaporated, and the residue was washed with cold *n*-pentane $(3 \times 2 \text{ mL})$ to afford an off-white powder after drying in vacuo (63 mg, 0.10 mmol, 53%). Crystals suitable for Xray diffraction studies were obtained from a PhMe/n-pentane solution at -80 °C. ¹H NMR (400 MHz, C₆D₆, rt): δ 7.20 (t, ³J_{HH} = 7.7 Hz, 2 H, 4-CH_{dipp}), 7.05 (d, ³J_{HH} = 7.7 Hz, 4 H, 3,5-CH_{dipp}), 6.21 (s, 2 H, CH_{NHC}), 2.56 (sept, ³J_{HH} = 6.9 Hz, 4 H, CH(CH₃)₂), 1.38 (d, ³J_{HH} = 6.9 Hz; 12 H, CH(CH₃)₂), 1.07 (d, ${}^{3}J_{HH} = 6.9$ Hz, 12 H, CH(CH₃)₂), 0.26 (s sat., ${}^{2}J^{117/119}_{SnH}$ = 26.6, 27.6 Hz, 9 H, Sn(CH₃)₃). ${}^{13}C{^{1}H}$ NMR (75 MHz, C₆D₆, rt): 183.4 (C_{NHC}), 145.8 (2,6-C_{dipp}), 134.8 (1- C_{dipp}), 130.7 (4- CH_{dipp}), 124.2 (3,5- CH_{dipp}), 122.1 (\dot{CH}_{NHC}), 29.0 $(CH(CH_3)_2)$, 25.2 $(CH(CH_3)_2)$, 23.7 $(CH(CH_3)_2)$, -7.4 (s sat., $I_J^{117/119}_{SnC}$ = 84.6, 88.3 Hz, Sn $(CH_3)_3$). ¹¹⁹Sn $\{^{1}H\}$ NMR (149.3 Hz, C_6D_6 , rt): δ –132.9. Mp: >110 °C dark-brown colorization, melting at >150 °C. Anal. Calcd for C₃₀H₄₅CuN₂Sn: C, 58.50; H, 7.36; N, 4.55. Found: C, 58.54; H, 7.40; N, 4.58.

[(*IMes*)*Cu*–*SiMe*₂*Ph*] (2*a*). In a nitrogen filled glovebox [(IMes)-Cu–OtBu] (100 mg, 0.23 mmol, 1.0 equiv) was dissolved in dry THF (1.5 mL), and pinB–SiMe₂Ph (66 mg, 0.25 mmol, 1.1 equiv) was added. After 30 min, *n*-pentane was added to the solution until it was turbid (ca. 3 mL), and the mixture was stored at –40 °C. After 2 h a small amount of a brownish oily material had separated. The supernatant light-brown/yellow solution was decanted into a Schlenk tube, layered with *n*-pentane (5 mL), and stored at –40 °C. After 2 d colorless crystals had separated, and the supernatant solution was decanted and the residue washed with *n*-pentane (2 × 2 mL) and dried in vacuo (42 mg, 0.08 mmol, 35%). ¹H NMR (400 MHz, C₆D₆, rt): δ 7.62 (br v dd, J_{HH} = 8.1, 1,4 Hz, 2 H, Ph), 7.31–7.19 (m, 3 H, Ph), 6.72 (s, 4 H, 3,5-CH_{mes}), 5.97 (s, 2 H, CH_{NHC}), 2.11 (s, 6 H, 4-C(CH₃)_{mes}), 1.94 (s, 12 H, 2,6-C(CH₃)_{mes}), 0.51 (s, 6 H, SiMe₂). ¹³C{¹H} NMR (100 MHz, C₆D₆, rt): 183.7 (C_{NHC}), 153.8 (C_{Ph}),

139.1 (4- C_{mes}), 135.8 (1- C_{mes}), 135.2 (CH_{Ph}), 134.8 (2,6- C_{mes}), 129.6 (3,5-CH_{mes}), 127.1 (CH_{Ph}), 125.9 (CH_{Ph}), 121.1 (CH_{NHC}), 21.1 (4-C(CH₃)_{mes}), 17.9 (2,6-C(CH₃)_{mes}), 4.4 (Si(CH₃)₂). ²⁹Si{¹H} NMR (79.5 MHz, C₆D₆, rt): δ –14.4. Mp: >110 °C black colorization, melting at 130 °C. Anal. Calcd for C₂₉H₃₅CuN₂Si: C, 69.21; H, 7.01; N, 5.57. Found: C, 69.31; H, 6.82; N, 5.29.

[(IMes)Cu-SiPh₃] (2b). In a nitrogen filled glovebox [(IMes)Cu-OtBu] (60 mg, 0.14 mmol, 1.0 equiv) and pinB-SiPh₃ (53 mg, 0.14 mmol, 1.0 equiv) were combined in dry toluene (3 mL). After 1 h at room temperature the solution was layered with *n*-pentane and cooled to -20 °C. After a few days, crystals had separated, and the supernatant solution was decanted. The colorless crystals (suitable for X-ray diffraction) were washed with *n*-pentane $(2 \times 2 \text{ mL})$ and dried in vacuo to give a colorless material (48 mg, 0.08 mmol, 57%). ¹H NMR (400 MHz, C_6D_6 , rt): δ 7.63–7.58 (m, 6 H, SiPh₃), 7.21–7.10 (m, 9 H, SiPh₃), 6.71 (s, 4 H, 3,5-CH_{mes}), 5.96 (s, 2 H, CH_{NHC}), 2.11 $(s, 6 H, 4-C(CH_3)_{mes}), 1.94 (s, 12 H, 2,6-C(CH_3)_{mes}).$ ¹³C{¹H} NMR (100 MHz, C₆D₆, rt): 182.8 (C_{NHC}), 147.5 (C_{Ph}), 139.2 (4-C_{mes}), 137.4 (CH_{Ph}), 135.7 (1- C_{mes}), 134.8 (2,6- C_{mes}), 129.6 (3,5- CH_{mes}), 127.3 (CH_{Ph}), 126.6 (CH_{Ph}), 121.6 (CH_{NHC}), 21.1 (4-C(CH_{3})_{mes}), 17.9 (2,6-C(CH₃)_{mes}). Mp: 163-166 °C. Anal. Calcd for C₃₉H₃₉CuN₂Si: C, 74.66; H, 6.27; N, 4.47. Found: C, 74.26; H, 6.33; N, 4.37.

[(ItBu)Cu–SiMe₂Ph] (**3a**). In a nitrogen filled glovebox [(ItBu)Cu–OtBu] (100 mg, 0.32 mmol, 1.0 equiv) and pinB–SiMe₂Ph (83 mg, 0.32 mmol, 1.0 equiv) were combined in dry toluene (2 mL). After 2 h the solution was layered with *n*-pentane and stored at -40 °C. After a few days crystals had separated, and the supernatant solution was decanted. The colorless crystals (suitable for X-ray diffraction) were washed with *n*-pentane (2 × 1 mL) and dried in vacuo to give a colorless material (80 mg, 0.21 mmol, 66%). ¹H NMR (600 MHz, C_6D_6 , rt): δ 8.14–8.10 (m, 2 H, CH_{Ph}), 7.48–7.43 (m, 2 H, CH_{Ph}), 7.31–7.26 (m, 1 H, CH_{Ph}), 6.26 (s, 2 H, CH_{NHC}), 1.39 (s, 18 H, C(CH₃)₃), 0.96 (s, 6 H, Si(CH₃)₂). ¹³C{¹H} NMR (150 MHz, C_6D_6 , rt): 180.3 (C_{NHC}), 153.9 (C_{Ph}), 135.0 (CH_{Ph}), 127.5 (CH_{Ph}), 126.2 (CH_{Ph}), 115.6 (CH_{NHC}), 57.7 (C(CH₃)₃), 31.9 (C(CH₃)₃), 5.0 (Si(CH₃)₂. ²⁹Si{¹H} NMR (79.5 MHz, C_6D_6 , rt): δ –14.8. Mp: 108–113 °C. Anal. Calcd for $C_{19}H_{31}CuN_2Si: C$, 60.20; H, 8.24; N, 7.39. Found: C, 60.11; H, 8.35; N, 7.34.

[(*ltBu*)*Cu*–*SiPh*₃] (*3b*). In a nitrogen filled glovebox [(*ltBu*)*Cu*–OtBu] (100 mg, 0.32 mmol, 1.0 equiv) and pinB–SiPh₃ (123 mg, 0.32 mmol, 1.0 equiv) were combined in dry toluene (2 mL). After 2 h the solution was layered with *n*-pentane and stored at –40 °C. After a few days crystals had separated, and the supernatant solution was decanted. The colorless crystals (suitable for X-ray diffraction) were washed with *n*-pentane (2 × 1 mL) and dried in vacuo to give a colorless material (121 mg, 0.24 mmol, 75%). ¹H NMR (600 MHz, C_6D_6 , rt): δ 8.05–8.01 (m, 6 H, CH_{Ph}), 7.38–7.33 (m, 6 H, CH_{Ph}), 7.26–7.23 (m, 3 H, CH_{Ph}), 6.26 (s, 2 H, CH_{NHC}), 1.38 (s, 18 H, $C(CH_3)_3$). ¹³C{¹H} NMR (150 MHz, C_6D_6 , rt): 179.5 (C_{NHC}), 147.8 (C_{Ph}), 137.4 (CH_{Ph}), 127.8 (CH_{Ph}), 127.0 (CH_{Ph}), 115.7 (CH_{NHC}), 57.7 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$). ²⁹Si{¹H} NMR (79.5 MHz, C_6D_6 , rt): δ –0.7. Mp: 151–155 °C. Anal. Calcd for $C_{29}H_{35}CuN_2Si: C$, 69.21; H, 7.01; N, 5.57. Found: C, 69.11; H, 7.18; N, 6.03.

 $[(Me_2|Me)Cu-SiMe_2Ph]_2$ (4a)₂. In a nitrogen filled glovebox [(Me₂IMe)Cu-OtBu] (30 mg, 0.12 mmol, 1.0 equiv) was dissolved in dry toluene (2 mL). Upon addition of pinB-SiMe₂Ph (31 mg, 0.12 mmol, 1.0 equiv) the initially pale solution turned immediately orangered. After 2 h the solution was layered with n-pentane and stored at -40 °C. After 48 h, orange crystals (suitable for X-ray diffraction) had separated. The supernatant solution was decanted and the residue washed with *n*-pentane $(2 \times 1 \text{ mL})$ and dried in vacuo to give an orange material (32 mg, 0.05 mmol, 83%). ¹H NMR (600 MHz, C₆D₆, rt): δ 7.85 (dd, 2 H, $J_{\rm HH}$ = 8.1, 1.3 Hz, $CH_{\rm Ph}$), 7.30–7.26 (m, 2 H, CH_{Ph}), 7.17–7.15 (m, 1 H, CH_{Ph} (overlapping with solvent signal)), 3.04 (s, 6 H, N(CH₃)_{NHC}), 1.32 (s, 6 H, C(CH₃)_{NHC}), 0.89 (s, 6 H, $Si(CH_3)_2$). ¹³C{¹H} NMR (150 MHz, C₆D₆, rt): 184.9 (C_{NHC}), 156.3 $(C_{\rm Ph})$, 134.3 $(CH_{\rm Ph})$, 127.1 $(CH_{\rm Ph})$, 125.1 $(CH_{\rm Ph})$, 123.2 $(C(CH_3)_{NHC})$, 34.4 $(N(CH_3)_{NHC})$, 8.3 $(C(CH_3)_{NHC})$, 7.1 $(Si(CH_3)_2)$. ²⁹Si{¹H} NMR (79.5 MHz, C_6D_6 , rt): δ –23.0. Mp: 127–131 °C.

UV-vis (PhMe): $\lambda_{max} = \sim 300$, 388 nm. Anal. Calcd for $(C_{15}H_{23}CuN_2Si)_2$: C, 55.78; H, 7.18; N, 8.67. Found: C, 55.89; H, 7.15; N, 8.34.

[(Me₂IMe)Cu–SiPh₃J₂ (4b)₂. In a nitrogen filled glovebox [(Me₂IMe)Cu–OtBu] (50 mg, 0.19 mmol, 1.0 equiv) and pinB–SiPh₃ (74 mg, 0.19 mmol, 1.0 equiv) were combined in dry toluene (2 mL). After 2 h the orange solution was layered with *n*-pentane and stored at -40 °C. After a few days, dark orange crystals (suitable for X-ray diffraction) had separated. The supernatant solution was decanted and the residue washed with *n*-pentane (2 × 1 mL) and dried in vacuo to give a deep orange material (78 mg, 0.09 mmol, 92%). ¹H NMR (600 MHz, C₆D₆, rt): δ 7.97 (br d, 6 H, ³J_{HH} = 7.2 Hz, CH_{ph}), 7.21 (br t, ³J_{HH} = 7.3 Hz, 6 H, CH_{ph}), 7.13 (tt, 3 H, ³J_{HH} = 7.3, 1.4 Hz, CH_{ph}), 2.73 (s, 6 H, N(CH₃)_{NHC}), 1.11 (s, 6 H, C(CH₃)_{NHC}). ¹³C{¹H} NMR (150 MHz, C₆D₆, rt): 183.2 (C_{NHC}), 149.0 (C_{Ph}), 13713 (CH_{ph}), 127.3 (CH_{ph}), 126.4 (CH_{ph}), 123.4 (C(CH₃)_{NHC}), 34.1 (N-(CH₃)_{NHC}), 8.1 (C(CH₃)_{NHC}). ²⁹Si{¹H} NMR (79.5 MHz, C₆D₆, rt): δ -10.1. Mp: 144–147 °C. Anal. Calcd for (C₂₅H₂₇CuN₂Si)₂: C, 67.15; H, 6.09; N, 6.27. Found: C, 66.62; H, 6.01; N, 6.10.

 $[(Me_2|Me)Cu-SnMe_3]_3$ (4c)₃. In a nitrogen filled glovebox [(Me₂IMe)Cu-OtBu] (50 mg, 0.19 mmol, 1.0 equiv) was dissolved in dry toluene (2 mL). Upon addition of ((C₂H₄)(*i*PrN)2)B-SnMe₃ (77 mg, 0.24 mmol, 1.3 equiv) the initially pale solution turned immediately dark. After 15 min at room temperature the solution was layered with *n*-pentane and stored at -40 °C. After 20 h bronze crystals had separated, and the supernatant solution was decanted; the crystals (suitable for X-ray diffraction) were washed with *n*-pentane (2 \times 1 mL) and dried in vacuo to give a bronze material (56 mg, 0.05 mmol, 84%). ¹H NMR (400 MHz, C₆D₆, rt): δ 3.55 (s, 6 H, N(CH₃)_{NHC}), 1.41 (s, 6 H, C(CH₃)_{NHC}), 0.58 (s sat., ${}^{2}J^{117/119}_{SnH} = 24.6$ Hz, 9 H, $Sn(CH_3)_3$). ¹³C{¹H} NMR (100 MHz, C₆D₆, rt): 185.6 (s sat., $C_{\rm NHC}$, ${}^{2}J_{\rm C}^{117/119}{\rm Sn}$ = 35 Hz), 123.6 (C(CH₃)_{NHC}), 35.8 (N- $(CH_3)_{NHC}$, 8.6 $(C(CH_3)_{NHC})$, -0.9 (s sat., $J_C^{117/119}_{Sn}$ = 67, 28 Hz, $Sn(CH_3)_3$). ¹¹⁹ $Sn{^1H}$ NMR (149.3 MHz, C_6D_6 , rt): δ -127.1 (s sat., $J_{119}_{Sn} = 2383 \text{ Hz}$.¹⁷ Mp: 86–93 °C (decomposition). UV-vis (PhMe): $\lambda_{max} = \sim 300$, 346, 414 (br shoulder) nm. Anal. Calcd for (C10H21CuN2Sn)3: C, 34.17; H, 6.02; N, 7.97. Found: C, 34.28; H, 6.01; N, 8.18.

[(Me₂IMe)Cu-Ph] (4d). In a nitrogen filled glovebox to a solution of [(Me₂IMe)Cu-OtBu] (50 mg, 0.19 mmol, 1.0 equiv) in dry toluene (1.5 mL) was added a solution of pinB-Ph (39 mg, 0.19 mmol, 1.0 equiv) in dry toluene (1.0 mL). After 3.5 h at room temperature the mixture was layered with *n*-pentane and stored at -40 °C. After a few days, colorless crystals had separated, and the supernatant solution was decanted; the crystals (suitable for X-ray diffraction) were washed with cold *n*-pentane $(2 \times 2 \text{ mL})$ and dried in vacuo to give a colorless material (40 mg, 0.15 mmol, 79%). ¹H NMR (600 MHz, C₆D₆, rt): δ 7.85 (v dd, 2 H, J_{HH} = 7.6, 1.4 Hz, CH_{Ph}), 7.62 (v t, 2 H, J_{HH} = 7.4 Hz, CH_{Ph}), 7.45 (tt, 1 H, J_{HH} = 7.3, 1.5 Hz, CH_{Ph}), 3.00 (br s, 6 H, $\Delta w_{1/2}$ = 14.7 Hz, N(CH₃)_{NHC}), 1.20 (s, 6 H, C(CH₃)_{NHC}). $^{13}C{^{1}H}$ NMR (150 MHz, C₆D₆, rt): 179.4 (C_{NHC}), 167.2 (C_{Ph}), 141.3 (CH_{Ph}), 126.9 (CH_{Ph}) , 124.8 (CH_{Ph}) , 123.8 $(C(CH_3)_{NHC})$, 34.7 $(N(CH_3)_{NHC})$, 8.1 (C(CH₃)_{NHC}). Mp: 95-100 °C. Anal. Calcd for C₁₃H₁₇CuN₂: C, 58.96; H, 6.47; N, 10.58. Found: C, 58.44; H, 6.66; N, 10.25.

X-ray Structure Determinations. The crystals were transferred into inert perfluoroether oil inside a nitrogen filled glovebox and, outside of the glovebox, rapidly mounted on top of a human hair and placed in the cold nitrogen gas stream on the diffractometer.^{21a} The data were either collected on an Oxford Diffraction Xcalibur E instrument using monochromated Mo K α radiation or on an Oxford Diffraction Nova A instrument, using mirror-focused Cu K α radiation. The reflections were indexed and integrated, and an empirical absorption correction was applied as implemented in the CrysAlisPro software.^{21b} The structures were solved employing the SHELXS, SHELXT, or SIR-92 programs and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on all F^2 using SHELXL software.^{21c-e} Generally, hydrogen atoms were refined employing a riding model; methyl groups were treated as rigid bodies and were allowed to rotate about the E–CH₃ bond. During refinement and

Table 1. Synthesis of [(NHC)Cu-R] by B-R Bond Cleavage

	$ \begin{array}{c} R^2 & \stackrel{R}{\searrow}^1 \\ R^2 & \stackrel{N}{\searrow} Cu - OtBu \\ R^2 & \stackrel{R}{R^1} \end{array} \xrightarrow{(B]-OtBu} \begin{array}{c} R^2 & \stackrel{R}{\searrow}^1 \\ R^2 & \stackrel{N}{\boxtimes} Cu - R \\ R^2 & \stackrel{N}{R^1} \end{array} $							
	[(NHC)Cu-OtBu]	[B]	R	$[(NHC)Cu-R]_n$ (yield)				
	$R^1 = dipp^a, R^2 = H$	pinB	SiPh ₃	1b (65%)				
	$R^1 = dipp^a, R^2 = H$	$((C_2H_4)(iPrN)_2)B$	SnMe ₃	1c (53%)				
	$R^1 = dipp^a, R^2 = H$	pinB	Ph	1d (86%) ^{6b,22}				
	$R^1 = dipp^a, R^2 = H$	pinB	C≡C-Ph	1e (47%) ^{19,23a,b}				
	$R^1 = mes^a$, $R^2 = H$	pinB	SiMe ₂ Ph	2a (35%)				
	$R^1 = mes^a$, $R^2 = H$	pinB	SiPh ₃	2b (57%)				
	$R^1 = tBu, R^2 = H$	pinB	SiMe ₂ Ph	3a (66%)				
	$\mathbf{R}^1 = t\mathbf{B}\mathbf{u}, \ \mathbf{R}^2 = \mathbf{H}$	pinB	SiPh ₃	3b (75%)				
	$R^1 = Me, R^2 = Me$	pinB	SiMe ₂ Ph	$(4a)_2 (83\%)$				
	$R^1 = Me, R^2 = Me$	pinB	SiPh ₃	$(4b)_2 (92\%)$				
	$R^1 = Me, R^2 = Me$	$((C_2H_4)(iPrN)_2)B$	SnMe ₃	$(4c)_3 (84\%)$				
	$R^1 = Me, R^2 = Me$	pinB	Ph	4d (79%)				
	$R^1 = Me, R^2 = Me$	pinB	C≡C-Ph	$4e^{b}$ (63%)				
^{<i>a</i>} dipp:	2,6-di-isopropyl-phenyl.	mes: 2,4,6-trimethyl-phenyl. ^b The	e actual composition is $\{[\langle (Me_2IMe_2IMe_3)] \}$	$[e_{2},Cu_{2},(PhC\equiv C),Cu_{2}][(PhC\equiv C),Cu_{2}]$				

 $[\langle (Me_2IMe)_2Cu \rangle \langle (PhC \equiv C)_2Cu \rangle] \}.$

Table 2. Selected Structural Parameters of 1a,b,c, 2a,b, and 3a,b

	$C_{\rm NHC}$ – $Cu/Å$	Cu-E [E]/Å	C _{NHC} -Cu-E	
1a ^{4a}	1.9333(1)	2.2783(4) [Si]	170.53(4)°	H–Ct: 3.15 Å ^a
1b ¹⁸	$1.929(2)/1.933(2)^{b}$	2.2671(5)/2.2738(6) ^b [Si]	171.43(5)°/171.35(5)° ^b	H–Ct: 3.13/3.23 Å ^{<i>a,b</i>}
1c ¹⁸	1.925 ^c	2.474^{c} [Sn]	163.4°°	H–Ct: 3.8° Å ^a
2a	1.943(1)	2.2914(4) [Si]	173.57(4)°	H–Ct: 4.12 Å ^a
2b	1.925(2)	2.2777(6) [Si]	171.18(6)°	H–Ct: 3.48 Å ^a
3a	1.941(6)	2.267(2) [Si]	$177.8(2)^{\circ}$	H–Ct: 4.83 Å ^{<i>a</i>} ; $\tau = 79.5(5)^{\circ d}$
$3a(PhMe)_{1/2}$	$1.938(5)/1.940(5)^{b}$	$2.260(2)/2.264(2)^{b}$ [Si]	$175.2(2)^{\circ}/174.2(2)^{\circ b}$	H–Ct: 4.63, 4.02, 4.14 Å ^{<i>a,b</i>} ; $\tau = 71.0(5)/6.3(5)^{\circ b,d}$
3b	1.935(1)	2.2645(4) [Si]	174.65(4)°	H–Ct: 3.96 Å ^{<i>a</i>}

^{*a*}H–Ct: shortest distance for a hydrogen atom on the R group to the centroid of an adjacent aromatic ring (see figures).¹⁸ ^{*b*}The values refer to different independent molecules in the asymmetric unit. ^{*c*}Averaged values (see text).¹⁸ ^{*d}</sup>\tau: N–C_{NHC}–Si–C_{ipso} torsion angle</sup>*

analysis of the crystallographic data, the programs WinGX, PLATON, Mercury, and Diamond were used. $^{\rm 21f-i}$

RESULTS AND DISCUSSION

Synthesis. As versatile access to [(NHC)Cu-R] complexes, the reaction of the [(NHC)Cu-OtBu] complex with a suitable boronic acid ester derivative pinB-R (R = SiMe₂Ph, SiPh₃, Ph, C=C-Ph) or $((C_2H_4)(iPrN)_2)B$ -SnMe₃, respectively, has been employed (Table 1). The resulting complexes **1a**-4e were obtained in good to excellent yields, usually typically directly in crystalline form suitable for crystal structure determination.

While this σ -bond metathesis reaction pathway is established for a range of boronic acid derivatives, its scope is here significantly extended on the side of the NHC ligand as well as with respect to the R substituent.^{3a,b,4a,5a,24a,25} Moreover, using an adopted procedure the phosphine complex [(Me₃P)₃Cu– SiMe₂Ph] was obtained from PMe₃, CuO*t*Bu, and pinB– SiMe₂Ph extending this reaction to non-NHC copper alkoxido complexes.¹⁸

The complexes obtained (1a-4e) are stable in pure form under an inert atmosphere in the dark at -40 °C as solids for several months and in solution at least for several days. In general, the monomeric complexes with sterically more hindered NHC ligands (vide infra) have been found to be quite stable while the dimeric complexes appear to be more prone to decomposition. Nonetheless, NMR spectroscopic characterization in solution was possible for all compounds. However, it was in our hands restricted to studies at ambient temperature, as the stability of the (multinuclear) complexes did not allow (heteronuclear) NMR studies at elevated temperatures.

Structural Study. X-ray diffraction structure determinations were successfully performed for all synthesized complexes (Tables 2 and 3).¹⁸ The solid state molecular structures of the complexes 1–3a (R = SiMe₂Ph), 1–3b (R = SiPh₃), and 1c (R = SnMe₃) and the sterically demanding NHCs IDipp (1a–c), IMes (1a,b), and ItBu (1a,b) show the anticipated monomeric linear structures (Table 2).^{4a} Similar structures have also been reported for related complexes with, e.g., R = C₆H₄OMe, C₆H₂Me₃, boryl, SnPh₃, Si(TMS)₃, and SiEt(TMS)₂ (vide supra).^{3,5a,7,8,23c,24}

While a comparative discussion of the individual molecular structures of $R = SiMe_2Ph (1-3a)$, $SiPh_3 (1-3b)$, and $SnMe_3 (1c)$ appears mandatory, first selected features of the crystal structures are briefly described.

Complex 1b crystallizes in space group $P\overline{1}$ with two molecules in the asymmetric unit (Figure 2).¹⁸ The two independent molecules adopt virtually identical conformations differing only slightly in the geometrical parameters (Table 2).¹⁸ In contrast, 2a and 2b crystallize with one molecule in the asymmetric unit in a monoclinic (C2/c) and an orthorhombic

Table 3. Selected Structural Parameters of $(4a)_2$ and $(4b)_2$

					$(4b)_2$ at 100 K ^a		
			$(4a)_2$	(4b) ₂ at 127 K	molecule 1	molecule 2	
Cu-C _{NHC} (Å)							
	Cu1	C1	1.925(2)	1.939(2)	1.951(5)	1.936(4)	
	Cu2	C8		1.937(2)	1.937(5)	1.941(4)	
Cu–Si (Å)							
	Cu1	Si1	2.4396(7)	2.5041(8)	2.618(2)	2.554(2)	
		Si1'/2	2.5550(7)	2.3978(8)	2.422(2)	2.398(2)	
	Cu2	Si1		2.4897(7)	2.385(2)	2.413(2)	
		Si2		2.5602(8)	2.523(2)	2.599(2)	
Cu…Cu (Å)							
			2.2503(6)	2.2691(4)	2.2879(6)	2.2729(6)	
C _{NHC} -Cu-E (deg)							
C1	Cu1	Si1	126.51(7)	121.13(8)	125.6(2)	117.0(1)	
		Si1'/2	106.99(7)	119.58(8)	124.8(2)	120.8(1)	
C8	Cu2	Si1		119.79(8)	122.9(2)	118.1(1)	
		Si2		126.42(8)	123.0(2)	122.1(1)	
Si-Cu-Si (deg)							
Si1	Cu1	Si1'/2	126.50(2)	119.28(2)	109.56(5)	121.93(5)	
	Cu2	Si2		113.77(2)	114.6(5)	119.48(5)	
Cu-Si-Cu (deg)							
Cu1	Si1	Cu2	53.50(2)°	54.05(2)	54.18(3)	54.38(3)	
	Si2	Cu2		54.35(2)	55.07(3)	53.93(3)	
ϕ^{b}			0.0°	34.35(3)	42.55(4)	25.19(6)	
[wo independent molecul	es in the asym	metric unit. ${}^{b}\phi$	interplanar angle in	cluded by the two [E,Cu,	Cu] planes.		

Figure 2. Top: View of the asymmetric unit of **1b** approximately parallel to the $[-1 \ 0 \ -1]$ vector. Bottom left: Molecular structure of **2a**. Bottom right: Molecular structure of **2b**. Only selected hydrogen atoms are shown.²⁶

(*Pnma*) space group, respectively (Figure 2). While 2a exhibits no molecular symmetry, the triphenylsilyl complex 2b resides on a mirror plane perpendicular to the NHC heterocycle and one of the of the phenyl moieties (through the atoms C1, Cu1, Si1, C18, and C21).

For the SiMe₂Ph complex 3a, two pseudopolymorphic structures were obtained, one containing a single molecule of 3a in the asymmetric unit in an orthorhombic space group type $P2_12_12_1$ and a second one with an asymmetric unit comprising

two molecules of **3a** and one molecule of PhMe in a monoclinic space group $P2_1$ (Figure 3 and Table 2).¹⁸ In the latter, two distinct conformations of **3a** differing in the relative orientation of the silyl group to the NHC ligand are realized [illustrated by



Figure 3. Top: View of the asymmetric unit of $3a(PhMe)_{1/2}$ parallel to the *b* axis (inset shows overlay of the two independent molecules). Bottom left: Molecular structure of **3a**. Bottom right: Molecular structure of **3b**. Only selected hydrogen atoms are shown.²⁶

the N–C_{NHC}–Si–C_{ipso} torsion angles, Figure 3 (inset), Table 2].¹⁸

The triphenylsilyl complex of the *tert*-butyl substituted NHC **3b** crystallizes in a monoclinic space group $(P2_1/c)$ with one molecule in the asymmetric unit (Figure 3 and Table 2).¹⁸

The individual molecular structures of 1a,b, 2a,b, and 3a,b may be best characterized by their respective $C_{\rm NHC}$ -Cu and Cu-E distances and $C_{\rm NHC}$ -Cu-E angles (Table 2, Figures 2 and 3). The $C_{\rm NHC}$ -Cu distances are in a small range around 1.93 Å for the silyl complexes (1a,b, 2a,b, 3a,b). For related phenyl and alkynyl complexes (1d,e), shorter $C_{\rm NHC}$ -Cu distances of around 1.90 Å are found, resembling the reduced donor properties of the latter ligands (reduced trans influence).¹⁸ These data are complemented by Cu-Si distances around 2.27 Å, lying in the range reported for various copper silyl complexes.¹³

A linear angle C_{NHC} -Cu-E may be expected for these monomeric (NHC)Cu-SiR₃ complexes; however, especially for the IDipp and IMes ligands (1a,b and 2a,b) bearing aromatic N-substituents, these angles deviate significantly from 180° (Table 2). A tentative rationalization on a molecular level may be the subtle interplay between repulsion due to steric bulk and attractive dispersive π -HC interactions between the aromatic Nsubstituent and CH moieties within the anionic ligand. The latter may be illustrated by the shortest H-Ct distances (with Ct being the centroid of the aromatic system) found for the individual complexes (Figure 2 and Table 2). It should be emphasized that positions of the H atoms were obtained by Xray diffraction employing suitable riding models and are not freely refined. While these distances must be considered with due caution, the riding models (including refinement of the orientation of methyl groups) should give reasonably reliable data for this tentative analysis.¹⁸ Moreover, the occurrence of these short distances corresponds generally reasonably well with the orientation of the bend C_{NHC} -Cu-E unit.^{24d,27} Nonetheless, into this simplified picture packing effects, and hence intermolecular interactions, certainly have to be included.

The reported complexes $[(ItBu)Cu-Si(TMS)_3]$ and $[(ItBu)Cu-SiEt(TMS)_2]$, analogous to **3a,b**, but featuring bulkier silyl groups, exhibit geometrical parameters in the same range: Cu-C_{NHC} 1.937(2) Å, Cu-Si 2.2636(5) Å, C_{NHC}-Cu-Si 178.60(5)°, and Cu-C_{NHC} 1.948(2) Å, Cu-Si 2.2754(5) Å, C_{NHC}-Cu-Si 178.29(5)°, respectively.⁸ However, the C_{NHC}-Cu-Si angles are significantly closer to linearity, tentatively an effect of the increased steric restraints due to the demanding silyl groups and the lack of π -HC interactions (vide supra).

The heavier homologues of the discussed silyl complexes, the stannyl complexes [(IDipp)Cu-SnMe₃] (1c) and [(IDipp)-Cu-SnPh₃], also fit into this picture. However, for 1c the crystallographic data have to be considered with some care as the crystal structure determination is complicated by the occurrence of a superstructure (three independent molecules per asymmetric unit) associated with twinning and possibly an additional modulation (Table 2 and Figure 4).¹⁸ As a consequence, only the mean geometrical data of the three independent molecules are discussed. Nonetheless, in comparison with the reported data for [(IDipp)Cu-SnPh₃] (C_{NHC}-Cu 1.914(2) Å, Cu–Sn 2.469(5) Å, C_{NHC} –Cu–Sn 169.6(8)°), similar Cu–Sn and C_{NHC}–Cu distances are observed, while the C_{NHC}-Cu distance is significantly shorter than that in the silyl complexes 1a,b, 2a,b, and 3a,b.7 The coordination geometry at the Cu atom shows for 1c with 17° the largest deviation from linearity for all discussed [(NHC)Cu-E] complexes. While this



Figure 4. View of the asymmetric unit of **1c** approximately along the [101] vector. Hydrogen atoms are omitted for clarity.^{18,26}

might be surprising considering the comparably small $SnMe_3$ ligand, it fits into the picture outlined above with the relevance of not only repulsive but also attractive interactions for the conformation of these complexes.¹⁸

In contrast to the above-discussed linear, mononuclear complexes, the silyl/stannyl complexes of the sterically little demanding Me₂IMe adopt more peculiar polynuclear structures. The silyl complexes $(4a)_2$ and $(4b)_2$ crystallize as dimers, similar to the reported complexes $[(IDipp)Cu-H]_2$ and $[(IMe)Cu-SiEt(TMS)_2]_2$, while the stannyl complex $(4c)_3$ adopts a trimeric structure.^{6a,8} In the dimeric silyl complexes a three-coordinated Cu¹ ion is coordinated by one NHC ligand and two bridging μ -silyl ligands. The structures of the symmetrical Cu₂Si₂ core may be described generally as butterfly type with a remarkably short Cu…Cu distance. However, a closer look on the crystal structures 5-8).¹⁸



Figure 5. Molecular structure of complex $(4a)_2$. Hydrogen atoms are omitted for clarity.²⁶

Complex $(4a)_2$ crystallizes in a triclinic space group $P\overline{1}$ with half of a dimeric molecule $(4a)_2$ in the asymmetric unit; hence,



Figure 6. Molecular structure of $(4b)_2$ at 127 K. Hydrogen atoms are omitted for clarity.²⁶



Figure 7. View of the asymmetric unit of $(4b)_2$ at 100 K [inset shows packing pattern of $(4b)_2$ at 100 K (only Si (light blue) and Cu (orange and purple) atoms shown; in red, approximate unit cell at 127 K for comparison)]. Hydrogen atoms are omitted for clarity.²⁶



Figure 8. Molecular structure of complex $(4c)_3$ and detail of the $[Cu_3Sn_3(C_{NHC})_3]$ subunit with selected distances. Hydrogen atoms are omitted for clarity.²⁶

it is located on a center of inversion (Figure 5).¹⁸ This crystallographic site symmetry requires a planar Cu₂Si₂ core (interplanar angle ϕ , Table 3) with a planar coordination environment at the two equivalent copper ions (Σ (Cu) 360°). However, the two Cu–Si interactions are not equivalent as shown by the different C_{NHC}–Cu–Si angles and Cu–Si distances.

Generally, complex $(4b)_2$ exhibits the same structural motif as $(4a)_2$, a Cu₂Si₂ core with planar coordinated Cu atoms, but it is lacking any crystallographic site symmetry. This allows for a nonplanar Cu₂Si₂ core with interplanar angles ϕ of 25–43° and also a variation in the C_{NHC}-Cu-Si and Si-Cu-Si angles (Table 3, Figures 6 and 7). Moreover, $(4b)_2$ shows complex structural changes depending on the temperature. At 127 K, a higher symmetric structure in an orthorhombic space group with one independent molecule in the asymmetric unit is realized while at 100 K a lower symmetric monoclinic cell with two independent molecules in the asymmetric unit is found (Table 3 and Figure 7).¹⁸ However, this transition is associated with twinning via a C-centered orthorhombic unit cell.¹⁸ Upon this transition, the geometric parameters of the molecular structure of $(4b)_2$ change appreciably (Table 3). Most significantly, the interplanar angle ϕ splits from 34° at 127 K into 43° and 25° at 100 K for the now two independent molecules in the asymmetric unit. The Cu-Cu distances for the two independent molecules are very short throughout and may, if at all, increase marginally upon cooling (Table 3).

It is illustrative to compare $(4a)_2$ and $(4b)_2$ with the closely related complex [(IMe)Cu-SiEt(TMS)₂]₂ (Cu-C_{NHC} 1.949(4) Å, Cu-Si 2.4232(9)/2.5922(8) Å, Cu-Cu 2.2854(9) Å, C_{NHC}-Cu-Si 115.2(1)/123.8(1)°, Si-Cu-Si 120.93(3)°, Cu-Si-Cu 54.09(2)°, ϕ 24.76°)⁸ as well as with the monomeric silyl complexes 1a,b and 3a,b (Table 2). All these structures reveal a quite narrow range of Cu-C_{NHC} distances of 1.93-1.95 Å despite the change in the coordination number at the Cu ion. However, the Cu-Si distances increase, as expected, significantly upon dimerization and, hence, upon increasing the coordination number at the silicon atom. For all dimeric complexes $((4a)_2, (4b)_2)$ $[(IMe)Cu-SiEt(TMS)_2]_2)$ a slightly unsymmetrical coordination of the μ -silyl groups is observed as evidenced by significantly different Cu-Si distances for each silyl group and differences in the C_{NHC}-Cu-Si angles. The coordination environment at each copper atom is within the significance planar as shown by sums of angles of $360 \pm 0.5^{\circ}$. Nonetheless, the individual angles at each Cu atom vary significantly, as does, connected with that, the interplanar angle ϕ .

However, the most remarkable feature of these dimers is the extraordinarily short Cu…Cu distance. In fact, $(4a)_2$ and $(4b)_2$ are, together with $[(IDipp)Cu-H]_2$ and $[(IMe)Cu-SiEt(TMS)_2]_2$ (vide supra), to the best of our knowledge, the only structurally well-characterized Cu complexes featuring a Cu…Cu distance below 2.3 Å.¹⁰ While the distance shows some variation within $(4a)_2$, $(4b)_2$, and $[(IMe)Cu-SiEt(TMS)_2]_2$, it stays always below 2.3 Å and is far shorter than the interatomic distance in elemental copper (2.56 Å) or the double van der Waals radius (2.8 Å).²⁸ Complexes featuring the motif of two Cu ions bridged by a silyl group are well-established, but typically two Cu ions are bridged by only one silyl ligand, resulting in Cu…Cu distances in the range 2.36–2.45 Å.¹³ Computational studies on the bonding situation in these and also related complexes, such as (CuH)₂, suggest the presence of a three-center-two-electron bond including the two copper

and the silicon atoms, potentially, but not necessarily, accompanied by closed-shell $d^{10}{-}d^{10}$ interaction. 9,13c

The stannyl homologue $(4c)_3$ realizes in the solid state an unsymmetrical trimeric structure exhibiting similar structural motifs as discussed above for $(4a)_2$ and $(4b)_2$: Cu-Cu units bridged by a ER₃ moiety. However, the three Cu atoms in $(4c)_{3}$, occupying the corners of a triangle, are inequivalent. The structure may be formally described as a dimer (as found for $(4a)_2$ and $(4b)_2$) embodied by the atoms Cu1, Cu3, Sn1, Sn2, C15, and C1, and additional SnMe₃ (Sn3) and (NHC)Cu^I (Cu2, C8) moieties bridging the Cu1…Cu3 unit (Figure 8). Alternatively, $(4c)_3$ may be described as two μ^3 -stannyl ligands (Sn1, Sn2) located above the faces of a $(Cu)_3$ -triangle and one μ^2 -stannyl ligand (Sn3) additionally located above one edge of the $(Cu)_3$ triangle. The coordination environment of the Cu atoms is then completed by three NHC ligands each coordinating one Cu atom. The copper atoms are inequivalent with respect to their coordination environments exhibiting coordination numbers of five (Cu2) and six (Cu1, Cu3), respectively. Although the Cu-Cu distances within the (Cu)₃ triangle vary slightly, they are very short (2.3–2.5 Å) but longer than those in the silvl complexes $(4a)_2$ and $(4b)_2$. The C_{NHC}-Cu distances are slightly longer than those in the related mononuclear complexes [(IDipp)Cu-SnPh₃] ((C_{NHC}-Cu 1.914(2) Å, Cu-Sn 2.469(5) Å, $C_{\rm NHC}$ -Cu-Sn 169.6(8)°)) or in 1c (vide supra).⁷ The Cu-Sn distances are significantly increased, and quite varying, as expected for a change to a (slightly unsymmetrical) μ^2/μ^3 coordination mode.

The observation of bridging coordination modes of the ER₃ ligands in $[(NHC)Cu-ER_3]$ complexes once the formation of aggregated species is not sterically prohibited by the sterics of the NHC ligand provoked the question regarding whether complexes with other anionic ligands exhibit similar structures. We synthesized the aryl complexes **1d** and **4d** as well as the alkynyl complexes **1e** and **4e**. For both ligand, the ability to form bridged Cu^I complexes (Table 1) is well-documented.^{9e,11,12}

However, the phenyl complexes [(IDipp)Cu–Ph] 1d and [(Me₂IMe)Cu–Ph] 4d both exhibit similar mononuclear linear structures despite the significantly different steric demand of the NHC ligands.¹⁸ The characteristic distances $C_{\rm NHC}$ –Cu and Cu–C_{Ph} are similar, while a more linear $C_{\rm NHC}$ –Cu–Ph angle is observed for the sterically less encumbered complex 4d ($C_{\rm NHC}$ –Cu: 1.906(3) Å/1.892(3) Å (1d), 1.902(3) Å (4d); Cu–C_{Ph}: 1.898(3) Å/1.907(3) Å (1d), 1.914(3) Å (4d); Cu–C_{Ph}: 1.898(3) Å/1.907(3) Å (1d), 179.1(1)° (4d)).¹⁸ The geometrical data also agree well with those of related [(NHC)Cu–Ar] complexes.²⁴

Here, it may be also stated that the complex $[(IMe)Cu-Si(TMS)_3]$ bearing the sterically demanding tris(trimethylsilyl)silyl group does not form dimeric complexes as observed in the related complexes $(4a)_2$, $(4b)_2$, and $[(IMe)Cu-SiEt(TMS)_2]_2$ (vide supra).⁸

The alkynyl complex [(IDipp)Cu–C≡C–Ph] (1e) exhibits, as expected and in agreement with the literature precedent, a linear, two-coordinated Cu^I ion.^{18,19,23} Surprisingly, the alkynyl complex with the formal composition [(Me₂IMe)Cu–C≡C– Ph] **4e** does not exhibit a similar structure but rather comprises [(Me₂IMe)₂Cu]⁺ cations and [(PhC≡C)₂Cu]⁻ anions that are present in distinct building blocks: [(PhC≡C)₂Cu]⁻, [\langle (Me₂-IMe)₂Cu \rangle_2 \langle (PhC≡C)₂Cu \rangle]⁺, and [\langle (Me₂IMe)₂Cu \rangle \langle (PhC≡ C)₂Cu \rangle].¹⁸ The occurrence of this structural motif is unexpected as μ -coordinating alkynyl ligands are very welldocumented, e.g., for related phosphine Cu^{I} complexes.¹¹ However, the ions $[(PhC \equiv C)_2 Cu]^-$ and $[(NHC)_2 Cu]^+$ themselves have also been reported independently.²⁹

Finally, it should be mentioned that an attempt to replace the NHC ligand in the dimeric complex $(4a)_2$ by a small phosphine (PMe₃) did not lead to the isolation of a polynuclear copper complex but the isolation of the mononuclear complex [(Me₃P)₃Cu-SiMe₂Ph] exhibiting a four-coordinate Cu¹ ion.¹⁸

Spectroscopic Characterization. While the molecular structures of the complexes **1a**–**4e** in the solid state are readily established by X-ray diffraction, insight into their solution behavior is not straightforward to obtain. However, heteronuclear NMR spectroscopy may give some indication on the solution state behavior.

For the linear, mononuclear dimethylphenyl silyl complexes, 1a, 2a, and 3a²⁹Si NMR chemical shifts in a narrow range of -14.4 ± 0.4 ppm are observed (in C₆D₆). In line with that, the related triphenylsilyl complexes 1b and 3b show ²⁹Si NMR chemical shifts in C_6D_6 of -0.4 and -0.7 ppm, respectively. In contrast to that, the dimeric complexes $(4a)_2$ and $(4b)_2$ give ²⁹Si NMR signals at -23.0 ppm $(4a)_2$ and at -10.1 ppm $(4b)_2$, respectively (in C_6D_6). Hence, significant shifts of the ²⁹Si NMR signals by about 9 ppm compared to the monomeric complexes are observed. This consistent and systematic difference in the ²⁹Si NMR data suggests a different electronic environment, in particular, different coordination numbers, in solution. This is in agreement with the data of the cuprates $[Cu_2{Si(TMS)_3}_2BrLi(thf)_3]$ and $[{Li_7(OtBu)_6}_{Cu_2}(Si (TMS)_3)_3$], respectively, where similarly distinct ²⁹Si NMR shifts are observed for bridging and terminal silvl groups within a single molecule.^{13b,c} In conclusion, in the solid state, monomeric and dimeric complexes exhibit characteristic and consistent specific sets of ²⁹Si NMR shifts suggesting different solution state structures. This may be rationalized by the solution structures resembling the monomeric and dimeric molecular structures in the solid state.

The unique NMR properties of tin comprising two spin 1/2 nuclei (¹¹⁷Sn and ¹¹⁹Sn) in virtually equal, relatively high natural abundances (7.68 and 8.59%) enable a more detailed study of the solution state structure for (**4**c)₃.

Especially indicative for the solution state structure of $(4c)_3$ are those signals with significant coupling to ^{117/119}Sn nuclei (Figure 9). ¹³C NMR spectroscopy reveals, for the carbene carbon atom beside the central signal (185.6 ppm), a doublet arising from coupling to one NMR active Sn nucleus $(J({}^{13}C-{}^{117/119}Sn) = 35 Hz$, averaged coupling constants to ${}^{117}Sn$ and ${}^{119}Sn$ are used throughout this analysis). In addition, a second set of signals, a triplet partly overlapping with the above signals, is recognizable, though just significant. It can account for a ${}^{13}C-{}^{117/119}Sn$ coupling to two ${}^{117/119}Sn$ nuclei. The intensity of both satellite signals agrees with the respective natural abundances.¹⁷ For the stannyl methyl carbon atom signal (-0.9 ppm) a better s/n ratio is obtained, and three distinct sets of signals are clearly observable: (a) the main signal not experiencing any ${}^{13}C - {}^{117/119}Sn$ coupling; (b) a doublet $(J({}^{13}C - {}^{117/119}Sn) = 67 \text{ Hz})$ due to coupling with one directly bound ^{117/119}Sn atom; (c) a doublet $(J({}^{13}C-{}^{117/119}Sn) = 28$ Hz) due to coupling with one ${}^{117/119}Sn$ atom not directly bound, with doubled intensity with respect to the previous satellite signal. Furthermore, two couplings to two ^{117/119}Sn atoms have to be included in the simulations for optimal agreement with the experimental data. These arise from coupling to one directly bound and one remote $^{117/119}\mathrm{Sn}$



Figure 9. Selected regions from experimental and simulated $^{13}C\{^{1}H\}$ NMR and $^{119}Sn\{^{1}H\}$ NMR spectra of $(4c)_{3}.^{18}$

atom and to two remote ^{117/119}Sn atoms, respectively. Again, the intensities of all satellite signals agree with their respective natural abundances.¹⁸ At last, the ¹¹⁹Sn NMR signal shows satellites arising from ¹¹⁹Sn-¹¹⁷Sn coupling ($J(^{119}Sn-^{117}Sn) = 2383$ Hz), again with intensities fitting the expected values for a trinuclear complex on the basis of the natural abundances.¹⁸

In summary it can be stated that the ¹³C and ¹¹⁹Sn NMR spectroscopic data are in agreement with a trimeric solution state structure of $(4c)_3$ similar to that present in the solid state; however, unlike in the solid state the spectra indicate the equivalence of all three tin atoms. This may be explained with a rapid interconversion of the two different types of tin atoms (μ^3 (Sn1, Sn2) and μ^2 (Sn3) coordinating, Figure 8) found in the solid state or by an alternative static symmetrical trimeric structure. The direct evidence for a trimeric nature of the stannyl complex (4c)₃ in solution supports the assumption of dimeric solution structures of the silyl complexes (4a)₂ and (4b)₂.

Catalysis. Copper(I) catalyzed silylation reactions of aldehydes and α,β -unsaturated carbonyls employing silylboranes have recently been intensely studied. In particular, **1a** has been employed as a model catalyst and enabled the characterization of a number of relevant intermediates.^{4a-c} It has been shown that under the reaction conditions the precatalyst (NHC)CuOtBu is converted to the catalytically crucial silyl complex upon reaction with pinB–SiMe₂Ph (vide supra).^{4a-c} To gain a first systematic insight into the impact of the sterics of the NHC ligand on the catalytic activity the complexes, [(ItBu)CuOtBu] and [(Me₂IMe)CuOtBu] were employed as precatalysts in the 1,2-/1,4-silylation of *p*-tolylaldehyde and hex-3-en-4-one as exemplary organic substrates (Table 4).

For both (pre)catalysts efficient conversion to the expected 1,2- and 1,4-silylation products at ambient temperature was observed, and the silylated compounds were isolated in good (unoptimized) yields (Table 4). Moreover, in comparison to those of the established (IDipp)Cu system significantly faster reaction rates were observed. Full conversion was reached after less than 1 h, while for the IDipp ligand significantly longer reaction times were reported.^{4b,c}



Table 4. Exemplary Catalytic Silylation with [Me₂IMe)CuOtBu] or [ItBu)CuOtBu] as Precatalyst

	^a Approximate	time	required	for	full	conversion	(GC/MS).	^b Isolated
•	yield.							

p-tolyl aldehyde

hex-3-en-4-one

<1 h

<1 h

59%

62%

CONCLUSION

 $R^1 = Me, R^2 = Me$

 $R^1 = Me$, $R^2 = Me$

A series of silyl and stannyl [(NHC)Cu–ER₃] complexes (ER3 = SiMe₂Ph, SiPh₃, SnMe₃) was synthesized by reaction of [(NHC)Cu–OtBu] complexes with the respective stannyl- and silylboranes significantly extending the scope of this versatile and easy-to-use access to copper silyl/stannyl complexes. Moreover, this reaction pathway has also been used to synthesize the related phenyl and alkynyl complexes [(NHC)-Cu–R] (R = Ph, C=C–Ph) as well as the phosphine complex [(Me₃P)₃Cu–SiMe₂Ph].

Single X-ray structure determinations of the compounds [(NHC)Cu-ER₃] revealed two major structure types in the solid state. For the sterically demanding NHC ligands IDipp, IMes, and ItBu, monomeric approximately linear Cu^I complexes were found for $ER_3 = SiMe_3Ph_1$, $SiPh_3$, $SnMe_3$ as well as for Ph and $C \equiv C$ —Ph. However, for the sterically little demanding methyl substituted NHC (Me₂IMe) dimeric silyl complexes comprising a butterfly shaped Cu_2Si_2 core with μ silyl ligands bridging the two Cu ions were obtained as reported earlier for the related complex $[(IMe)Cu-SiEt(TMS)_2]_2$ Similarly a structurally related trimeric complex was obtained for the trimethylstannyl complex. These complexes feature ultrashort Cu…Cu distances around 2.3 Å, among the shortest known today. In contrast, for the phenyl ligands the monomeric and linear complex [(Me₂IMe)Cu-Ph] is obtained while for the alkynyl ligand the formation of $[(Me_2IMe)_2Cu_2]^+$ and $[(PhC \equiv C)_2 Cu]^-$ ions was observed in the solid state, despite the well-documented ability of phenyl and alkynyl ligands to realize bridging coordination modes in Cu^I complexes. The heteronuclear solution NMR spectroscopic data of the silyl and stannyl complexes are consistent with different modes of coordination of the silvl and stannyl ligands with dependence on the NHC ligand present as observed in the solid state.

A case study of the catalytic properties of sterically less encumbered (NHC)Cu–SiMe₂Ph complexes for the silylation of aldehydes and $\alpha_{,\beta}$ -unsaturated ketones with silylboranes was conducted. The complexes (ItBu)CuOtBu and (Me₂IMe)- CuOtBu were found to be effective (pre)catalysts for the silylation of an aldehyde and an $\alpha_{,\beta}$ -unsaturated ketone, presumably via the intermediate monomeric ([(ItBu)Cu-SiMePh₂]) and dimeric ([(Me₂IMe)Cu-SiMePh₂]₂) complexes, respectively. Moreover, significantly faster reactions were observed than those with the established, sterically more demanding IDipp ligand. However, no significant difference was observed between the ItBu and Me₂IMe ligand.

The findings are of direct relevance to the growing field of Cu^{I} catalyzed silylation reaction, in particular those involving NHC- Cu^{I} complexes, where mononuclear complexes are widely assumed to be the active species. The study suggests that the coordination chemistry of NHC- Cu^{I} silyl complexes is more diverse, and aggregation and in particular bridging coordination of silyl ligands must be considered. Forthcoming experimental as well as computational studies, regarding the solution structure of NHC- Cu^{I} silyl complexes as well as a detailed analysis of the ultrashort Cu-Cu-Cu distances, will provide further insight into these intriguing and highly valuable class of compounds. Moreover, further comparative studies of the reactivity of monomeric and dimeric/aggregated NHC- Cu^{I} silyl complexes should impact on the further development of Cu^{I} catalyzed silylation reactions with silylboranes.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00210. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc. cam.ac.uk/structures.

Additional experimental, analytical, and crystallographic data (PDF) Crystallographic data (ZIP)

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Notes

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