

SUPPORTING INFORMATION

FOR

Mechanochemically directed metathesis in Group 2 chemistry: Calcium amide formation without solvent

*Isaiah R. Speight^a, Stephen C. Chmely^a, Timothy P. Hanusa^{*a},
and Arnold L. Rheingold^b*

^aDepartment of Chemistry, Vanderbilt University, VU Station B #351822,
Nashville, Tennessee 37235 USA

^bDepartment of Chemistry and Biochemistry, University of California,
San Diego, La Jolla, California 92093, USA

Experimental Synthetic Procedures	S2
Powder XRD Procedures and Data.....	S3
Figure S1: Powder XRD of Unextracted Milled Sample.....	S3
Figure S2: ¹ H NMR of [Ca(N(SiMe ₃) ₂) ₂] from a 1:1 CaI ₂ : [KN(SiMe ₃) ₂] reaction	S4
Table S1: Crystal Data and Summary of X-Ray Collection.....	S5

Experimental Synthetic Procedures

General Considerations. All manipulations were performed with the exclusion of air and moisture using standard glovebox techniques. Proton (^1H) NMR spectra were obtained on a Bruker AV-400 spectrometer at 400 MHz, and were referenced to the residual proton resonances of C_6D_6 . Elemental analysis was performed by ALS, Tucson, AZ.

Materials. Calcium iodide, chloride, bromide, fluoride and potassium hexamethyldisilazide were purchased from commercial suppliers and used as received. Toluene was degassed with argon and dried over activated alumina using a solvent purification system, then stored over 4A molecular sieves in a glovebox. Benzene- d_6 was obtained from Cambridge Isotopes and stored over 4A molecular sieves.

Mechanochemical protocol. Ball milling reactions used either 2 stainless steel (440 grade) ball bearings ($5/16$ in (8 mm), 3.5 g) or 50 stainless steel (440 grade) ball bearings ($3/16$ in (4.8 mm), 0.44 g) that were thoroughly cleaned with detergent and water, then washed with acetone, and dried in a 125 °C oven prior to use. Planetary milling was performed with a Retsch PM100 mill, 50 mL stainless steel grinding jar type C, and a safety clamp for air-sensitive grinding. Mixer milling was performed with a Retsch MM400 mill with a 15 mL stainless steel Formtech Smartsnap grinding jar taped shut for air-sensitive grinding. A typical reaction involved ca. 250 mg total sample weight (1:1 grinding reactions), sealed under an inert atmosphere. The ground mixture was extracted with minimal toluene (<70 mL) and filtered through a fine porosity ground glass frit. The extraction is designed to dissolve the complex, and the filtration removes traces of KI. The filtrate was then dried under vacuum prior to NMR analysis.

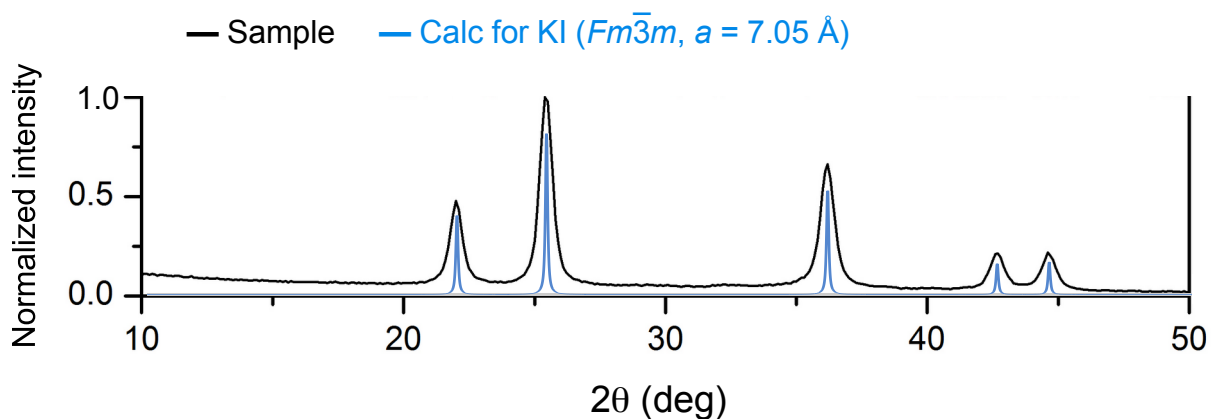
Typical preparation of $[\text{Ca}(\text{N}(\text{SiMe}_3)_2)_2]$. Details for a 1:1 reaction are given here. Inside a glovebox, CaI_2 (146.9 mg, 0.50 mmol) and $\text{K}[\text{N}(\text{SiMe}_3)_2]$ (99.7 mg, 0.50 mmol) were added to a 15 mL stainless steel milling jar with two 8 mm stainless steel ball bearings. The jar was closed tightly, sealed with electrical tape at the seam, brought out of the glovebox, and milled for 10 min at 30 Hz. The jar, still taped, was placed in a C-clamp and returned to the glovebox. When opened, the inside of the jar and balls were coated in a white powder that, when extracted with one ca. 30 mL portion of room temperature toluene and filtered through a fine-porosity ground glass frit, yielded a colorless filtrate. Removal of solvent under vacuum yielded a white solid (61 mg, 68% yield (w.r.t. limiting reagent)). The compound was identified by its characteristic NMR shift (A. M. Johns, S. C. Chmely, T. P. Hanusa, *Inorg. Chem.* 2009, **48**, 1380-1384). ^1H NMR (δ /ppm, 400 MHz, C_6D_6): 0.31 (SiMe_3).

Larger scale preparation of $[\text{Ca}(\text{N}(\text{SiMe}_3)_2)_2]$. Details for a scaled-up 1:1 reaction are given here. Inside a glovebox, CaI_2 (817 mg, 2.7 mmol) and $\text{K}[\text{N}(\text{SiMe}_3)_2]$ (554 mg, 2.7 mmol) were added to a 50 mL stainless steel grinding jar with 50 stainless steel ball bearings. The jar was

sealed with a safety clamp and milled for 10 minutes at 600 rpm. The reaction was then returned to the glovebox after milling. The jar was opened to reveal a white powder that was extracted with one 60 mL portion of room temperature toluene followed by a second 30 mL portion of the same. The extracts were filtered through a fine-porosity ground glass frit, yielding a colorless filtrate. Removal of solvent under vacuum left a white solid (423 mg, 84% yield (w.r.t. limiting reagent)). **¹H NMR** (C₆D₆, δ/ppm, 400 MHz): 0.31 (SiMe₃). Anal. Calcd for C₁₂H₃₆CaN₂Si₄ (i.e., Ca[N(SiMe₃)₂]₂): Ca, 11.11; K, 0; calcd for C₁₈H₅₄CaKN₃Si₆ (i.e., [KCa(N(SiMe₃)₂)₃]): Ca, 7.15; K, 6.98. Found: Ca, 11.54; K, 0.64.

X-ray Diffraction (XRD) Measurements. XRD analysis was performed on a Rigaku SmartLab diffractometer equipped with a Cu-K α radiation source and D/teX Ultra 250 detector operating at 40 kV and 44 mA. XRD samples were prepared by placing raw reaction powder onto a zero-background quartz holder.

Figure S1: Powder XRD of Unextracted Milled Sample (1 Ca₂ : 2 [KN(SiMe₃)₂])



IRS-2-134, planetary 1:1 $\text{CaI}_2:\text{KN}(\text{SiMe}_3)_2$

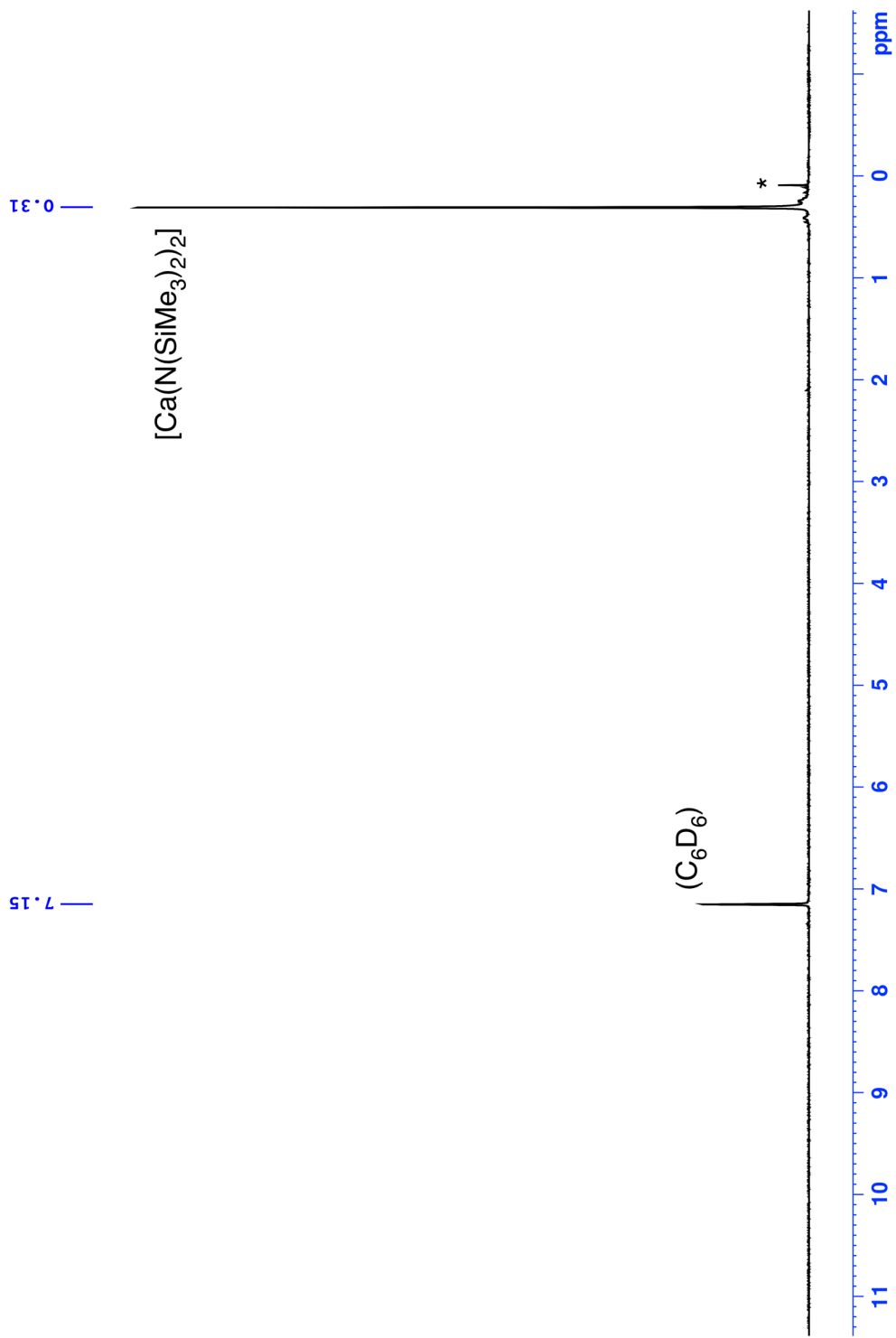


Figure S2. ^1H NMR of $[\text{Ca}(\text{N}(\text{SiMe}_3)_2)_2]$ *silicone grease

Table S1: Crystal Data and Summary of X-Ray Collection

Identification code	vand70	
Empirical formula	C ₁₈ H ₅₄ CaKN ₃ Si ₆	
Formula weight	560.36	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 8.6477(8)$ Å	$\alpha = 93.148(5)^\circ$
	$b = 11.2357(9)$ Å	$\beta = 91.419(2)^\circ$
	$c = 19.398(2)$ Å	$\gamma = 111.817(2)^\circ$
Volume	1745.0(3) Å ³	
Z	2	
Density (calculated)	1.066 g/cm ³	
Absorption coefficient	0.516 mm ⁻¹	
$F(000)$	612	
Crystal size	0.32 x 0.28 x 0.24 mm ³	
Crystal color, habit	Colorless block	
Theta range for data collection	1.96 to 27.01°	
Index ranges	-11 ≤ h ≤ 10, -14 ≤ k ≤ 14, 0 ≤ l ≤ 24	
Reflections collected	25 442	
Independent reflections	7444 [R(int) = 0.0000]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7444 / 0 / 263	
Goodness-of-fit on F^2	1.062	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0327$, $wR_2 = 0.0794$	
R indices (all data)	$R_1 = 0.0422$, $wR_2 = 0.0840$	
Largest diff. peak and hole	0.358 and -0.289 e Å ⁻³	
Twinning	Full rotational twin (50/50)	