# **Electronic Supporting Information**

# Application of a Stable and Soluble Dibenzylbarium Reagent in the Synthesis of a Barium Imido Cluster

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# 1. Spectroscopic characterization



Figure S1. <sup>1</sup>H NMR (600.13 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of (DMAT)<sub>2</sub>Ba·(THF)<sub>2</sub>.



Figure S2. <sup>1</sup>H-<sup>1</sup>H COSY NMR (600.13 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of (DMAT)<sub>2</sub>Ba·(THF)<sub>2</sub>.



Figure S3. <sup>13</sup>C NMR (150.92 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of (DMAT)<sub>2</sub>Ba·(THF)<sub>2</sub>.



Figure S4. <sup>13</sup>C(DEPT-135) NMR (150.92 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of (DMAT)<sub>2</sub>Ba·(THF)<sub>2</sub>.



Figure S5. <sup>1</sup>H <sup>13</sup>C HSQC NMR (600.13/150.92 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of (DMAT)<sub>2</sub>Ba·(THF)<sub>2</sub>.



Figure S6. <sup>13</sup>C NMR (100.62 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of (DMAT)<sub>2</sub>Ba·(THF)<sub>2</sub> without <sup>1</sup>H decoupling.



Figure S7. <sup>29</sup>Si NMR (119.22 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of (DMAT)<sub>2</sub>Ba·(THF)<sub>2</sub>.



Figure S8. Temperature dependent <sup>1</sup>H NMR (600.13 MHz, tol-d8) of (DMAT)<sub>2</sub>Ba·(THF)<sub>2</sub>.



**Figure S9.** Stack of <sup>1</sup>H NMR (600.13 MHz, 298 K,  $C_6D_6$ ) of (DMAT)<sub>2</sub>Ba·(THF)<sub>2</sub> heated at 60 °C in benzene for 1, 2 and 3 days. Slow decomposition was observed. Formation of ethylene (5.25 ppm) indicates deprotonation of the THF ligand as main decomposition pathway.



**Figure S10.** Stack of <sup>1</sup>H NMR (600.13 MHz, 298 K, THF-*d8*) of (DMAT)<sub>2</sub>Ba·(THF)<sub>2</sub> heated at 60 °C in THF for 1, 2 and 3 days. Slow decomposition was observed.



Figure S11. <sup>1</sup>H NMR (600.13 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of [(Ph<sub>3</sub>SiN)Ba·(THF)]<sub>4</sub>.



Figure S12. <sup>1</sup>H-<sup>1</sup>H COSY NMR (600.13 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of [(Ph<sub>3</sub>SiN)Ba·(THF)]<sub>4</sub>.



<sup>150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20</sup> chemical shift [ppm]

Figure S13. <sup>13</sup>C NMR (150.92 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of [(Ph<sub>3</sub>SiN)Ba·(THF)]<sub>4</sub>.



Figure S14. <sup>1</sup>H <sup>13</sup>C HSQC NMR (600.13/150.92 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of [(Ph<sub>3</sub>SiN)Ba·(THF)]<sub>4</sub>.



Figure S15. <sup>29</sup>Si NMR (119.22 MHz, 298 K,  $C_6D_6$ ) of [(Ph<sub>3</sub>SiN)Ba·(THF)]<sub>4</sub>.



Figure S16. <sup>1</sup>H NMR (600.13 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of [(Ph<sub>3</sub>SiN)Sr·(THF)]<sub>4</sub>·0.31THF.



Figure S17. <sup>1</sup>H-<sup>1</sup>H COSY NMR (600.13 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of [(Ph<sub>3</sub>SiN)Sr·(THF)]<sub>4</sub>·0.31THF.



165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 chemical shift [ppm]

Figure S18. <sup>13</sup>C NMR (150.92 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of [(Ph<sub>3</sub>SiN)Sr · (THF)]<sub>4</sub>·0.31THF.



Figure S19. <sup>1</sup>H <sup>13</sup>C HSQC NMR (600.13/150.92 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>) of [(Ph<sub>3</sub>SiN)Sr·(THF)]<sub>4</sub>·0.31THF.



00 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -3( chemical shift [ppm]

Figure S20. <sup>29</sup>Si NMR (119.22 MHz, 298 K,  $C_6D_6$ ) of [(Ph<sub>3</sub>SiN)Sr·(THF)]<sub>4</sub>·0.31THF.

### 2. Crystal structure determination

The crystal structure data of the compounds mentioned below have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2074746 for [(DMAT)<sub>2</sub>Ba·(THF)<sub>2</sub>]·THF, 2074747 for [(Ph<sub>3</sub>SiN)Ba·(THF)]<sub>4</sub>(THF)<sub>2</sub> and 2074748 for [(Ph<sub>3</sub>SiN)Sr·(THF)]<sub>4</sub>·0.31THF contain the supplementary crystallographic data for the compounds. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data\_request/cif</u>.

#### [(DMAT)2Ba·(THF)2]·THF (1)

A yellow crystal of the composition [(DMAT)<sub>2</sub>Ba·(THF)<sub>2</sub>]·THF was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100.0(3) K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on an Agilent SuperNova diffractometer with Atlas S2 detector using a MoKα microfocus source. The measured data was processed with the CrysAlisPro (v40.67a) software package.<sup>[S1]</sup> Using Olex2,<sup>[S2]</sup> the structure was solved with the ShelXT<sup>[S3]</sup> structure solution program using Intrinsic Phasing and refined with the ShelXL<sup>[S4]</sup> refinement package using Least Squares Minimization. All non-hydrogen atoms were refined anisotropically. Most hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Since the benzylic hydrogen atoms at C1 and C13 deviate slightly from the idealized geometry, their positions were located from difference Fourier maps and refined.

Disorder of two THF ligands and of the co-crystallized THF was observed. The disorder was modeled with the help of similarity restraints (SIMU, SADI). The relative occupancies of the two alternative orientations of each moiety were refined to 0.511(13)/0.489(13) (Ligand 1), 0.860(13)/0.140(13) (Ligand 2) and 0.686(5)/0.314(5) (co-crystallized THF), respectively.

Crystallographic and refinement data are summarized in Table S1.

Table S1. Crystal data and structure refinement for [(DMAT)<sub>2</sub>Ba·(THF)<sub>2</sub>]·THF.

hasj180523a
$C_{36}H_{64}BaN_2O_3Si_2$
766.41
100.0(3)
triclinic
P-1
10.0143(2)
10.3100(2)
20.0630(4)
93.9528(18)
91.8778(18)
105.4458(19)

1090 09(9)
1909.00(0)
2
1.280
1.092
804.0
0.31 × 0.159 × 0.091
Μο Κα (λ = 0.71073)
4.44 to 59.68
$-13 \le h \le 13,  -14 \le k \le 14,  -22 \le l \le 27$
38081
10059 [ $R_{int} = 0.0344, R_{sigma} = 0.0379$ ]
10059/585/508
1.054
R <sub>1</sub> = 0.0315, wR <sub>2</sub> = 0.0644
R <sub>1</sub> = 0.0370, wR <sub>2</sub> = 0.0665
0.70/-0.54





#### $[(Ph_3SiN)Ba \cdot (THF)]_4(THF)_2(2)$

A colorless crystal of the composition [(Ph<sub>3</sub>SiN)Ba·(THF)]<sub>4</sub>(THF)<sub>2</sub> was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100.0(6) K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on an Agilent SuperNova diffractometer with Atlas S2 detector using a MoKα microfocus source. The measured data was processed with the CrysAlisPro (v40.67a) software package.<sup>[S1]</sup> Using Olex2,<sup>[S2]</sup> the structure was solved with the ShelXT<sup>[S3]</sup> structure solution program using Intrinsic Phasing and refined with the ShelXL<sup>[S4]</sup> refinement package using Least Squares Minimization. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

Disorder of two THF ligands was observed. The disorder was modeled with the help of similarity restraints (SIMU, SADI). The relative occupancies of the two alternative orientations of each moiety were refined to 0.813(9)/0.187(9) (THF 1) and 0.57(2)/0.43(2) (THF 2), respectively.

Crystallographic and refinement data are summarized in Table S2.

Table S2. Crystal data and structure	refinement for [(Ph₃SiN	)Ba·(THF)]4(THF)2
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Identification code	hasj200205a
Empirical formula	C <sub>96</sub> H <sub>108</sub> Ba <sub>4</sub> N <sub>4</sub> O <sub>6</sub> Si <sub>4</sub>
Formula weight	2075.58
Temperature/K	100.0(6)
Crystal system	monoclinic
Space group	P21
a/Å	13.8251(2)
b/Å	14.5060(2)
c/Å	22.6463(3)
α/°	90
β/°	95.1929(14)
γ/°	90
Volume/Å <sup>3</sup>	4523.00(13)
Z	2
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.524
µ/mm⁻¹	1.826
F(000)	2080.0
Crystal size/mm <sup>3</sup>	0.213 × 0.18 × 0.129
Radiation	Μο Κα (λ = 0.71073)
2O range for data collection/°	4.35 to 59.014
Index ranges	-17 ≤ h ≤ 17, -18 ≤ k ≤ 19, -31 ≤ l ≤ 31
Reflections collected	39704
Independent reflections	21085 [ $R_{int} = 0.0344$ , $R_{sigma} = 0.0538$ ]
Data/restraints/parameters	21085/447/1110





**Figure S22.** Solid state structure of  $[(Ph_3SiN)Ba \cdot (THF)]_4(THF)_2$ . Ellipsoids represent 50% probability. Cocrystallized THF and hydrogen atoms have been omitted for clarity.

#### [(THF)Sr(NSiPh<sub>3</sub>)]<sub>4</sub> (3)

A colorless crystal of the composition [(Ph<sub>3</sub>SiN)Sr·(THF)]<sub>4</sub>·0.31THF was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100.0(6) K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on an Agilent SuperNova diffractometer with Atlas S2 detector using a CuKα microfocus source. The measured data was processed with the CrysAlisPro (v40.67a) software package.<sup>[S1]</sup> Using Olex2,<sup>[S2]</sup> the structure was solved with the ShelXT<sup>[S3]</sup> structure solution program using Intrinsic Phasing and refined with the ShelXL<sup>[S4]</sup> refinement package using Least Squares Minimization. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

Disorder of two THF ligands and one phenyl group was observed. The disorder was modeled with the help of similarity restraints (SIMU, SADI). The relative occupancies of the alternative orientations of each moiety were refined to 0.500(3)/0.308(3)/0.192(3) (THF 1), 0.772(8)/0.228(8) (THF 2) and 0.692(2)/0.308(2) (phenyl), respectively. Additionally, there is a cavity, which is either empty or filled with a disordered THF, depending on the orientation of the disordered phenyl moiety next to it. The site occupancy factors for this partially present solvent molecule are 0.166(3) and 0.142(3).

Crystallographic and refinement data are summarized in Table S3.

Identification code	hasj200220b
Empirical formula	$C_{89.23}H_{94.46}N_4O_{4.31}Si_4Sr_4$
Formula weight	1754.66
Temperature/K	100.0(6)
Crystal system	monoclinic
Space group	P21/n
a/Å	14.45103(6)
b/Å	23.75812(13)
c/Å	24.44540(11)
α/°	90
β/°	99.7196(4)
γ/°	90
Volume/Å <sup>3</sup>	8272.35(7)
Z	4
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.409
µ/mm⁻¹	4.253
F(000)	3601.0
Crystal size/mm <sup>3</sup>	0.322 × 0.236 × 0.172
Radiation	Cu Kα (λ = 1.54184)
20 range for data collection/°	7.236 to 145.766

#### Table S3. Crystal data and structure refinement for [(Ph<sub>3</sub>SiN)Sr·(THF)]<sub>4</sub>·0.31THF

Index ranges Reflections collected Independent reflections Data/restraints/parameters Goodness-of-fit on  $F^2$ Final R indexes [I>=2 $\sigma$  (I)] Final R indexes [all data] Largest diff. peak/hole / e Å<sup>-3</sup>  $\begin{array}{l} -17 \leq h \leq 17, \ -29 \leq k \leq 21, \ -29 \leq l \leq 29 \\ 63701 \\ 16118 \ [R_{int} = 0.0215, \ R_{sigma} = 0.0163] \\ 16118/854/1169 \\ 1.073 \\ R_1 = 0.0298, \ wR_2 = 0.0716 \\ R_1 = 0.0316, \ wR_2 = 0.0732 \\ 1.37/-1.29 \end{array}$ 



**Figure S23.** Solid state structure of [(Ph<sub>3</sub>SiN)Sr·(THF)]<sub>4</sub>·0.31THF. Ellipsoids represent 50% probability. Co-crystallized THF and hydrogen atoms have been omitted for clarity.

## 3. DFT calculations

All calculations were carried out using Gaussian 16A.<sup>5</sup> All methods were used as implemented. All structures were fully optimized on a B3PW91/def2tzvp level of theory.<sup>6</sup> In all cases Grimme`s third dispersion correction with Becke-Johnson damping (GD3BJ) was added.<sup>7</sup> Charges were calculated via NBO Analyses.<sup>8</sup>

#### Comparison calculated and experimental structure



**Figure S24.** Selected bond lengths for the optimized geometries of complexes [(Ph<sub>3</sub>SiN)Sr·(THF)]<sub>4</sub>·(left) and [(Ph<sub>3</sub>SiN)Ba·(THF)]<sub>4</sub>·(right).at the B3PW91/def2tzvp (GD3BJ) level. Calculated bond lengths are shown in green boxes, the average of the experimental values determined by X-ray diffraction analysis are shown in red boxes.

#### Natural Population Analysis (NPA)



**Figure S25.** Selected NPA charges calculated for  $[(Ph_3SiN)Sr \cdot (THF)]_4 \cdot (left)$  and  $[(Ph_3SiN)Ba \cdot (THF)]_4 \cdot (right)$ .

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