

Synthesis of Homoleptic Barium Alkoxides and Aryloxides and Their Reactions with $\text{Al}(\text{CH}_3)_3$: a Convenient Route to Heterometallic Species

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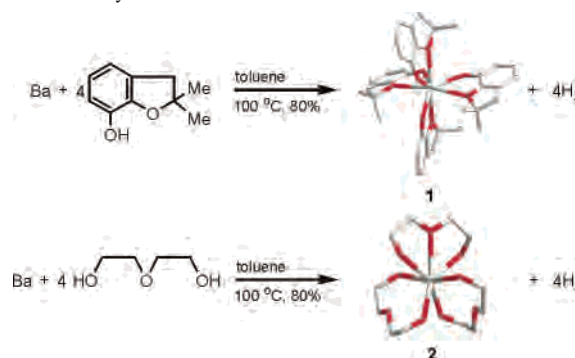
Received March 1, 2005

Reactions of metallic Ba with benzofuranol (dbbfoH) or diethylene glycol give homoleptic and homonuclear complexes $\text{Ba}(\text{dbbfo})_2$ – $(\text{dbbfoH})_2 \cdot 3\text{dbbfoH}$ and $\text{Ba}\{\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\}\{\text{O}(\text{CH}_2\text{CH}_2\text{OH})_2\}_2$ (60–89%). Both compounds and formerly described $\text{Ba}\{\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{Me}\}_2$ react with $\text{Al}(\text{CH}_3)_3$ to yield trinuclear heterobimetallic low-coordinated barium compounds with structure and geometry depending on the reaction stoichiometry and crystallization procedure.

Heavier alkaline-earth metal complexes remain in the zone of growing interest because of their potential as precursors for materials of numerous applications. These metal alkoxides and aryl oxides especially with low nuclearity, high thermal stability, and volatility are highly desirable for the preparation of superconducting thin films by metal organic chemical vapor deposition.¹ Lately, they also find increasing utility as catalysts, e.g., for dehydrogenative coupling of hydrosilanes with terminal alkynes² or polymerization of lactones.³ In turn, heterometallic alkoxides⁴ are precursors to numerous ceramic materials.

Numerous barium alkoxides and aryloxides have been synthesized to date.⁵ Unfortunately, they are usually oxo species forming large aggregates. The first structurally characterized homoleptic tetrabarium alkoxide was reported in 1994 by Caulton et al.^{6a} In 2002, Chi and co-workers presented a structure of Ba with a four-coordinated polyether-

Scheme 1. Syntheses of 1 and 2



substituted fluoro alcohol.^{6b} To our knowledge, no other structures of homoleptic barium alkoxides have been reported since then. The population of structurally characterized heterometallic Ba compounds with alkoxo ligands is much bigger. Among the most investigated are Ba/Cu^{7,8b} and Ba/Y⁸ because of their physical properties and applicability, although today, organometallic Ba-containing compounds have become more and more interesting in this context.⁹

In this communication, we report the syntheses and partial characterization of a series of homoleptic mononuclear as well as heterobimetallic Ba compounds.

As shown in Scheme 1, an excess of O,O'-coordinating 2,3-dihydro-2,2-dimethyl-7-benzofuranol (dbbfoH), already utilized in our research,¹⁰ was combined with metal Ba under

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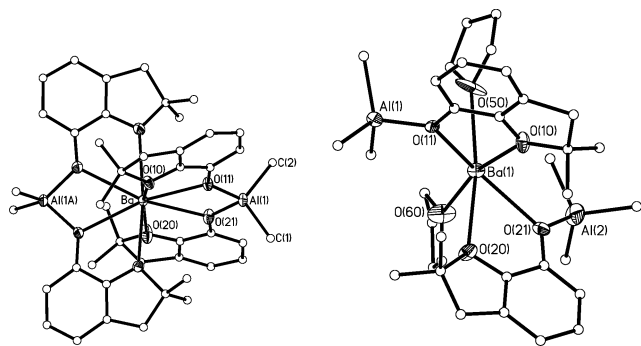


Figure 3. ORTEP views of **3** and **4**.

CH_3 /tetrahydrofuran (THF) mixture resulted in six-coordinated Ba complex $\text{Ba}\{\mu\text{-dbbfo}\}\text{Al}(\text{CH}_3)_3\}_2(\text{THF})_2$ (**4**).¹⁶ Here $\text{Al}(\text{CH}_3)_3$ simply coordinates to oxygen atoms. Figure 3 shows molecules of **3** and **4**.

(16) Crystallographic data for **4**: $\text{C}_{34}\text{H}_{56}\text{Al}_2\text{BaO}_6 \cdot 0.5\text{C}_7\text{H}_8$, FW = 798.16, monoclinic, $P2_1$, $a = 10.698(3)$ Å, $b = 38.025(6)$ Å, $c = 10.968(3)$ Å, $\beta = 97.99(3)^\circ$, $V = 4418.4(19)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 1.200$ g/cm³, $\mu = 0.975$ mm⁻¹, $R_1 = 0.0678$, $wR_2 = 0.1323$, GOF = 0.931.

A similar result was obtained in the reaction of previously reported $\text{Ba}\{\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{Me}\}_2$ ^{5c} with $\text{Al}(\text{CH}_3)_3$. Also in this case the reaction led to six-coordinated heterotrimetallic adduct $\text{Ba}\{\mu\text{-(Me)O}(\text{CH}_2\text{CH}_2\text{O})_2\text{Al}(\text{CH}_3)_2\}_2$ (**5**).

In conclusion, we have presented an easy and high-yield synthetic strategy to access homoleptic barium alkoxides. In these complexes, in order to satisfy the coordination requirements of the large Ba atom, usually neutral alcohol molecules are coordinated. We have demonstrated that they can easily be modified with metal organometallics into heterometallic alkoxides, potentially useful in material science. In future research, reagents other than $\text{Al}(\text{CH}_3)_3$ organometallic reagents will be tried in similar reactions.

Acknowledgment. We thank the Polish State Committee for Scientific Research (Grant 3 T09A 158 26) for support of this research.

Supporting Information Available: Text and tables giving experimental and crystallographic details. Crystallographic data are also available as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0503129