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Convenient Access to Homo- and Heterobimetallic Alkoxo Hydridozinc Clusters of Formula $[(HZnO\textit{t}Bu)_{4-n}(LiO\textit{t}Bu)_n]$ ($n = 0, 1, 2, 3$)

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Summary: A convenient and efficient route to the stable and soluble alkoxo hydridozinc clusters $\{[HZnOtBu]_3[Li(thf)OtBu]\}$, $\{[HZnOtBu]_2[Li(thf)OtBu]_2\}$, *and* $\{[HZnOtBu][Li(thf)OtBu]_3\}$ *is described by cluster core metathesis reactions between* $[HZnOtBu]_4$ *and [LiOtBu] aggregates in THF solutions. They are the first examples of alkoxo hydridozinc clusters structurally characterized and consist of heterocubane cores.*

The study of transition metal hydride compounds remains an extremely active area of chemical research.[1] This interest stems not only from their broad range of reactivity but also from their structural and spectroscopic properties.[2] Reduction of carbonyl compounds with metal hydride reagents has been widely utilized in organic synthesis, and numerous hydride systems have been developed. Many of them utilize zinc species or in particular zinc hydride derivatives such as alkali metal hydridozinc*ate* complexes.[3] Because ZnH_2 and HZnX (X = halides, alkyl), respectively, are inconvenient reagents due to their nonsolubility and instability, they are commonly synthesized in situ, starting from ZnX_2 (X = halide, alkyl) and alkali metal hydrides. They have found remarkable broad applications in stereoselective hydrozincations of unsaturated hydrocarbons.[4] However, neither a structure of a reactive intermediate in the aforementioned reactions involving zinc hydrides nor the nature of the active species could hitherto be identified unequivocally. Thus there is an enormous interest in gaining access to soluble and well-defined homo- and heterobimetallic hydridozinc species for extension of application fields using Zn−H species (e.g., stereoselective catalytic reductions). One promising class of structurally versatile and soluble Zn−H species represents alkoxo hydridozinc compounds, [HZnOR]. Our experiences in synthesizing homo- and heterobimetallic alkoxo alkylzinc heterocubane clusters of the type $[(RZnO\textit{t}Bu)_{4-n}(MO\textit{t}Bu)_n]$ (M = alkali metal, $n = 1, 2, 3$) and their use as metal organic single-source precursors for nanoscaled and heterometal-doped ZnO materials[5−7] prompted us to explore whether the related homo-

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(1) (a) Paneque, M.; Poveda, M. L.; Taboada, S. *J. Am. Chem. Soc.* **1994**, *116*, 4519. (b) Shapiro, P. J.; Cotter, W. D.; Schefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 623.

(2) (a) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (b) Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, G. R. K.; Jackson, S. A.; Eisenstein, O. J. *J. Am. Chem. Soc.* **1993**, *115*, 569, and references therein.

(3) (a) Aida, T,; Kuboki, N.; Kato, K.; Uchikawa, W.; Matsuno, C.; Okamoto, S. *Tetrahedron Lett.* **2005**, *46*, 1667. (b) Mimoun, H.; de Saint Laumer, J. Y.; Giannini, L.; Scopelliti, R.; Floriani, C. *J. Am. Chem. Soc.* **1999**, *121*, 6158. (c) Uchiyama, M.; Furumoto, S.; Saito, M.; Kondo, Y.; Sakamoto, T. *J. Am. Chem. Soc.* **1997**, *119*, 11425. (d) Ohkuma, T.; Hashiguchi, S.; Noyori, R. *J. Org. Chem.* **1994**, *59*, 217.

(4) Gao, Y.; Harada, K.; Hata, T.; Urabe, H.; Sato, F. *J. Org. Chem.* **1995**, *60*, 290, and references therein.

(5) (a) Driess M.; Merz, K.; Rell, S. *Eur. J. Inorg. Chem.* **2000**, 2517. (b) Driess, M.; Lu, L.; Merz, K. *Eur. J. Inorg. Chem.* **2003**, 51.

(6) Merz, K.; Block, S.; Schoenen, R.; Driess, M. *Dalton Trans.* **2003**, *17*, 3365.

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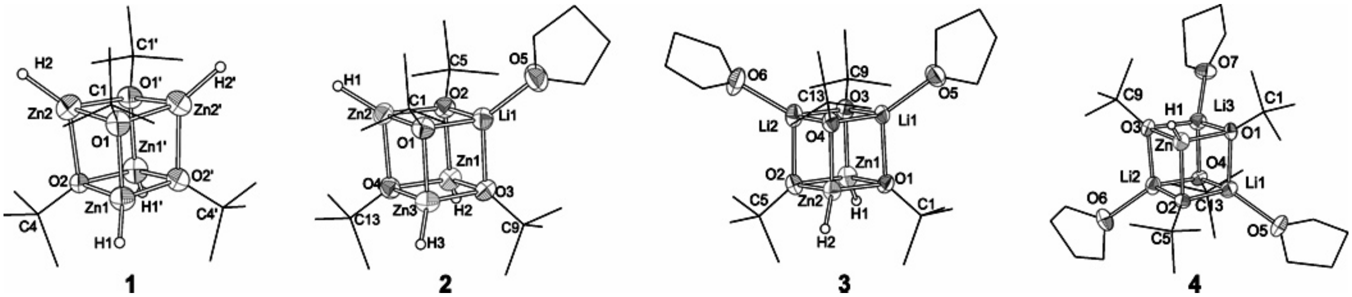
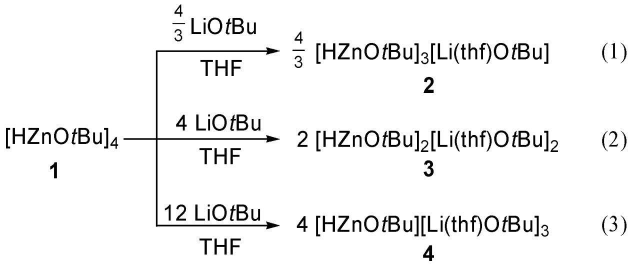


Figure 1. ORTEP view of **1**, **2**, **3**, and **4** with thermal ellipsoids drawn at the 50% probability level. The H atoms were omitted for clarity, except for the H atoms at zinc. Selected distances and angles: see Supporting Information.

and heterobimetallic alkoxo hydridozinc clusters $[(HZnO\textit{t}Bu)_{4-n}(MO\textit{t}Bu)_n]$ are accessible in an analogous manner, starting from ZnH_2, *t*BuOH, and *t*BuOM. ZnH_2 is a metastable compound that can be synthesized by the reaction of dimethylzinc with a diethyl ether solution of lithium tetrahydridoalanate.[8] Watkins and Ashby prepared ZnH_2 by reacting alkali metal hydrides with zinc halides in THF, but it was found difficult to obtain analytically pure ZnH_2.[9] To our knowledge, the best method described so far is the reaction of AlH_3•thf with Me_2Zn.[10] Neils and Burlitch already reported the reaction of *t*BuOH with ZnH_2, affording the tetrameric cluster $[HZnO\textit{t}Bu]_4$, which has merely been characterized by ^1H NMR spectroscopy and FAB-MS.[11] Similarly, $Me_2N(CH_2)_nOH$ ($n = 2$, 3) reacts with ZnH_2 to furnish dinuclear aggregates, but none of the products have been characterized structurally.[12] Up to now, only a few organonitrogen-substituted hydridozinc complexes have been characterized structurally, namely, $[HZnN(Me)(CH_2)_2NMe_2]_2$,[13] $[\{\eta_3\text{-}HB(3\text{-}RC_3N_2H_2)_3\}ZnH]$,[14] $[(Me_3PN)ZnH]_4$•THF,[15] and $[\{HC(CMeNAr)_2\}Zn(\mu\text{-}H)]_2$.[16] Here we report the convenient isolation and first structural characterization of a series of soluble alkoxo hydridozinc clusters with a cubane-like core, starting from $[HZnO\textit{t}Bu]_4$, **1**. The latter undergoes HZn/Li exchange reactions in the presence of [LiO*t*Bu] in THF solutions under retention of a cubic $[M_4O_4]$ cluster core. The homonuclear starting material **1** has been prepared in high yield according to the literature procedure[3] and recrystallized from THF, affording colorless crystals suitable for X-ray single-crystal determination, which proves the anticipated tetrameric structure (Figure 1). Compound **1** consists of a centrosymmetric cubic $[Zn_4O_4]$ cluster core. The Zn−O distances and Zn−O−Zn angles are similar to the values observed for the tetrameric alkoxo methylzinc derivative $[MeZnO\textit{t}Bu]_4$.[17] The positions of the Zn−H hydrogen atoms have been observed directly and refined. The Zn−H distances of 1.49(8) and 1.55(7) Å are inconspicuous in comparison with those in $[(Me_3PN)ZnH]_4$• THF[15] and $[HZnN(Me)(CH_2)_2NMe_2]_2$ (Zn−H: 1.42 to 1.67 Å).[13] Cryoscopic measurements prove that **1** retains its tetrameric aggregation in benzene solutions. Encouraged by previous results where we showed that the zinc atoms in $[Zn_4O_4]$ heterocubane cores in alkoxo alkylzinc tetramers can by replaced by alkali metal atoms M to give $[Zn_{4-n}M_nO_4]$ cores, we decided to investigate the possibility of cluster core metathesis between **1** and $[(LiO\textit{t}Bu)_n]$ aggregates ($[Li_6O_6]$ and $[Li_8O_8]$ cores in the solid state).[18] However, no HZn/Li cluster exchange reaction occurs in toluene at room temperature (^1H NMR), presumably because of the relatively high stability of **1** and the $[(LiO\textit{t}Bu)_n]$ aggregates in aromatic solvents. This situation is immediately changed if THF is used as a polar solvent. In fact, the heterobimetallic cluster $\{[HZnO\textit{t}Bu]_3[Li(thf)O\textit{t}Bu]\}$ (**2**) is readily obtainable in quantitative yield at ambient temperature by reaction of **1** with [LiO*t*Bu] in the molar ratio of 3:4 (Scheme 1, eq 1).

Scheme 1. Synthesis of 2, 3, and 4 by HZn/Li Alkoxide Cluster Exchange Reactions



Crystallization in THF at −18 °C affords colorless crystals of **2** suitable for single-crystal X-ray diffraction analysis (Figure 1). The IR and ^1H NMR spectra of **2** show resonances at 1793 cm^{-1} and 4.62 ppm, respectively, that can clearly be attributed to the Zn−H group. These values compare well to those found for $[Me_2NC_2H_4OZnH]_2$[12] (1740, 1650 cm^{-1} and 4.47 ppm). The δ ^1H values of the signals of the two different O*t*Bu-groups (1.46 (27H) vs 1.65 ppm (9H)) are similar to those observed for related heterobimetallic alkali metal−zinc alkoxides.[6] Remarkably, increasing the molar ratio of [LiO*t*Bu]:**1** to 4:1 and

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(7) (a) Merz, K.; Schoenen, R.; Driess, M. *J. Phys. IV Fr.* **2001**, *11*, 467. (b) Driess, M.; Merz, K.; Schoenen, R.; Rabe, R.; Kruis, F. E.; Roy, A.; Birkner, A. *C. R. Acad. Sci, Chim.* **2003**, *6* (3), 273. (c) Hambrock, J.; Rabe, S.; Merz, K.; Wohlfarth, A.; Birkner, A.; Fischer, R. A.; Driess, M. *J. Mater. Chem.* **2003**, *13*, 1731. (d) Kurtz, M.; Bauer, N.; Buescher, C.; Wilmer, H.; Hinrichsen, O.; Becker, R.; Rabe, S.; Merz, K.; Driess, M.; Fischer, R. A.; Muhler, M. *Catal. Lett.* **2004**, *92*, 49. (e) Polarz, S.; Roy, A.; Merz, M.; Halm, S.; Schröder, D.; Schneider, L.; Bacher, G.; Kruis, F. E.; Driess, M. *Small* **2005**, *1*, 2. (f) Ischenko, V.; Polarz, S.; Grote, D.; Stavarache, V.; Fink, K.; Driess, M. *Adv. Funct. Mater.* **2005**, *15*, 1945. (g) Schröder, D.; Schwarz, H.; Polarz, S.; Driess, M. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1049.

(8) Barabaras, G. D.; Dillard, C.; Finholt, A. E.; Wartlik, T.; Wilzbach, K. E.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1951**, *73*, 4585.

(9) Watkins, J. J.; Ashby, E. C. *Inorg. Chem.* **1974**, *13*, 2350.

(10) Ashby, E. C.; Watkins, J. J. *Inorg. Synth.* **1977**, *17*, 6.

(11) Neils, T. L.; Burlitch, J. M. *Inorg. Chem.* **1989**, *28*, 1607.

(12) (a) Bell, N. A.; Kassyk, A. L. *J. Organomet. Chem.* **1988**, *345*, 245. (b) Goeden, G. V.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 7354.

(13) Bell, N. A.; Moseley, P. Z.; Shearer, H. M. M.; Spencer, C. B. *J. Chem. Soc., Chem. Commun.* **1980**, 359.

(14) Han, R.; Gorrell, I. B.; Looney, A. G.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1991**, 717.

(15) Krieger, M.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1563.

(16) Hao, H.; Cui, C.; Roesky, H. W.; Bai, G.; Schmidt, H.-G.; Noltemeyer, M. *Chem. Commun.* **2001**, 1118.

(17) Herrmann, W. A.; Bagdanovic, S.; Behm, J.; Denk, M. *J. Organomet. Chem.* **1992**, *430*, C33.

(18) (a) Allan, J. F.; Nassar, R.; Specht, E.; Beatty, A.; Calin, N.; Henderson, K. W. *J. Am. Chem. Soc.* **2004**, *126*, 484. (b) Nekola, H.; Olbrich, F.; Behrens, U. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2076, and references therein.

12:1, respectively, leads to the formation of the desired heterobimetallic alkoxo lithium hydridozinc clusters **3** and **4** in quantitative yield, respectively (Scheme 1, eqs 2, 3). Thus, colorless crystals of the new clusters {[HZnO*t*Bu]$_2$[Li(thf)-O*t*Bu]$_2$} (**3**) and {[HZnO*t*Bu][Li(thf)O*t*Bu]$_3$} (**4**) suitable for X-ray diffraction analyses (Figure 1) have been isolated. Alternatively, **4** is also accessible in quantitative yield by the reaction of [Li$_3$ZnH$_5$][19] with 4 molar equiv of *t*BuOH. Interestingly, when crystalline **4** is dissolved in cyclohexane (or in other aprotic nonpolar solvents), crystals of **3** are formed immediately and the remaining solution contains only [LiO*t*Bu] (^{1}H NMR). Apparently, the degradation of **4** to **3** and [(LiO*t*Bu)$_n$] aggregates in a nonpolar medium is due to the lower polarity of the [Li$_2$-Zn$_2$O$_4$] framework and entropy contributions. The heterobimetallic clusters **3** and **4** have also been characterized by ^{1}H NMR, IR absorption, combustion analysis (see Supporting Information), and X-ray diffraction (Figure 1). Their resonance signals in the ^{1}H NMR and IR spectra are similar to those of **2**. Variable-temperature ^{1}H NMR studies of **2**, **3**, and **4** (from −70 to 28 °C in THF-d_8) did not show any significant changes of the spectra. This may indicate fast exchange and equilibria on the NMR time scale. The molecular structures of **1**, **2**, **3**, and **4** (Figure 1) are closely related, as all show distorted heterocubane cores. **2** crystallizes in the monoclinic space group $P2_1/n$ with a distorted [LiZn$_3$O$_4$] framework where the lithium atom coordinates in addition an THF ligand. The average Zn−O distances and Zn−O−Zn angles of the cubic [LiZn$_3$O$_4$] moiety resemble those determined for **1**. However, the Li−O(thf) distance (1.98 Å) in **2** is slightly shorter than that determined for {[MeZnO*t*Bu]$_2$[Li(thf)O*t*Bu]$_2$} (Li−O: 2.059 Å).[20] The Zn−H distances in **2** (1.41(5) and 1.50(4) Å) and **3** (1.49(5) and 1.54(4) Å) are similar to those described for **1** and other Zn−H complexes.[13−16] The molecular structure of **3** can be regarded as a hydrido analogue of {[MeZnO*t*Bu]$_2$[Li(thf)-O*t*Bu]$_2$},[20] which shows similar geometric features. The molecular structure of **4** consists of a [Li$_3$ZnO$_4$] cubic core with only one terminal Zn−H bond (1.61(4) Å), which is only slightly longer than that in **1**, **2**, and **3**.

In conclusion, we have provided a convenient route to soluble and well-defined alkoxo hydridozinc clusters by core metathesis reaction of the [Zn$_4$O$_4$] framework in **1** with LiO*t*Bu aggregates in THF solutions. The Zn:Li ratio can be tailored by using the appropriate molar ratio of the starting materials. The compounds **1**, **2**, **3**, and **4** are the first alkoxo hydridozinc derivatives that have been characterized structurally. Efficient access to these compounds now opens new opportunities to study their reactivity in organic synthesis and materials chemistry.

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Supporting Information Available: Experimental details for the synthesis and spectroscopic data of **1**, **2**, **3**, and **4** (PDF); crystallographic data for **1**, **2**, **3**, and **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] Ashby, E. C.; Watkins, J. J. *Inorg. Chem.* **1973**, *12*, 2493.

[20] Davies, R. P.; Linton, D. J.; Schooler, P.; Snaith, R.; Wheatley, A. E. H. *Chem. Eur. J.* **2001**, *7*, 3696.