Supporting Information for

Alkali Metal Oxides Encapsulated in Diethylzinc

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1. Synthesis

Starting Materials. Exercise caution as diethylzinc and reaction products are all pyrophoric! Diethylzinc (Zn 52 wt. %, neat), sodium hydroxide (reagent grade, 97%), potassium hydroxide (reagent grade, 90%), rubidium hydroxide·hydrate (Sigma Aldrich). All hydroxides were dried overnight using high vacuum and P_2O_5 prior to performing the reactions. We assume that there is still some water present, as hydroxides are difficult to dry. All reactions were performed under inert atmosphere using a glovebox or Schlenk techniques.

Synthesis of $Na_2(ZnEt_2)_3(\mu_5\text{-}O)$ (2). Method 1: 96 mg (2.4 mmol) of NaOH (ground with mortar and pestle and dried using the above procedure) was measured out and added to a 10 mL Schlenk tube containing 1.5 mL of diethylzinc (14.57 mmol) and a magnetic stir bar under inert N_2 atmosphere. After entering the diethylzinc, gas bubbles were observed. The temperature was raised to reflux (120°C). The bubbling of the gas was steady and the reaction was allowed to stir at refluxing temperatures for 2 hrs. Upon cooling to room temperature overnight, large crystals were observed to form on the sides of the Schlenk tube (see fig. S1). 117 mg of the product was isolated after filtration (leaving behind the darkened byproducts), rinsing with dry hexanes, and solvent removal via high vacuum corresponding to a yield of 23 % (0.5 equiv. **2** per 1 equiv. of NaOH).

Method 2: 96 mg (2.4 mmol) of NaOH (ground with mortar and pestle and dried using the above procedure) was measured out and added to a glass vial containing 2.0 mL of diethylzinc (19.43 mmol) and a magnetic stir bar. Shortly after addition of NaOH, small gas bubbles were observed and the reaction was allowed to stir for 2 hrs (if the mixture became too viscous or paste-like with solids, yield of product decreased to <15 mg of crystalline product in all r.t. experiments using NaOH). During this time white precipitate was observed to form in the reaction mixture making it more viscous. After two hours, the solution became thickened with precipitate which was difficult to filter from the remaining liquid. This clear solution of product in diethylzinc was added to one side of an H-tube (equal amount of dry hexanes was added to the other side) for crystallization by slow vapor diffusion. Colorless crystals were observed after 24 hours (room temperature). 65 mg of the product was isolated after filtration, rinsing with dry hexanes, and drying via high vacuum corresponding to 12.5 % yield. (0.5 equiv. **2** per 1 equiv. of NaOH). The lower yield can be rationalized due to the precipitation of product during the stirring period, which is filtered from the excess liquid used to grow high quality crystals.

Figure S1. Image of large crystals of **2** on the walls of a Schlenk tube.

Synthesis of $K_2(ZnEt_2)_4(\mu_6\text{-}O)$ (5). 135 mg (2.4 mmol) of KOH (ground with mortar and pestle and dried using the above procedure) was measured out and added to a glass vial containing 1.5 mL of diethylzinc (14.57 mmol) and a magnetic stir bar. The reaction was stirred for 2 hrs. inside of a glovebox under an inert N_2 atmosphere. During the stirring period, bubbles were observed in the reaction (evolution of gas). The liquid was passed through a filter leaving behind any solids formed during the reaction or any unreacted KOH (most of the solids agglomerated into larger lumps which could be separated easily before filtration). The clear, filtered liquid was carefully added to one side of an H-tube. Dry hexanes was then added (equal to the amount of clear, filtered liquid from the reaction) to the other side of the H-tube before sealing it and allowing for it to remain in the glovebox for crystallization. Colorless crystals were observed to form after 24 hours (at room temperature). 126 mg of the product was isolated after filtration, rinsing with dry hexanes, and drying via high vacuum corresponding to a yield of 18 % (0.5 equiv. **5** per 1 equiv. of KOH).

Crystallizations were also performed in standard NMR tubes by layering dry hexanes on top of the clear, filtered liquid from the reaction. Each method was found to yield large crystals.

Figure S2. Image of large clear crystals of **5** grown in an NMR tube.

Synthesis of $Rb_2(ZnEt_2)_4(\mu_6\text{-}O)$ (6). 100 mg (0.976 mmol) of $RbOH\cdot H_2O$ (dried using the above procedure) was measured out and added to a plastic disposable centrifuge tube (tested for compatibility with diethylzinc prior to running the experiment) containing 2.0 mL of diethylzinc (19.43 mmol) and a magnetic stir bar. The reaction was stirred for 2 hrs. within the glovebox under inert N_2. During the stirring period, bubbles were observed in the reaction. After stirring for 2 hours, the liquid was passed through a filter leaving behind any solids (like the KOH reaction, most of the solids agglomerated into larger lumps which could easily be separated from the excess liquid) formed during the reaction or any unreacted RbOH. The clear, filtered liquid was carefully added to one side of an H-tube. Dry hexanes was then added (equal to the amount of clear, filtered liquid from the reaction) to the other side of the H-tube before sealing it and allowing for it to remain in the glovebox for crystallization. Colorless crystals were observed after 24 hrs (room temperature). 58 mg of the product was isolated after filtration, rinsing with dry hexanes, and drying via high vacuum corresponding to a yield of 17 % (0.5 equiv. **6** per 1 equiv. of RbOH).

Crystals were also grown in NMR tubes by layering dry hexanes on top of the clear, filtered liquid from the reaction. Each method was found to yield large clear crystals.

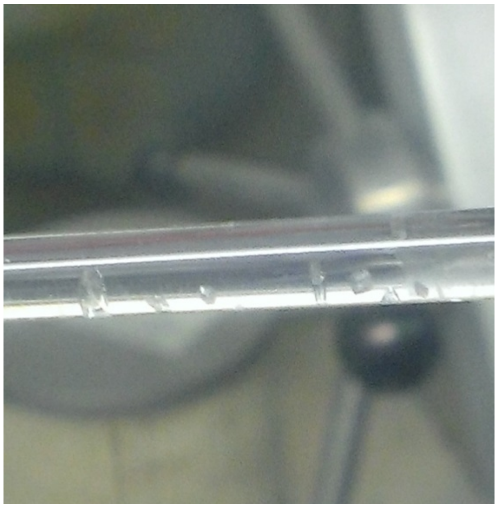

Figure S3. Image of large clear crystals of **6** grown in an NMR tube.

2. Nuclear Magnetic Resonance Spectroscopy

Crystals of each material were selected and dried using high vacuum techniques. In the glovebox, crystals were dissolved in d8-THF (99.5 atom % D) fresh from an argon-blanketed ampule. The samples were then transferred to clean, dry NMR tubes and sealed with a rubber septum which was also covered with parafilm to help slow decomposition (formation of ethane observed in extended ^{13}C runs at ~4.12 ppm and ^{1}H spectra at 0.85 ppm) by adventitious oxygen/moisture. All experiments were carried out on a Bruker AVANCE III 600 MHz spectrometer at frequencies of 600 MHz and 151 MHz for ^{1}H and ^{13}C, respectively. In each proton spectrum, the peaks are referenced to d8-THF (3.58 ppm). See additional PDF file for all spectra obtained.

$Na_2(ZnEt_2)_3(\mu_5\text{-}O)$ **(2)**: ^{1}H NMR (600 MHz, THF-d8): $\delta = 1.2$ (t, CH_3), -0.25 (q, CH_2).^{13}C NMR (151 MHz, THF-d8): $\delta = 9.64$ (CH_3), 0.00 (CH_2).

$K_2(ZnEt_2)_4(\mu_6\text{-}O)$ **(5)**: ^{1}H NMR (600 MHz, THF-d8): $\delta = 1.18$ (t, CH_3), -0.21 (q, CH_2).^{13}C NMR (151 MHz, THF-d8): $\delta = 11.97$ (CH_3), 3.16 (CH_2).

$Rb_2(ZnEt_2)_4(\mu_6\text{-}O)$ **(6)**: ^{1}H NMR (600 MHz, THF-d8): $\delta = 1.18$ (t, CH_3), -0.19 (q, CH_2).^{13}C NMR (151 MHz, THF-d8): $\delta = 13.55$ (CH_3), 5.07 (CH_2).

3. X-Ray Crystallography

All crystals were selected and mounted in an N_2-filled glove box. A single crystal of **2** or **5** was placed on a cryoloop (Hampton Research) using a minimum amount of Paratone-N oil (Hampton Research), and the cryoloop was tightly closed with a plastic cylinder. The assembly was taken out of the glove box, and the cryoloop with the crystal was opened and quickly transferred onto a goniometer head of the Bruker AXS SMART diffractometer equipped with an APEX-II CCD detector. In the case of **6**, the crystal was mounted into a glass capillary that was sealed on both ends before being removed from the glove box. Each crystal was cooled in a stream of cold N_2 gas to the desired data collection temperature. The data sets were recorded as ω-scans at 0.3° stepwidth and integrated with the Bruker SAINT software package.[S1] In all the experiments, a multi-scan adsorption correction was applied based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements (SADABS).[S2] The space group determination was performed with XPREP,[S3] while the solution and refinement of the crystal structures were carried out using the SHELX programs.[S4] The final refinement was performed with anisotropic atomic displacement parameters for all but H atoms. All H atoms were placed in calculated positions. A summary of pertinent information relating to unit cell parameters, data collection, and refinements is provided in Table S1.

S1. Bruker, *SMART and SAINT*; Bruker AXS Inc.: Madison, WI, USA, **2007**.

S2. Sheldrick, G. M. *SADABS*; University of Gottingen: Gottingen, Germany, **1996**.

S3. Sheldrick, G. M. *XPREP. Space group determination and reciprocal space plots.* Siemens Analytical X-ray Instruments: Madison, WI, USA, **1991**.

S4. G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *A64*, 112.

Table S1. Data collection and structure refinement parameters for compounds **2**, **5**, and **6**.

Formula	$Na_2Zn_3OC_{12}H_{30}$ (**2**)	$K_2Zn_4OC_{16}H_{40}$ (**5**)	$Rb_2Zn_4OC_{16}H_{40}$ (**6**)
CCDC number	988444	988445	988446
Space group	*P*6$_5$22	*P*4/*nnc*	*P*4/*nnc*
Unit cell parameters, Å and deg	*a* = 8.7801(5) *c* = 43.327(2)	*a* = 9.027(2) *c* = 14.145(3)	*a* = 9.446(3) *c* = 14.199(5)
V, Å^3	2892.6(4)	1152.6(5)	1266.8(9)
Z	6	2	2
Temperature	173 K	173 K	260 K
Crystal shape	block	block	block
Crystal color	colorless	colorless	colorless
Crystal size	0.15×0.12×0.08	0.30×0.28×0.21	0.55×0.35×0.30
λ, Å	0.71073 (Mo$K\alpha$)	0.71073 (Mo$K\alpha$)	0.71073 (Mo$K\alpha$)
ρ_{calc}, g cm^{-3}	1.490	1.695	1.785
μ, mm^{-1}	3.734	4.473	7.559
$2\theta_{\max}$, deg	28.29	28.14	28.21
Reflections collected	18994	5225	7169
R_{int}	0.025	0.030	0.063
Unique reflections	2329	697	774
Parameters refined	105	30	30
Restraints used	0	0	0
R_1, wR_2 [$F_o > 4\sigma(F_o)$]	0.023, 0.051	0.019, 0.038	0.047, 0.106
Goodness-of-fit	1.153	1.100	1.008
Diff. peak and hole, e/Å^3	0.24 and –0.35	0.46 and –0.22	0.54 and –0.45
Flack parameter	0.03(3)	–	–