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Supporting Information for

Base-Stabilized Silaimine and its Donor-Free Dimer Derived from the Reaction of NHC-Supported Silylene with $SiCl_4$

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Experimental Section

General considerations: All operations were carried out under an atmosphere of dry argon or nitrogen by using modified Schlenck line and glovebox techniques. All solvents were freshly distilled from Na and degassed immediately prior to use. Elemental analyses were carried out on an Elemental Vario EL analyzer. The ^{1}H, ^{13}C and ^{29}Si NMR spectroscopic data were recorded on Bruker Mercury Plus 300, 400 and 600 MHz NMR spectrometers. Infrared spectra were recorded on a Bio-Rad FTS 6000 spectrometer. The UV-vis spectra were recorded on a Shimadzu UV-2450 spectrometer and Emission spectra on an Edinburgh Analytical Instruments FL900CD spectrometer. $ArN(SiMe_3)Si(I\textit{i}Pr)Cl$ (**1**)[1] (Ar = 2,6-$^{i}Pr_2C_6H_3$, I*i*Pr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) was synthesized according to published procedure.

Synthesis of $ArN{=}SiCl_2(I\textit{i}Pr)$ (2): A solution of $SiCl_4$ (1.5 ml, 0.53 mmol, 0.35 M solution in Et_2O) was added to a stirred solution of **1** (0.26g, 0.5 mmol) in Et_2O (5mL) at room temperature. Soon white suspension formed. The mixture was allowed to stir for 2h. After filtration, the residue white power is neat **2** (0.05g，21.2%). M.p. 198-200 °C; ^{1}H NMR (400 MHz, C_6D_6): δ 0.95 (d, *J* = 7.0 Hz, 12H, $CH(CH_3)_2$), 1.34 (s, 6H, $=CCH_3$), 1.56 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$), 4.13 (m, 2H, Ar-$CH(CH_3)_2$), 6.62 (m, 2H, N-$CH(CH_3)_2$), 7.09 (m, 1H, Ar-*H*), 7.39 (d, 2H, Ar-*H*) ppm; ^{13}C NMR (100.61 MHz, d^8-THF): δ 10.69 ($=CCH_3$), 21.08 ($CH(CH_3)_2$), 24.16 ($CH(CH_3)_2$), 28.47 (Ar-$CH(CH_3)_2$), 51.73 (N-$CH(CH_3)_2$), 116.06, 122.01, 129.73, 139.90, 145.78 (Ar-*C*), 145.99 (N*C*N) ppm; ^{29}Si NMR (79.49 MHz, d^8-THF): δ -107.03 ppm; Elemental analysis (%) calcd for $C_{23}H_{37}Cl_2N_3Si$: C, 60.77; H, 8.20; N, 9.24; Found: C, 60.26; H, 8.53; N, 8.93; IR (cm^{-1}): ν 469.71, 541.48, 638.24, 757.49, 809.22, 915.63, 1038.81, 1104.74, 1171.35, 1209.04, 1244, 1312.82, 1373.38, 1622.99, 1963.51, 2274.55, 2324.13, 2976.06.

Synthesis of $ArN(SiMe_3)SiCl_3$ (3): A solution of $SiCl_4$ (1.5 ml, 1.36 mmol) in hexane (15 mL) was added to a stirred suspension of **1** (0.49 g, 1 mmol) in hexane (70 mL) at room temperature. Soon the suspension became clarified. The mixture was allowed to stir for overnight whereupon a white precipitate formed. After filtration (the residual solid was I*i*Pr·$SiCl_4$) and removal of solvents under vacuum afforded colorless solid **3** (0.35 g, 91.4%). M.p. 127°C-130°C; ^{1}H NMR (400 MHz, C_6D_6): δ 7.07 – 6.94 (m, 3H, Ar-*H*), 3.45 (m, 2H, $CH(CH_3)_2$), 1.25 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.16 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 0.19 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (100.61 MHz, C_6D_6): δ 147.3, 138.5, 127.2, 124.8 (Ar-*C*), 28.5 ($CH(CH_3)_2$), 25.4 and 24.7

(CH(*C*H_3)$_2$), 1.7 (Si(*C*H_3)$_3$). ^{29}Si NMR (79.49 MHz, C_6D_6): δ -27.3 (*Si*Cl_3) ppm. Elemental analysis (%) calcd for $C_{15}H_{26}Cl_3NSi_2$: C, 47.05; H, 6.84; N, 3.66; Found: C, 47.01; H, 6.86; N, 3.61.

Path b for I*i*Pr·$SiCl_4$: Neat $SiCl_4$ (0.2 ml, 1.8 mmol) was added to a stirred solution of I*i*Pr (0.09g, 0.5 mmol) in toluene (10 mL) at ambient temperature. The mixture was allowed to stir for 1h, and then the volatiles were removed under vacuum. The residue was washed with n-hexane (5 ml) to afforded white powder I*i*Pr·$SiCl_4$ (0.14g, 80.0%). : ^{1}H NMR (400 MHz, C_6D_6): δ 6.00 (s, 2H, C*H*(CH_3)$_2$), 1.33 (s, 6H, =CC*H*$_3$), 1.13 (d, *J* = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100.61 MHz, C_6D_6): δ 154.59 (N*C*N), 125.64 (CH$_3$*C*=), 52.19 (*C*H(CH$_3$)$_2$), 20.76 (CH(*C*H$_3$)$_2$), 10.19 (=C*C*H$_3$). ^{29}Si NMR (79.49 MHz, C_6D_6): δ -104.95 (*Si*Cl_4) ppm.

Synthesis of ArN(SiMe$_3$)$SiCl_2SiCl_3$ (4') and (ArN$SiCl_2$)$_2$ (4): A suspension of **1** (0.25g, 0.5 mmol) in hexane (15mL) was added to a stirred solution of $SiCl_4$ (1.5 ml, 0.53 mmol, 0.35 M solution in Et_2O) in hexane (15 mL) at room temperature. The mixture was stirred overnight. After filtration (the residue white power was I*i*Pr·$SiCl_4$) and removal solvents, the remaining residue (a mixture of **4'** (about 70%), **3**, and undefined coproducts) was dissolved in toluene (15 ml) and heated at 80 °C for 16 h. Concentration to ca. 1~2 mL and storage at -10 °C afforded colorless crystals of **4** (0.09 g, 64.3%). **4'**: ^{1}H NMR (400 MHz, C_6D_6): δ 7.05 – 6.93 (m, 3H, Ar-*H*), 3.46 (m, 2H, C*H*(CH$_3$)$_2$), 1.25 (d, 6H, CH(C*H*$_3$)$_2$), 1.16 (d, 6H, CH(C*H*$_3$)$_2$), 0.18 (s, 9H, Si(C*H*$_3$)$_3$) ppm. ^{13}C NMR (100.61 MHz, C_6D_6): δ 147.28, 138.54, 124.77, 28.49, 25.46, 24.63, 1.74 ppm. **4**: Sublimation at 260 °C; ^{1}H NMR (400 MHz, C_6D_6): δ 7.06-7.12 (m, 6H, Ar-*H*), 3.86 (m, 4H, C*H*(CH$_3$)$_2$), 1.29 (d, *J* = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$) ppm; ^{13}C NMR (100.61 MHz, C_6D_6): δ 147.44, 129.43, 127.50 and 125.09 (Ar-*C*), 28.64 (*C*H(CH$_3$)$_2$), 25.66 (CH(*C*H$_3$)$_2$) ppm; ^{29}Si NMR (79.49 MHz, d^8-THF): δ -43.15 (*Si*Cl_2) ppm; Elemental analysis (%) calcd for $C_{24}H_{34}Cl_4N_2Si_2$: C, 52.55; H, 6.25; N, 5.11; Found: C, 52.37; H, 6.03; N, 5.56;

X-ray Structural Determinations. All intensities for compounds **2** and **4** were collected with a Rigaku Saturn 724 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 113(2) K. The structure was solved by direct methods (*SHELXS-97*)[2] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (*SHELXL-97*).[3] Crystals of **2** suitable for X-ray analysis were grown from mixture of THF and toluene. And crystals of **4** suitable for X-ray analysis were grown from toluene. Crystallographic data for **2** and **4** are given in Table S1.

Table S1: Crystallographic data for **2** and **4**.

Compound	**2**	**4**
CCDC No.	1418863	1418862
Empirical formula	$C_{23}H_{37}Cl_2N_3Si•C_7H_8$	$C_{24}H_{34}Cl_4N_2Si_2$
Formula weight	546.68	548.51
Temperature/K	113(2)	113(2)
Wavelength /Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
space group	P2(1)/n	P2(1)/n
a/Å	9.490(4)	9.730(6)
b/Å	14.842(6)	11.344(7)
c/Å	21.882(9)	13.051(8)
α (°)	90	90
β (°)	91.321(7)	96.115(9)
γ (°)	90	90
V/ Å^3	3081(2)	1432.3(15)
Z	4	2
$d_{calcd.}$ (g/cm^3)	1.179	1.272
F(000)	1176.0	576
Limiting indices	-11≤h≤10 -17≤k≤17 -26≤l≤26	-8≤h≤12, -14≤k≤14 -17≤l≤16
Reflections collected / unique	23056 / 5427	12871 / 3411
GOF	1.073	0.923
R_1 ($I > 2\sigma(I)$)	0.0656	0.0343
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1669	0.0791
R_1 (all data)	0.0825	0.0476
$wR(F^2)$ (all data)	0.1781	0.0818

References

1. Cui, H.; Cui, C. *Dalton Trans.* **2011**, *40*, 11937.

2. Sheldrick, G. M. SHELXS-90/96, *Program for Structure Solution*, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

3. Sheldrick, G. M. *SHELXL 97*, *Program for Crystal Structure Refinement*, University of Goettingen, Goettingen, Germany, **1997**.