Inorg. Chem. **2008**, *47*, 5971−5977

Inorganic Chemistry
Article

A Reactivity Change of a Strontium Monohydroxide by Umpolung to an Acid

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Received February 15, 2008

Controlled hydrolysis of strontium amide $LSrN(SiMe_3)_2(thf)$ ($L = CH(CMe2,6\text{-}i\text{-}Pr_2C_6H_3N)_2$) (**1**) gave an unprecedented example of a hydrocarbon-soluble strontium hydroxide, $[LSr(thf)(\mu\text{-}OH)_2Sr(thf)_2L]$ (**2**). In compound **2**, the tetrahydrofuran (THF) molecules can easily replaced by benzophenone and triphenylphosphine oxide to yield $[LSr(\mu\text{-}OH)(OCPh_2)]_2$ (**3**) and $[LSr(\mu\text{-}OH)(OPPh_3)]_2$ (**4**) compounds. Among the two strontium atoms of **2**, one is coordinated to a single THF molecule, while the other is coordinated to two THF molecules. Interestingly, strontium hydroxide complex **2** behaves as an acid in its reaction with $Zr(NMe_2)_4$ and results in a heterobimetallic oxide, $[LSr(\mu\text{-}O)Zr(NMe_2)_3]_2$ (**5**). Compound **5** is dimeric in the solid state and contains a $Sr_2Zr_2O_2$ core.

Introduction

The so-called water effect in organometallic compounds has resulted in the formation of various interesting hydroxide complexes.[1] The reaction of these hydroxides with suitable metal precursors generally leads to the formation of polymetallic oxides[2] that are emerging as an important class of compounds due to their potential application in catalysis.[3] Therefore, we have prepared various p-block hydroxides and have been successful in assembling novel heterobi- and heteropolymetallic oxides by utilizing the acidic character of these hydroxide complexes.[4] For example, the heterodimetallic compound $LAl(Me)(\mu\text{-}O)Zr(Me)Cp_2$ ($L = CH(CMe2,6\text{-}i\text{-}Pr_2C_6H_3N)_2$) has been obtained by the reaction of $LAl(Me)OH$ with Cp_2ZrMe_2, and we have demonstrated that it is a versatile catalyst in ethylene polymerization.[5] Also, the cubic silicon−titanium μ-oxo complex obtained by the reaction of an aminosilanetriol with $Ti(OEt)_4$ showed excellent catalytic activity in the epoxidation of cyclohexene and cyclooctene by *t*-butyl hydroperoxide.[6] In view of this importance, one may think of a possible extension of these principles to group 2 elements. Nevertheless, two major issues that need to be addressed are the synthesis of stable and soluble group 2 hydroxides and the basicity of these hydroxides. The preparation of group 2 hydroxides, mainly those with heavier metals, is difficult (due to the large atomic radii and high ionic character of these elements),[7] and

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10.1021/ic800284u CCC: $40.75

consequently only a few group 2 hydroxide complexes are reported. Two hydroxide complexes for magnesium[8] and one example for calcium[9] are known. Apart from the magnesium hydroxide complex $\{[Tp^{Ar,Me}]Mg(\mu\text{-}OH)\}_2$ (stabilized by tris(1-pyrazolyl)hydroborate ligand ($Tp^{Ar,Me}$); Ar = p-$t$$BuC_6H_4$), the other two examples have been obtained by exploiting the unique property of the β-diketiminato ligand, L. All of these complexes are dimeric in the solid state and contain coordinated tetrahydrofuran (THF) molecules except $\{[Tp^{Ar,Me}]Mg(\mu\text{-}OH)\}_2$.[8a] They can be exchanged with other donors such as benzophenone.[9] Surprisingly, no reactivity study based on these complexes has been reported. Group 2 metals except Be react with water and form metal hydroxides by the elimination of hydrogen gas. These metal hydroxides exist as $M_{(aq)}^{2+}$ and $OH_{(aq)}^{-}$ ions in aqueous solution. The basic strength increases within this group from Mg to Ba and can be determined by pH measurements. This basic knowledge informs us that the aforementioned group 2 hydroxide complexes might behave as a base. To shed light into this issue and to find out the exact nature of the OH functionality in these complexes, we prepared a novel strontium hydroxide complex, $[LSr(thf)(\mu\text{-}OH)_2Sr(thf)_2L]$ (**1**), by the controlled hydrolysis of strontium amide and carried out a series of experiments on this hydroxide.

Herein, we report the first molecular hydrocarbon-soluble strontium monohydroxide, **2**, and a heterobimetallic compound, $[LSr(\mu\text{-}O)Zr(NMe_2)_3]_2$ (**5**), obtained by the reaction of strontium hydroxide **2** with $Zr(NMe_2)_4$, where compound **2** behaves as an acid instead of its expected reactivity as a base. Such an umpolung is unprecedented in group 2 hydroxide chemistry.

Results and Discussion

The reaction of LH with 2 equiv of $KN(SiMe_3)_2$ in THF was carried out for 5 h. Addition of this reaction mixture to a slurry of SrI_2 in THF at room temperature led to the formation of the strontium amide, $LSrN(SiMe_3)_2(thf)$ (**1**), as colorless crystals (77.9% yield). Compound **1** is soluble in a number of organic solvents. It has been well-characterized by mass spectrometry, NMR spectroscopy (^1H, ^{13}C, and ^{29}Si), X-ray single-crystal structure analysis, and elemental analysis. The ^1H and ^{29}Si NMR spectra of compound **1** show a singlet (0.14 ppm) for trimethylsilyl protons and a singlet (−15.95 ppm) for the trimethylsilyl silicon atoms, respectively. The molecular ion peak corresponding to **1** was not observed in its electron impact (EI) mass spectrum. Colorless crystals of **1** suitable for structural analysis were obtained when a concentrated solution of **1** in n-hexane was allowed to stand at room temperature for 12 h.

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with a molecule of THF coordinated to the metal center. The structure of **1** (Figure 1) confirms the presence of a six-membered C_3N_2Sr ring. This ring has an envelope conformation with the strontium atom at a distance of 0.724 Å above the plane of the planar C_3N_2 framework. This can be compared with the magnesium and calcium amides where the respective metals are at a distance of 0.428 and 1.206 Å, respectively, above the plane of the planar C_3N_2 framework.[10,11] The Sr center is four-coordinate with two nitrogen atoms of the β-diketiminate ligand, a nitrogen atom of the amide moiety, and an oxygen atom of the THF. The strontium atom has a distorted tetrahedral geometry, while that around the nitrogen atom of the amide is trigonal-planar.

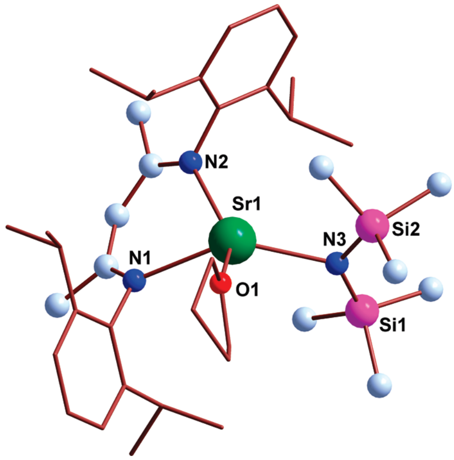

Figure 1. Crystal structure of **1**. All of the hydrogen atoms have been omitted for clarity.

Controlled hydrolysis of amide **1** with a stoichiometric amount of degassed water in THF at −60 °C gave strontium hydroxide **2** as a colorless solid (55.2% yield; Scheme 1). Colorless crystals suitable for X-ray structural analysis were obtained either by keeping a dilute solution of **2** in THF at −32 °C or by concentrating its THF solution at room temperature.

Compound **2** is freely soluble in common organic solvents such as benzene, toluene, and THF. Compound **2** was characterized by NMR spectroscopy (^1H and ^{13}C), EI mass spectrometry, and elemental and X-ray structural analysis. The complete disappearance of the $SiMe_3$ resonance (0.14 ppm) of **1** clearly indicates the formation of compound **2**. As expected, the resonances for the γ-CH (4.74 ppm) and OH (−0.72 ppm) protons appear as singlets in the ^1H NMR spectrum. The absence of the molecular ion peak in the EI mass spectrum of **2** shows its instability under these conditions. The hydroxide stretching frequency of **2** appears as a sharp absorption band (3677 cm^{-1}) in the IR spectrum and is comparable to those of the inorganic anhydrous strontium dihydroxide (3618 cm^{-1}).[12] The strontium hydroxide crystallizes in the triclinic space group $P\bar{1}$ with two molecules of THF as colorless crystals. The structure of **2** (Figure 2) reveals its dimeric nature and shows the presence of two six-membered C_3N_2Sr rings. These six-membered

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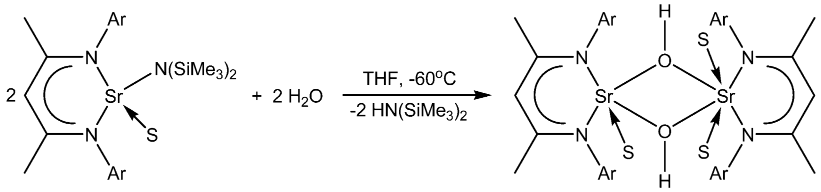
Scheme 1. Preparation of β-Diketiminate Supported Strontium Hydroxide Complex



1

Ar = 2,6-*i*-$Pr_2C_6H_3$; S = THF

2

Table 1. Crystallographic and Structure Refinement Data

param	**1**	**2**·2THF	**3**·C_6H_6	**4**·0.5toluene + 0.5benzene	**5**·toluene
empirical formula	$C_{39}H_{67}N_3OSi_2Sr$	$C_{78}H_{124}N_4O_7Sr_2$	$C_{90}H_{110}N_4O_4Sr_2$	$C_{100.5}H_{121}N_4O_4P_2Sr_2$	$C_{77}H_{126}N_{10}O_2Sr_2Zr_2$
fw	737.76	1405.05	1487.06	1686.27	1581.56
T (K)	133(2)	100(2)	100(2)	133(2)	100(2)
cryst syst	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	11.5102(6)	12.958(3)	12.829(1)	15.6034(6)	12.296(1)
b (Å)	18.3156(7)	14.612(3)	12.912(1)	13.3159(4)	13.611(1)
c (Å)	20.0293(11)	22.946(3)	15.205(1)	23.0252(8)	13.597(1)
α (deg)	*90*	85.33(3)	94.26(1)	90	77.80(1)
β (deg)	91.165(4)°	73.94(3)	110.54(1)	106.277(3)	65.73(1)
γ (deg)	*90*	66.34(3)	116.63(1)	90	84.98(1)
V (Å^3)	4221.6(4)	3822.0(13)	2026.1(3)	4592.3(3)	2027.6(3)
Z	4	2	1	2	1
ρ_{calcd} (mg/m^3)	1.161	1.221	1.219	1.219	1.295
F(000)	1584	1504	786	1780	830
μ (Mo Kα)	1.365	2.246	2.126	1.248	4.091
θ range for data collcn (deg)	2.02−24.73	3.30−59.09	3.23−59.42	1.41−24.83	3.32−59.04
no. of reflcns collcd/unique obsd reflns [$I > 2\sigma(I)$]	58275/7166 (R_{int} = 0.0994)	77913/11259(R_{int}= 0.0577)	18352/5471 (R_{int}= 0.0573)	66801/7919 (R_{int} = 0.0895)	20752/5672 (R_{int} = 0.0305)
data/restraints/params	7166/0/431	11259/525/ 961	5471/2/469	7919/0/518	5672/63/468
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
GOF on F^2	1.000	1.047	1.093	0.981	1.047
R1, wR2 [I 2$\sigma(I)$]	0.0387, 0.777	0.0309, 0.0772	0.0510, 0.1394	0.0347, 0.0743	0.0211, 0.0542
R1, wR2 (all data)	0.0599, 0.0839	0.0374, 0.0820	0.0636, 0.1503	0.0519, 0.0790	0.0219, 0.0546
largest diff peak/hole (e Å^3)	0.453 and −0.266	0.568 and −0.513	1.652 and −0.778	0.635 and −0.327	0.386 and −0.290

rings are connected to each other by means of two μ-OH groups, which results in the formation of a four-membered Sr_2O_2ring. The six-membered rings possess an envelope conformation and are perpendicular to each other (89.6°). The four-membered Sr_2O_2 ring is planar and forms an angle of 53.3° and 38.1° with the two six-membered rings.

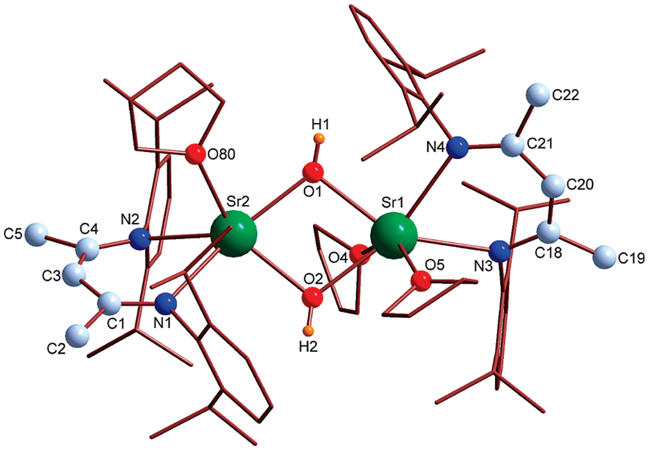


Figure 2. Crystal structure of **2**·2THF. The two noncoordinate THF molecules and all of the hydrogen atoms except those of hydroxyl groups have been omitted for clarity.

Interestingly, the strontium atoms have an environment that differs in the number of coordinated THF molecules. Thus, one of the strontium atoms is penta-coordinate and has distorted trigonal-bipyramidal geometry with two nitrogen atoms of the β-diketiminate ligand, two oxygen atoms of the two hydroxyl groups, and an oxygen atom of the THF molecule. The other strontium atom has a similar environment but contains one additional THF molecule in its coordination sphere, which makes it hexa-coordinate with distorted octahedral geometry. This observation is in contrast to the magnesium and calcium hydroxides ([LMg(μ-OH)(thf)]$_2$ and [LCa(μ-OH)(thf)]$_2$), where the alkaline earth metal centers have the same coordination geometry. As anticipated, the Sr−O bond distances in hydroxide **2** (2.402(2)$_{av}$ Å) are longer than the Mg−O (1.988(2) Å) and Ca−O (2.225(6)$_{av}$ Å) distances found in the magnesium[8b] and calcium congeners.[9] The Sr−O−Sr and O−Sr−O bond angles in **2** (103.83(9)$_{av}$° and 76.17(7)$_{av}$°) are comparable with the Ca−O−Ca (103.49(11)°) and O−Ca−O (76.51(11)°) bond angles present in [LCa(μ-OH)(thf)]$_2$. Crystallographic and structure refinement data are presented in Table 1.

We have tried the possibility for preparing a monomeric strontium hydroxide by exploiting the ligand exchange phenomenon observed in alkaline earth metal complexes.[9] The addition of 2 equiv of benzophenone and triphenylphosphine oxide at room temperature to [LSr(thf)(μ-OH)$_2$Sr-(thf)$_2$L] (**2**) in benzene resulted in the precipitation of [LSr(μ-OH)(OCPh$_2$)]$_2$ (**3**) as reddish orange crystals and in toluene led to the formation of [LSr(μ-OH)(OPPh$_3$)]$_2$ (**4**) as a yellowish compound (78.3% yield) at room temperature, respectively. Compound **4** is soluble in benzene and toluene. Compound **4** shows a singlet (4.89 ppm) for the γ-CH proton and another one for the hydroxyl group (-0.479 ppm). The ^{31}P NMR spectrum contains only one singlet (29.5 ppm) for the triphenylphosphine oxide. The SrO$-$H stretching frequency of **3** (3676 cm^{-1}) and **4** (3680 cm^{-1}) matches with that of **2** (3677 cm^{-1}). The molecular ion peak corresponding to **3** and **4** was not observed in the EI mass spectra.

The strontium hydroxide **3** (Figure 3) with coordinate benzophenone molecules crystallizes in the triclinic space group $P\bar{1}$ as orange-red diamond-shaped crystals containing half of a molecule of benzene in the asymmetric unit. Similar to the structure of **2**, the structure of **3** contains three heterocyclic rings, but their orientation differs significantly. The enveloped six-membered C$_3$N$_2$Sr rings are exactly parallel to each other, caused by the crystallographic inversion center, and form an angle of 32.3° with the planar four-membered Sr$_2$O$_2$ ring. Both of the strontium atoms are pentacoordinate (with two nitrogen atoms of ligand L, two oxygen atoms of the hydroxyl groups, and an oxygen atom of the benzophenone molecule) and adopt a distorted square pyramidal geometry.

Yellow crystals of **4** suitable for structural analysis were obtained when a concentrated solution of **4** in toluene was kept at -5 °C for 1 day. Compound **4** crystallizes in the monoclinic space group $P2_1/n$ with a disordered toluene molecule. The structure of **4** (Figure 4) reveals the dimeric nature of **4** and rules out the possibility of a monomeric strontium hydroxide. Both of the strontium atoms are pentacoordinate with two nitrogen atoms of the β-diketiminato ligand, two oxygen atoms of the hydroxyl groups, and an oxygen atom of the triphenylphosphine oxide. In addition, they adopt distorted trigonal-bipyramidal geometry, with the oxygen atom of a hydroxyl group and a nitrogen atom of the β-diketiminato ligand occupying the apical positions. The structure of **4** contains two enveloped C$_3$N$_2$Sr six-membered rings and a planar Sr$_2$O$_2$ four-membered ring. The six-membered rings are exactly parallel to each other and form an angle of 43.95° with the four-membered ring. This angle shows that the structure of **4** is more twisted than the structure of the strontium hydroxide with coordinated benzophenone molecules, where the same angle is 32.3°. The reason might be the more bulky triphenylphosphine oxide ligand compared to the benzophenone molecule.

A reactivity study of strontium hydroxide complex **2** with non-cyclopentadienyl complexes of group 4 metal unveiled its unprecedented mild acidic character. Interestingly, the reaction of **2** with 2 equiv of Zr(NMe$_2$)$_4$ in toluene at -60 °C led to the intermolecular elimination of 2 equiv of Me$_2$NH and resulted in the μ-oxo-bridged heterobimetallic complex [LSr(μ-O)Zr(NMe$_2$)$_3$]$_2$ (**5**) as a colorless solid (69.1% yield; Scheme 2). The special electronic and steric effect offered by the β-diketiminate ligand may be the reason for the umpolung of the hydroxide group in complex **2**. Although, we anticipate that the facile formation of the Zr$-$O$-$Sr bond may be the driving force for the change of the polarity in the hydroxide group of complex **2**.

Compound **5** is freely soluble in common organic solvents such as benzene and toluene. Compound **5** was characterized by NMR spectroscopy (^{1}H and ^{13}C), EI mass spectrometry, and X-ray structural and elemental analyses. The complete disappearance of the OH resonance and the stretching frequency of **2** in the ^{1}H NMR and IR spectra of **5**, respectively, clearly indicates its formation. The ^{1}H NMR spectrum shows a singlet for the γ-CH (4.72 ppm) and NMe$_2$ (2.62 ppm) protons, respectively. No molecular ion peak was observed in the EI mass spectrum of **5**, and only fragment ions are formed. Colorless crystals suitable for X-ray structural analysis were obtained by keeping a concentrated solution of **5** in toluene at -5 °C.

Compound **5** crystallizes in the triclinic space group $P\bar{1}$ together with a disordered toluene molecule (Figure 5). The structure reveals the dimeric nature of **5**, and this dimerization

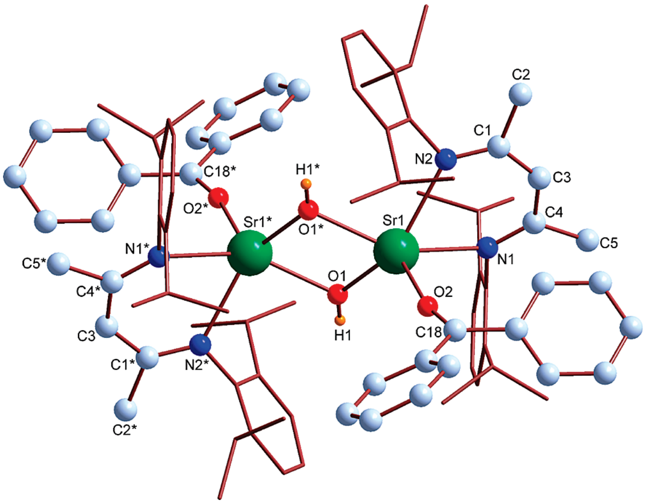


Figure 3. Crystal structure of **3**·C$_6$H$_6$. The benzene molecule and all of the hydrogen atoms except those of hydroxyl groups have been omitted for clarity.

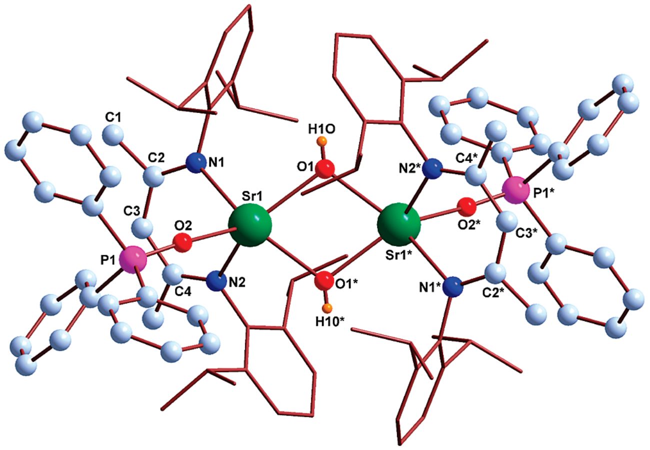
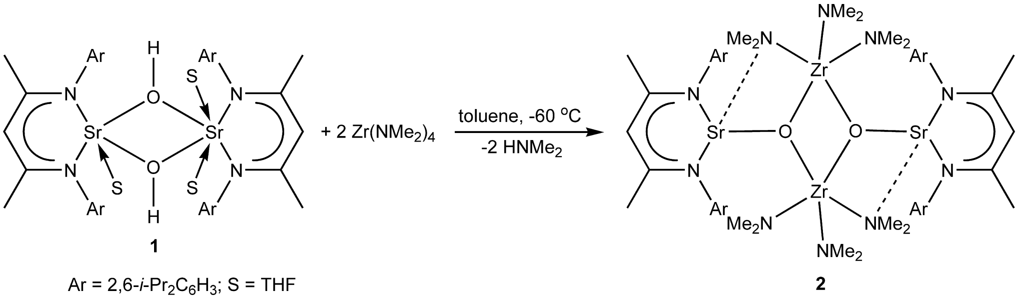


Figure 4. Crystal structure of **3**·0.5toluene + 0.5benzene. The disordered solvent molecules and all of the hydrogen atoms except those of hydroxyl groups have been omitted for clarity.

Scheme 2. Preparation of Heterobimetallic Compound $[LSr(\mu\text{-}O)Zr(NMe_2)_3]_2$



results in the formation of a planar four-membered Zr_2O_2 ring. The zirconium atoms are penta-coordinate (with three nitrogen atoms of the dimethylamino groups and two oxygen atoms) and adopt a distorted trigonal-bipyramidal geometry. Among the three nitrogen atoms of the dimethylamino groups, one nitrogen atom takes up the apical position and the other two nitrogen atoms are arranged on equatorial positions. One of the equatorial diaminomethyl nitrogen atoms on each zirconium atom forms a coordinate bond with the strontium atom, and consequently two puckered four-membered SrONZr rings are assembled. Interestingly, both the strontium atoms rest almost on the plane of the planar Zr_2O_2 ring, and the nitrogen atoms that bridge the zirconium and strontium atoms lie at a distance of 1.51 Å above and below the $Sr_2Zr_2O_2$ plane. The strontium atoms are tetra-coordinate (with two nitrogen atoms of the β-diketiminato ligand, a nitrogen atom of one of the dimethylamino groups, and an oxygen atom) and create two six-membered C_3N_2Sr rings due to the bidentate mode of binding offered by the β-diketiminato ligands. In contrast to the enveloped C_3N_2Sr rings present in the strontium amide $LSrN(SiMe_3)_2(thf)$ and strontium hydroxide **2**, the C_3N_2Sr rings of **5** are nearly planar. Additionally, the C_3N_2Sr rings of **5** are exactly parallel to each other and are almost perpendicular (89.71°) to the $Sr_2Zr_2O_2$ plane. Selected bond distances and angles for **1**−**5** are given in Table 2.

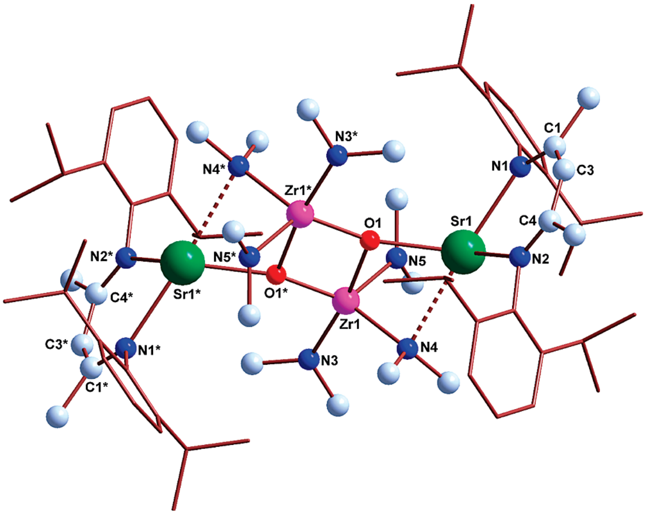


Figure 5. Crystal structure of **5**·toluene. The toluene molecule and all of the hydrogen atoms have been omitted for clarity. The dashed coordinate bonds represent the weak interactions between the strontium atoms and the $-NMe_2$ groups.

Experimental Section

General Procedures. All manipulations were performed under a dry and oxygen-free N_2 atmosphere by using Schlenk and glovebox techniques. SrI_2 and $KN(SiMe_3)_2$ (95%), Ph_2CO, Ph_3PO (98%), and $Zr(NMe_2)_4$ were purchased from Aldrich and used as obtained. ^1H and ^{13}C NMR spectra were recorded on either a Bruker Avance 300 or 500 NMR spectrometer. Chemical shifts are reported in parts per million with reference to $SiMe_4$ (external). All NMR measurements were carried out at room temperature. IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer in the range of 4000 to 350 cm^{-1} as nujol mulls. EI mass spectra were obtained using a Finnigan MAT 8230 or a Varian MAT CH5 instrument (70 eV). Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus and are uncorrected. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.

Synthesis of 1. LH (2.931 g, 7.00 mmol) and $KN(SiMe_3)_2$ (2.933 g, 14.70 mmol) were dissolved in THF (60 mL) and stirred for 5 h at room temperature. This clear solution was added to a suspension of SrI_2 (2.390 g, 7.00 mmol) in THF (60 mL) at room temperature. It was stirred for another 18 h. After that, the solvent was removed, and the residue was extracted with *n*-hexane (90 mL) and filtered. Removal of the solvent from the filtrate in a vacuum gave compound **1** as a pale yellow solid. The solid upon crystallization from *n*-hexane at a low temperature gave an analytically pure sample of **1**. Yield: 4.02 g, 5.45 mmol, 77.9%. mp: 116−118 °C. ^1H NMR (500 MHz, C_6D_6): δ 7.14−7.11 (m, 6 H, *m*-, *p*-Ar−H), 4.78 (s, 1H, γ-C*H*), 3.31 (m, 4H, $O-CH_2-CH_2$), 3.18 (sept, 4H, $CH(CH_3)_2$), 1.69(s, 6H, CH_3), 1.33−1.32 (d, 12H, $CH(CH_3)_2$), 125−1.24 (d, 12H, $CH(CH_3)_2$), 1.11 (m, 4H, $O-CH_2-CH_2$), 0.14 (s, 18H, $SiMe_3$). ^{13}C {^1H} NMR(125.77 MHz, C_6D_6): δ 164.96, 147.27, 140.95, 124.31, 124.05, 92.49, 68.75, 28.42, 25.52, 25.05, 24.89, 24.51, 5.77. ^{29}Si NMR (75 MHz, C_6D_6): δ −15. 95 (s, 2Si, *Si*Me₃). MS (70 eV): *m*/*z* (%) 505.16 (100) $[M^+-N(SiMe_3)_2-THF]$. Anal. calcd for $C_{39}H_{67}N_3OSi_2Sr$ (737.76): C, 63.49; H, 9.15; N, 5.70. Found: C, 62.45; H, 9.20; N, 5.61.

Synthesis of 2. Distilled and degassed water (24 μL, 1.36 mmol) was added to a solution of $LSrN(SiMe_3)_2(thf)$ (1.00 g, 1.36 mmol) in THF (50 mL) at −60 °C. Then, it was taken to room temperature and stirred for 1 h. Filtration followed by removal of the solvent in a vacuum to give compound **2** as an off-white solid. It was washed with a small amount of *n*-hexane and crystallized from THF at −32 °C to exhibit compound **2** as colorless crystals. Yield: 0.47 g, 0.37 mmol, 55.2%. mp: 172−176 °C. ^1H NMR (300.132 MHz, C_6D_6): δ 7.15−7.06 (m, 12H, *m*-, *p*-Ar−H), 4.74 (s, 2H, γ-C*H*), 3.44 (m, 12H, $O-CH_2-CH_2$), 3.19 (sept, 8H, $CH(CH_3)_2$), 1.72 (s, 12H, CH_3), 1.40 (m, 12H, $O-CH_2-CH_2$), 1.25−1.22 (d, 24H, $CH(CH_3)_2$), 1.09−1.07 (d, 24H, $CH(CH_3)_2$), −0.72 (s, 2H, Sr−O*H*). ^{13}C NMR (75.48 MHz, C_6D_6): δ 163.48, 147.81, 141.46, 123.48, 123.34, 93.15, 68. 25, 28.00, 25.55, 25.15, 24.50, 24.36. IR (nujol):

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**−**5**

Compound **1**			
Sr1−N1, 2.554(2)	Sr1−N2, 2.514(2)	Sr1−N3, 2.446(2)	Sr1−O1, 2.536(2)
N1–Sr1–N2 74.13(7)	N1–Sr1–N3 138.55(7)	N2–Sr1–N3 118.24(7)	N1–Sr2−O1, 94.36(7)
N2–Sr1-01 140.77(7)	N3–Sr1–01 95.43(7)		
Compound **2**			
Sr1−N4, 2.658(2)	Sr1−O1, 2.411(2)	Sr1−O2, 2.430(2)	Sr1−O4, 2.642(2)
Sr1−O5, 2.621(2)	Sr2−N1, 2.599(3)	Sr2−O1, 2.384(2)	Sr2−O2, 2.383(2)
Sr2−O80, 2.564(2)	Sr1···Sr2, 3.7811(14)		
N3−Sr1−N4, 70.75(8)	O1−Sr1−O2, 75.48(7)	O1−Sr1−N3, 146.21(8)	O2−Sr1−N4, 150.47(8)
N2−Sr2−N1, 71.81(8)	O1−Sr2−O2, 76.86(7)	O2−Sr2−N2, 128.47(7)	O2−Sr2−N1, 94.88(8)
O1−Sr2−N2, 128.16(8)			
Compound **3**			
Sr1−N1, 2.565(3)	Sr1−N2, 2.601(4)	Sr1−O1, 2.351(3)	Sr1−O1*, 2.381(3)
Sr1−O2, 2.531(3)	Sr1···Sr1*, 3.7306(9)		
N1−Sr1−N2, 72.99(11)	O1−Sr1−O1*, 75.94(13)	O1−Sr1−N1, 100.94(11)	O1*−Sr1−N2, 90.63(11)
O2−Sr1−N1, 99.92(10)			
Compound **4**			
Sr1−N1, 2.623(2)	Sr1−N2, 2.580(2)	Sr1−O1, 2.368(2)	Sr1−O1*, 2.379(2)
Sr1−O2, 2.538(2)	P1−O2, 1.496(2)	Sr1···Sr1*, 3.786(1)	
N1−Sr1−N2, 72.18(6)	O1−Sr1−O1*, 74.20(8)	O1−Sr1−N2, 126.18(7)	O1*−Sr1−N1, 150.18(7)
N2−Sr2−N1, 72.18(6)	O1−Sr1−O2, 130.33(7)	Sr−O1−Sr*, 105.80(8)	
Compound **5**			
Sr1−N1, 2.5421(17)	Sr1−N2, 2.5484(16)	Sr1−N4, 2.7865(17)	Sr1−O1, 2.3423(14)
Zr1−O1, 2.1992(13)	Zr1−O1*, 1.9778(13)	Zr1···Zr1*, 3.2870(4)	
N1−Sr1−N2, 72.17(5)	O1−Sr1−N1, 115.88(5)	O1−Sr1−N2, 117.67(5)	O1−Sr1−N4, 68.11
Zr1−O1−Zr1*, 103.67(6)	O1−Zr1−O1*, 76.33(6)	Zr1−O1−Sr1, 96.63(5)	

$\tilde{\nu}$ 3677, 3053, 1917, 1624, 1549, 1510, 1429, 1408, 1379, 1314, 1254, 1225, 1166, 1100, 1042, 1018, 924, 890, 828, 783, 758, 724, 668, 618, 523, 437, 348 cm^{-1}. MS (70 eV): *m/z* (%) 403 (100) [L$^+$−Me]. Anal. calcd for $C_{70}H_{108}N_4O_5Sr_2$ (M = 1260.87): C, 66.68; H, 8.63; N 4.44. Found: C, 65.23; H, 8.57; N, 4.53.

Synthesis of 3. A solution of benzophenone (0.072 g, 0.397 mmol) in benzene (2 mL) was added to a colorless solution of compound **2** (0.25 g, 0.198 mmol) in benzene at room temperature (6 mL). Compound **3** was formed instantaneously and separated out of the solution as orange-red crystals. Yield: 0.15 g, 0.109 mmol, 55.2%. mp: 147−149 °C (dec.). IR (Nujol): $\tilde{\nu}$ 3676, 3059, 2278, 1667, 1641, 1626, 1596, 1576, 1551, 1508, 1465, 1364, 1321, 1286, 1255, 1227, 1175, 1167, 1099, 1078, 1056, 1018, 999, 946, 937, 925, 852, 827, 806, 793, 784, 769, 757, 729, 706, 640, 622, 532, 504, 434, 412, 352 cm^{-1}. MS (70 eV) *m/z* (%): 403(100) [L$^+$−Me]. Anal. calcd for $C_{84}H_{104}N_4O_4Sr_2$ (M = 1408.99): C, 71.60; H, 7.44; N, 3.98. Found: C, 71.63; H, 7.49; N, 3.79.

Synthesis of 4. [LSr(thf)(μ-OH)$_2$Sr(thf)$_2$L] (0.35 g, 0.28 mmol) and Ph_3PO (0.156 g, 0.56 mmol) were dissolved in toluene (15 mL) and stirred for 0.5 h at room temperature. Removal of the solvent from the filtrate in a vacuum gave compound **4** as a yellow solid. The solid upon crystallization from toluene at −5 °C gave an analytically pure sample of **4**. Yield: 0.348 g, 0.217 mmol, 78.3%. mp: 189−191 °C. ^{1}H NMR (300.132 MHz, C_6D_6): δ 7.69−7.66 (m, 30H, Ar−*H*), 7.13−7.01 (m, 12H, *m-*, *p*-Ar−*H*), 4.89 (s, 2H, γ-C*H)*, 3.31 (sept, 8H, C*H*(CH$_3$)$_2$), 1.79 (s, 12H, CH$_3$), 1.09−1.07 (d, 24H, CH(C*H*$_3$)$_2$), 0.98−0.97 (d, 24H, CH(C*H*$_3$)$_2$), −0.479 (s, 2H, Sr−O*H*). ^{13}C NMR (75.48 MHz, C_6D_6): δ 163.26, 149.45, 141.00, 132.87, 132.79, 132.13, 132.03, 125.64, 123.23, 122.89, 92.63, 27.77, 25.64, 25.08, 24.39. ^{31}P NMR (75 MHz, C_6D_6): δ 29.5 (s, 2P, O*P*Ph*$_3$)*. IR (nujol): $\tilde{\nu}$ 3680, 3049, 1965, 1909, 1683, 1624, 1591,1548, 1507, 1380, 1362, 1338, 1313, 1275, 1253, 1225, 1174, 1118, 1100, 1072, 1053, 1028, 1015, 998, 935, 923, 857, 827, 807, 794, 785, 751, 727, 693, 619, 598, 537, 512, 465, 436, 346 cm^{-1}. MS (70 eV) *m/z* (%): 403 (100) [L$^+$−Me]. Anal. calcd for $C_{94}H_{114}N_4O_4P_2Sr_2$ (1601.12): C, 70.51; H, 7.18; N 3.50. Found: C, 70.92; H, 7.42; N 3.26.

Synthesis of 5. A toluene solution of [LSr(thf)(μ-OH)$_2$Sr(thf)$_2$L] (**1**) (0.5 g, 0.397 mmol) was added drop by drop to a solution of Zr(NMe$_2$)$_4$ (0.212 g, 0.73 mmol) in toluene at −60 °C using a cannula. After the addition was complete, the solution was brought to room temperature and stirred for 1 day. Then, the solvent was removed *in vacuo* to get the crude sample of **5**. Colorless crystals were obtained when a toluene solution of **5** was kept at −5 °C for 3 days. Yield: 0.408 g, 0.274 mmol, 69.1%. mp: 252−254 °C. ^{1}H NMR (500.132 MHz, C_6D_6): δ 7.14−7.09 (m, 12H, Ar−H), 4.72 (s, 2H, γ-C*H*), 3.24 (sept, 8H, C*H*(CH$_3$)$_2$), 2.62 (s, 36H, N(C*H*$_3$)$_2$), 1.69 (s, 12H, C*H*$_3$), 1.34−1.33 (d, 24H, CH(C*H*$_3$)$_2$), 1.25−1.23 (d, 24H, CH(C*H*$_3$)$_2$). ^{13}C NMR (75.48 MHz, C_6D_6): δ 165.12, 147.56, 141.32, 124.34, 123.98, 91.77, 43. 22, 28.64, 25.25, 24.93, 24.45. MS (70 eV) *m/z* (%): 505.2 (15) [M$^+$−OZr(NMe$_2$)$_3$)], 403 (100) [L$^+$−Me]. Anal. calcd for $C_{70}H_{108}N_{10}O_2Sr_2Zr_2$ (M = 1489.44): C, 56.45; H, 7.99. Found: C, 56.52; H, 7.59.

Crystallographic Details for Compounds 1−5. The data for compounds **1** and **4** were collected on a STOE IPDS II instrument. In the case of **2**, the data were collected using a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector on a nonmerohedrally twinned crystal. There were three twin domains with a refined fractional contribution of 0.5485(7):0.3979(7): 0.0536(7). The data for compounds **3** and **5** were also collected on the same diffractometer used for **2**. In the structure of **2**, one coordinated THF molecule and two noncoordinated THF molecules are disordered. The solvent molecule toluene in both **4** and **5** was found to be disordered. They were refined with distance restraints and restraints for the anisotropic displacement parameters. All of the structures were solved by direct methods with SHELXS-97[13] and were refined with SHELXL-97[14] on F^2.

Conclusion

In summary, a novel strontium hydroxide, **2**, was prepared from strontium amide **1** and water. The reaction of strontium hydroxide **2** with Zr(NMe$_2$)$_4$ gave the unprecedented het-

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erobimetallic oxide **5** and reveals for the first time the acidic character of an alkaline earth metal hydroxide, **2**. The stability and good solubility of **5** has made it possible to prepare hitherto unknown strontium oxide complexes. Compound **5** can also act as a precursor for polymetallic complexes in view of its replaceable NMe_2 groups. Such studies are currently in progress in our laboratory.

Acknowledgment. Support of the Göttinger Akademie der Wissenschaften is highly acknowledged. S.N. thanks the Alexander von Humboldt foundation for a postdoctoral research fellowship.

Supporting Information Available: X-ray data for **1**−**5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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