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NHC Supersilyl Silver Complex [Ag(IPr)Si*t*Bu$_3$] as a Promising Agent for Substitution Reactions

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Abstract. The NHC supersilyl silver complex [Ag(IPr)Si*t*Bu$_3$] (IPr = NHC$_{\mathrm{IPr}}$) was prepared by treatment of Ag(IPr)Cl with Na(thf)$_2$[Si*t*Bu$_3$] in benzene/thf at room temperature. X-ray quality crystals of the NHC supersilyl silver complex [Ag(IPr)Si*t*Bu$_3$] (monoclinic, space group $P2_1/m$) were grown from heptane at room temperature. The ^{29}Si NMR spectrum of a solution of [Ag(IPr)Si*t*Bu$_3$] in C_6D_6 revealed two doublets caused by coupling to ^{107}Ag and ^{109}Ag nuclei. We further investigated the possibility of a conversion of triel halides EX_3 by treatment with [Ag(IPr)Si*t*Bu$_3$]. At ambient temperature the reaction of [Ag(IPr)Si*t*Bu$_3$] with an excess of EX_3 yielded *t*Bu$_3$SiEX$_2$ (E = B, Al; X = Cl, Br; E = Ga; X = Cl) and IPr·EX$_3$ (EX$_3$ = BCl$_3$, BBr$_3$, AlCl$_3$, AlBr$_3$, GaCl$_3$). The identity of *t*Bu$_3$SiEX$_2$ and IPr·EX$_3$ was confirmed by comparison with authentic samples.

Introduction

Over the past decades silanides $[SiR_3]^-$ (R = organyl) have been widely investigated in basic academic research.[1–5] Both supported and unsupported silanides are potent nucleophiles and it has been shown that their donor strength correlates to their reduction behavior.[6] For instance K[Si*t*Bu$_3$] as a very strong Brønsted base already deprotonates benzene at room temperature.[6] It is therefore not surprising, that the supersilyl anion [Si*t*Bu$_3$]$^-$ can also easily release one electron to form the related supersilyl radical ·Si*t*Bu$_3$. As shown in Figure 1, one can consider four possible isomers of the supersilyl radical ·Si*t*Bu$_3$.[7]

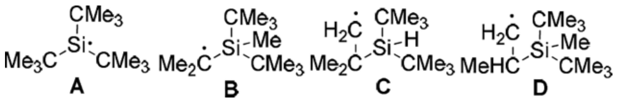


Figure 1. Isomers of the supersilyl radical ·Si*t*Bu$_3$ (**A**).

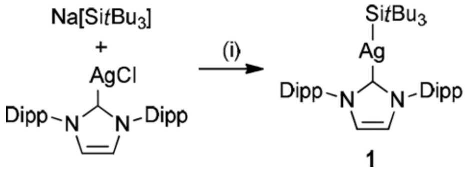
DFT calculations have shown that the silicon-centered radical ·Si*t*Bu$_3$ (**A**) is not the lowest-energy structure. Instead the carbon-centered radical **B**, where a methyl group has migrated from one *t*Bu group to the silicon atom, is significantly lower in energy than **A**. These calculations also revealed that structures **C** and **D** formed by 1,2 H-shifts are more disfavored than **B**.[7,8]

In many cases Na[Si*t*Bu$_3$][4,6] is able to reduce transition metal cations to the respective elements.[4] For example by the reaction of Ag$^+$ with supersilylsodium elemental silver along with the supersilyl radical dimer *t*Bu$_3$SiSi*t*Bu$_3$ was formed.[6] To gain supersilyl silver complexes there is a need for complexation of Ag$^+$ to lower the redox potential. In pursuit of a stable silver supersilanide we decided to treat NHC-stabilized Ag$^+$ cations with supersilylsodium.

Disupersilylated trielanes of the type (*t*Bu$_3$Si)$_2$EX (E = B, Al, Ga, In, Tl; X = F, Cl, Br)[9–12] can be prepared from EX$_3$ and Na[Si*t*Bu$_3$].[4,6] However, when EX$_3$ in pentane was treated with one or two molar equivalents of Na[Si*t*Bu$_3$][4,6] in both cases, reaction of EX$_3$ with Na[Si*t*Bu$_3$][4,6] exclusively yielded the disupersilylated compound (*t*Bu$_3$Si)$_2$EX. Thereby no monosupersilylated compound *t*Bu$_3$SiEX$_2$ was formed.[10] In these reactions the second substitution step must be much faster than the first one. We also suggested that in solution an equilibrium of (*t*Bu$_3$Si)$_2$EX and EX$_3$ with the ion pair [*t*Bu$_3$Si-E-Si*t*Bu$_3$][EX$_4$] exists.[10] The previously published preparation protocols revealed quite low yields for *t*Bu$_3$SiEX$_2$. As an example, *t*Bu$_3$SiAlBr$_2$ was obtained in 34 % yield by treatment of [Zn(Si*t*Bu$_3$)$_2$] with AlBr$_3$.[11] The purpose of this paper is to establish a direct conversion of triel halides EX$_3$ by supersilyl silver with forming monosupersilylated trielanes *t*Bu$_3$SiEX$_2$.

Results and Discussion

The NHC-supported silver complex [Ag(IPr)Si*t*Bu$_3$] (**1**) was prepared by the reaction of [Ag(IPr)Cl] with Na(thf)$_2$[Si*t*Bu$_3$][4,6] in a mixture of benzene and thf at room temperature, as shown in Scheme 1.



Scheme 1. Preparation route for the NHC supersilyl silver complex [Ag(IPr)Si*t*Bu$_3$] (**1**). (i) –NaCl; benzene/thf, room temperature.

After removing all volatiles, the residue was extracted into heptane. The NMR spectra of the reaction mixture solely

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showed resonances due to the silver complex **1**. Single crystals of **1** were grown from filtered heptane solution at room temperature. The NHC supersilyl silver complex **1** could be characterized by X-ray crystallography (monoclinic, space group $P2_1/m$).

The molecular structure of **1** is shown in Figure 2 (selected bond lengths and angles are in the Figure caption). The complex **1** is located on a crystallographic mirror plane with only half a molecule in the asymmetric unit. Besides two other silyl complexes $[Ag(IPr)SiEt(SiMe_3)_2]$[13] and $[Ag(IPr)Si(SiMe_3)_3]$,[13] the supersilyl silver complex **1** is the third IPr silyl silver complex which could be characterized by X-ray crystallography. Due to the bulky supersilyl group the Si–Ag distance in **1** [Si–Ag 2.4244(9) Å] is somewhat longer than the appropriate Si–Ag bonds found in $[Ag(IPr)SiEt(SiMe_3)_2]$ [Si–Ag bond lengths: 2.4006(6) Å][13] and $[Ag(IPr)Si(SiMe_3)_3]$ [Si–Ag bond lengths: 2.3936(5) Å],[13] respectively. One of the *t*Bu groups in **1** is disordered over two position with a site occupation factor of 0.521(9) for the major occupied site. Bond lengths and angles in the two disordered sites were restrained to be equal. The molecules of **1** are arranged in an alternate fashion, as shown in Figure 3.

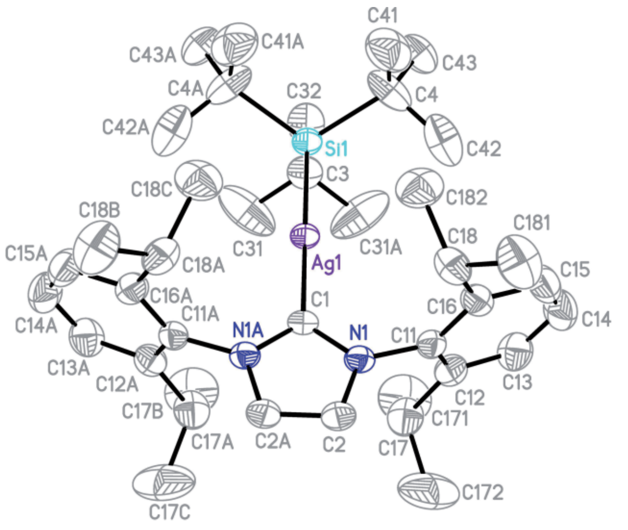


Figure 2. Structure and parameters of the supersilyl silver NHC complex $[Ag(IPr)SitBu_3]$ (**1**) (monoclinic, space group $P2_1/m$). Selected bond lengths /Å and angles /°: Ag(1)–C(1) 2.155(3), Ag(1)–Si(1) 2.4244(9), Si(1)–C(3) 1.966(4), Si(1)–C(4) 1.974(3), N(1)–C(1) 1.358(2), N(1)–C(2) 1.391(3), N(1)–C(11) 1.442(3), C(1)–N(1)#1 1.358(2), C(2)–C(2)#1 1.358(5), C(1)–Ag(1)–Si(1) 176.54(8), C(3)–Si(1)–C(4) 108.32(13), C(4)#1–Si(1)–C(4) 111.0(3), C(3)–Si(1)–Ag(1) 110.79(13), C(4)–Si(1)–Ag(1) 109.21(12), C(1)–N(1)–C(2) 111.94(19), C(1)–N(1)–C(11) 122.34(17), C(2)–N(1)–C(11) 125.63(19), N(1)–C(1)–N(1)#1 103.7(2), N(1)–C(1)–Ag(1) 128.15(12). Symmetry transformation used to generate equivalent atoms: #1 x, –*y* + 1/2, z.

As shown in Table 1, the structure of **1** features C–Si–C angles smaller than 110°, indicating a negatively polarized Si atom comparable to those of $Na(thf)_2[Cu(SitBu_3)_2]$[14] and $Na(thf)_4[Cu(SitBu_3)_2]$.[14] Whereas the C–Si–C values of group 12 supersilanides are in the "normal" range for neutral supersilyl compounds.

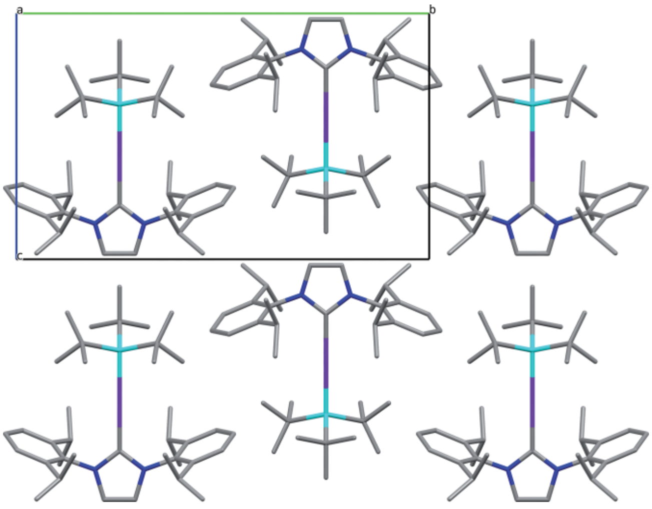


Figure 3. Packing diagram of the supersilyl silver NHC complex $[Ag(IPr)SitBu_3]$ (**1**).

Table 1. Structural parameters /Å,° of group 11 and 12 supersilanides.

	M–Si	Si–C a)	C–Si–C a)
$Na(thf)_2[Cu(SitBu_3)_2]$ [14]	2.361(1) a)	1.978(5)	108.7(2)
$Na(thf)_4[Cu(SitBu_3)_2]$ [14]	2.307(2)	1.972(6)	108.5(2)
$[Ag(IPr)SitBu_3]$ (**1**)	2.424(1)	1.971(3)	109.2(3)
$[Zn(SitBu_3)_2]$ [15]	2.384(1)	1.943(4)	111.8(2)
$[Cd(SitBu_3)_2]$ [15]	2.524(2)	1.943(4)	111.9(2)
$[Hg(SitBu_3)_2]$ [15]	2.495(2)	1.937(8)	112.2(4)

a) Average.

The $^{29}Si\{^1H\}$ NMR spectrum of a solution of **1** in C_6D_6 revealed two doublets caused by coupling to ^{107}Ag and ^{109}Ag nuclei, as shown in Figure 4. When considering the ^{29}Si spectra of the group 11 and 12 supersilanides certain trends can be observed. As is to be expected, the signals of the silicon nuclei of the group 11 as well as the group 12 element supersilanides are shifted upfield as the element is changed from up to down in the periodic table (Table 2).

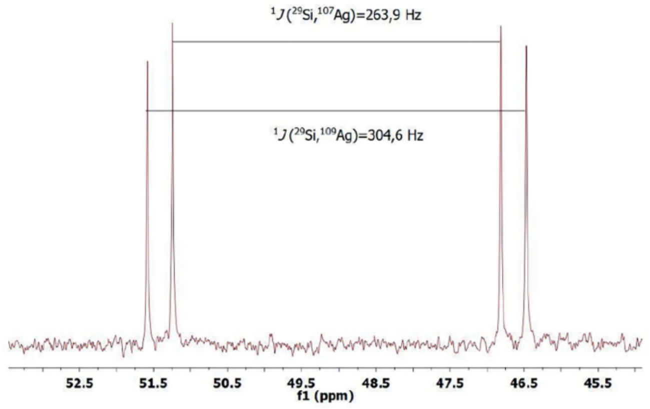


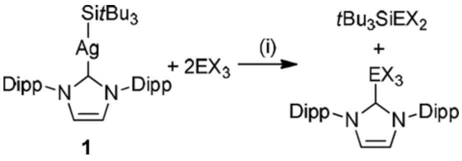
Figure 4. $^{29}Si\{^1H\}$ NMR spectrum (59.6 MHz) of $[Ag(IPr)SitBu_3]$ (**1**) in C_6D_6: $\delta = 49.0$ ppm.

We further investigated the possibility of a conversion of triel halides EX_3 by treatment with **1**. As shown in Scheme 2, we found 100 % conversion of the silver silanide **1** in all these

Table 2. ^{29}Si NMR resonances of group 11 and 12 supersilanides in C_6D_6.

	δ(^{29}Si*t*Bu$_3$) /ppm
Na(thf)$_x$[Cu(Si*t*Bu$_3$)$_2$] [14]	23.2
[Ag(IPr)Si*t*Bu$_3$] (**1**)	49.0
[Zn(Si*t*Bu$_3$)$_2$] [15]	25.9
[Cd(Si*t*Bu$_3$)$_2$] [15]	47.6
[Hg(Si*t*Bu$_3$)$_2$] [15]	88.3

reactions. Thereby the related monosupersilylated trielanes *t*Bu$_3$SiEX$_2$ and the NHC complexes IPr·EX$_3$ were formed (E = B, Al; X = Cl, Br; E = Ga; X = Cl). The identity of *t*Bu$_3$SiEX$_2$ as well as IPr·EX$_3$ was confirmed by comparison with authentic samples.



Scheme 2. Reaction of of triel halides EX$_3$ (E = B, Al; X = Cl, Br; E = Ga; X = Cl) by treatment with the NHC-supported silver complex [Ag(IPr)Si*t*Bu$_3$] (**1**). i) -AgX, cyclohexane, room temperature.

Experimental Section

All experiments were carried out in a dry argon or nitrogen atmosphere using standard Schlenk and glove box techniques. Alkane solvents were dried with sodium and freshly distilled prior to use. Benzene and thf were distilled from sodium/benzophenone. Na(thf)$_2$[Si*t*Bu$_3$][6] was prepared according to the published procedure. All other starting materials were purchased from commercial sources and used without further purification.

Synthesis of [Ag(IPr)Si*t*Bu$_3$] (1). A mixture of [Ag(IPr)Cl] (99 mg, 0.186 mmol) in 4 mL benzene and 0.4 M solution of Na(thf)$_x$[Si*t*Bu$_3$][6] (0.2 mmol) in 0.5 mL thf was stirred for 1 d at room temperature in an Ar-atmosphere. The NMR spectra of the reaction mixture showed resonances due to the silver complex **1**. After removing all volatiles, the residue was extracted into 10 mL heptane. Colorless crystals of **1** were grown from filtered heptane solution at room temperature. Yield: 110 mg (85 %). **^{1}H NMR** (300.1 MHz, C_6D_6): δ = 1.07 [d, ^3J(H,H) = 6.9 Hz; 12 H; CH(C*H*$_3$)], 1.25 [s, 27 H, C(C*H*$_3$)$_3$], 1.43 [d, $^3J_{H,H}$ = 6.9 Hz; 12 H; CH(C*H*$_3$)], 2.58 [m, 4 H, C*H*(CH$_3$)], 6.35 (s, 2 H, =C*H*), 7.05–7.23 ppm (m, Ar*H*). **^{13}C{^{1}H} NMR** (75.5 MHz, C_6D_6): δ = 23.7 [CH(*C*H$_3$)], 24.0 [d, $^3J_{13C,107/109Ag}$ = 9.8 Hz; *C*(CH$_3$)$_3$], 24.6 [*C*H(CH$_3$)], 28.6 [CH(*C*H$_3$)], 33.4 [d, $^4J_{13C,107/109Ag}$ = 3.8 Hz; C(*C*H$_3$)$_3$], 122.0 (=*C*H), 123.8, 130.1, 135.1, 145.7 ppm (Ar*C*). **^{29}Si{^{1}H} NMR** (59.6 MHz, C_6D_6): δ = 49.0 (d, $^1J_{29Si,107Ag}$ = 263.9 Hz; d, $^1J_{29Si,109Ag}$ = 304.6 Hz; *Si*tBu$_3$) ppm. $C_{39}H_{63}AgN_2Si$ (695.88): calcd. C 67.31, H 9.13; N 4.03 %; found: C 66.42, H 9.03, N 3.57 %.

Reaction of 1 with EX$_3$: A solution of [Ag(IPr)Si*t*Bu$_3$] (**1**) (**1** for BCl$_3$: 8 mg, 0.012 mmol; **1** for BBr$_3$: 9 mg, 0.013 mmol; **1** for AlCl$_3$: 11 mg, 0.016 mmol; **1** for AlBr$_3$: 12 mg, 0.017 mmol; **1** for GaCl$_3$: 8 mg, 0.012 mmol) in 1 mL cyclohexane was combined with an excess of EX$_3$ (BCl$_3$: 0.11 mmol, BBr$_3$: 33 mg, 0.13 mmol, AlCl$_3$: 30 mg, 0.23 mmol, AlBr$_3$: 53 mg, 0.20 mmol, GaCl$_3$: 8 mg, 0.046 mmol). After filtering out insoluble AgX (X = Cl, Br) the solutions were examined by NMR spectroscopy. The resonances of *t*Bu$_3$SiEX$_2$ (E = B, Al; X = Cl, Br; E = Ga; X = Cl) and IPr·EX$_3$ (IPr·EX$_3$ = IPr·BCl$_3$,[16] IPr·BBr$_3$,[17] IPr·AlCl$_3$, IPr·AlBr$_3$, IPr·GaCl$_3$[18]) were observable in the NMR spectra of these solutions.

^{29}Si NMR resonances of *t*Bu$_3$SiEX$_2$ recorded by ^{1}H/^{29}Si HETCOR NMR spectroscopy in C_6D_{12}: δ = –1.6 (E = B, X = Cl); 0.3 (E = B, X = Br); 14.3 (E = Al, X = Cl); 15.1 (E = Al, X = Br); 13.5 ppm (E = Ga; X = Cl).

Note: Treatment of a mixture of AlX$_3$ (AlCl$_3$: 20 mg, 0.15 mmol, AlBr$_3$: 44 mg, 0.16 mmol) in 6 mL heptane with IPr (IPr for AlCl$_3$: 50 mg, 0.13 mmol, IPr for AlBr$_3$: 50 mg, 0.13 mmol) yielded quantitatively IPr·AlX$_3$ according to the NMR spectra.

IPr·AlCl$_3$: ^{1}H NMR (300.1 MHz, C_6D_6): δ = 0.94 [d, $^3J_{H,H}$ = 6.9 Hz; 12 H; CH(C*H*$_3$)], 1.43 [d, $^3J_{H,H}$ = 6.9 Hz; 12 H; CH(C*H*$_3$)], 2.71 [m, 4 H, C*H*(CH$_3$)], 6.40 (s, 2 H, =C*H*), 6.94–7.24 ppm (m, Ar*H*). **^{13}C{^{1}H} NMR** (75.5 MHz, C_6D_6): δ = 22.3 [CH(*C*H$_3$)], 25.5 [*C*H(CH$_3$)], 28.8 [CH(*C*H$_3$)], 124.1 (=*C*H), 125.1, 131.2, 133.5, 145.3 ppm (Ar*C*).

IPr·AlBr$_3$: ^{1}H NMR (300.1 MHz, C_6D_6): δ = 0.94 [d, $^3J_{H,H}$ = 6.9 Hz; 12 H; CH(C*H*$_3$)], 1.43 [d, $^3J_{H,H}$ = 6.9 Hz; 12 H; CH(C*H*$_3$)], 2.67 [m, 4 H, C*H*(CH$_3$)], 6.41 (s, 2 H, =C*H*), 6.95–7.22 ppm (m, Ar*H*). **^{13}C{^{1}H} NMR** (75.5 MHz, C_6D_6): δ = 23.7 [CH(*C*H$_3$)], 25.3 [*C*H(CH$_3$)], 28.7 [CH(*C*H$_3$)], 124.2 (=*C*H), 125.7, 131.5, 133.6, 145.5 ppm (Ar*C*).

X-ray Crystallography of 1: Data were collected on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using Mo-K_α radiation (λ = 0.71073 Å) and were scaled using frame scaling procedure in the *X-AREA* program system.[19] An empirical absorption correction with the program PLATON was performed for both structures. The structure[20] was solved by direct methods using the program *SHELXS* and refined with full-matrix least-squares on F^2 using the program *SHELXL*.[21]

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1941530 (**1**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

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Keywords: Silanide; Silicon; Silver; Triel; X-ray diffraction

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