Synthesis of Arene-Soluble Mixed-Metal Zr/Ce, Zr/Y, and Related $\{[Zr_2(O^iPr)_9]LnX_2\}_n$ Complexes Using the Dizirconium Nonaisopropoxide Ligand

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The utility of polydentate monoanionic $[Zr_2(O^iPr)_9]^-$ in generating arene-soluble, unsolvated, mixed-metal Zr/Ce and Zr/Y complexes is described. The synthesis of other mixed-metal zirconium lanthanide complexes was also studied to explore the relationship of metal size to structure. Lanthanide trihalides react in THF with $KZr_2(O^iPr)_9$ to form unsolvated dimers, $\{[Zr_2(O^iPr)_9]LnCl_2\}_2$, with the larger metals, Ln = Ce (**1**), Ho (**2**), Y (**3**), and unsolvated monomers, $[Zr_2(O^iPr)_9]LnCl_2$, with the smaller elements, Ln = Er (**4**), Yb (**5**). The synthesis of a monomeric iodide analogue, $[Zr_2(O^iPr)_9]TmI_2$, **6**, by reduction of $Zr_2(O^iPr)_8(^iPrOH)_2$ with $TmI_2(DME)_3$ is also reported. In all of these complexes, the $[Zr_2(O^iPr)_9]^-$ subunit is tetradentate. **1**−**6** are compared with related cyclopentadienyl halide complexes to evaluate the special features of the dizirconium nonaisopropoxide ligand versus cyclopentadienide.

Introduction

Recent investigations of heterometallic lanthanide zirconium isopropoxide chemistry showed that the $[Zr_2(O^iPr)_9]^-$ dizirconium nonaisopropoxide (dzni) subunit[1] could solubilize Nd, Eu, and Sm metal halides in arene solvents.[2] It seemed likely that this approach could also provide easy access to soluble mixed-metal Zr/Ce and Zr/Y complexes which could be of interest as precursors to Zr/Ce and Zr/Y oxides. These mixed-metal oxides are of interest due to their oxide transport and storage capacity and find use in automotive exhaust catalysts[3] and solid oxide fuel cells.[4] These mixed-metal materials are commonly prepared from individual components by traditional mix/grind/calcine techniques, since convenient mixed-metal molecular precursors were previously unavailable. Accordingly, we have examined the synthesis of dzni complexes of Ce and Y.

We have also extended the study to other members of the lanthanide series since arene-soluble lanthanide dihalides can be valuable starting materials in general. This investigation also allowed us to further examine the utility of the monoanionic polyhapto dzni ligand in comparison with the popular cyclopentadienyl ligands[5] which have the same charge and similar coordination capacity.[2,6] This study also provides a series of soluble, unsolvated $[(\text{ancillary ligand})LnX_2]_n$ complexes, a class of starting materials which is rare in lanthanide chemistry.

We report here the synthesis and structures of five new examples of $\{[Zr_2(O^iPr)_9]LnCl_2\}_n$ complexes and contrast them with the previously reported neodymium complex, $\{[Zr_2(O^iPr)_9]NdCl_2\}_2$.[2] In addition we describe the use of the only known molecular divalent thulium complex in the literature, $TmI_2(DME)_3$,[7] in the reduction of $Zr_2(O^iPr)_8(^iPrOH)_2$ to form an arene-soluble heterometallic Zr(IV)/Tm(III) complex. The reduction chemistry of this highly reactive compound has been relatively unexplored, and there are few reports of the controlled reactivity of Tm(II) to date.[8]

Experimental Section

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox techniques. Solvents were purified as previously described.[9] $K[Zr_2(O^iPr)_9]$,[1b] $LnCl_3$,[10] and $TmI_2(DME)_3$[7] were prepared by

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literature methods. NMR spectra were recorded and magnetic moments were measured by the method of Evans[11] using a Bruker DRX400 or a General Electric GE500 spectrometer. Infrared spectra were recorded as thin films on a React IR instrument or as KBr pellets on a Perkin FTIR. All magnetic moments were recorded in THF. Elemental analyses were performed by Analytische Laboratorien, Lindlar, Germany, and Desert Analytics, Tucson, AZ 85719.

$\{[Zr_2(O^iPr)_9]CeCl_2\}_2$, 1. A solution of $KZr_2(O^iPr)_9$ (923 mg, 1.23 mmol) in 5 mL of THF was added to a gently heated suspension of $CeCl_3$ (356 mg, 1.30 mmol) in 3 mL of THF. The resultant white solution was further stirred for 24 h and then centrifuged to remove a white precipitate. The solution volume was reduced to 2 mL by rotary evaporation to afford clear crystals suitable for X-ray diffraction (542 mg, 42%). Anal. Calcd for $C_{27}H_{63}O_9Cl_2Zr_2Ce$: C, 35.05; H, 6.61. Found: C, 36.05; H, 6.61. IR (thin film): 2972 s, 2860 s, 1969 w, 1459 m, 1366 s, 1289 m, 1173 m, 1065 s, 1031 m, 914 m, 663 w cm^{-1}. Magnetic susceptibility: $\chi_g^{298\ K} = 1.54 \times 10^{-6}$, $\mu_{eff}^{298\ K} = 1.8\ \mu_B$. Melting point: 262 °C.

$\{[Zr_2(O^iPr)_9]HoCl_2\}_2$, 2. A solution of $KZr_2(O^iPr)_9$ (1.054 g, 1.40 mmol) in 5 mL of THF was added to stirred suspension of $HoCl_3$ (0.400 g, 1.47 mmol) in 3 mL of THF. The cloudy white solution was stirred for 24 h and then centrifuged to remove white material. The supernatant was dried using a rotary evaporator, and the remaining pink solid was recrystallized from 2 mL of toluene at −20 °C, to afford pink-orange crystals suitable for X-ray diffraction (0.84 g, 63%). IR (thin film): 2968 s, 2930 m, 2864 m, 2629 w, 1756 w, 1463 m, 1366 s, 1339 w, 1166 s, 1131 s, 1019 s, 953 m, 849 w, 802 w, 702 m cm^{-1}. Magnetic susceptibility: $\chi_g^{298\ K} = 4.70 \times 10^{-5}$, $\mu_{eff}^{298\ K} = 10.4\ \mu_B$. Melting point: 253 °C.

$\{[Zr_2(O^iPr)_9]YCl_2\}_2$, 3. A solution of $KZr_2(OPr^i)_9$ (908 mg, 1.21 mmol) in 5 mL of THF was added to a gently heated suspension of YCl_3 (218 mg, 1.30 mmol) in 7 mL of THF. The resultant colorless solution was further stirred for 24 h and then centrifuged to remove white material. The supernatant was evaporated using a rotary evaporator, and the remaining solid was recrystallized from a 1:1 toluene/hexanes mixture (3 mL) at −20 °C to produce crystals suitable for X-ray crystallography (0.75 g, 71 %). NMR (C_6D_6): ^1H, δ 4.56 m (5H, $OCH(CH_3)_2$), 4.24 m (4H, $OCH(CH_3)_2$), 1.82 d (12H, $OCH(CH_3)_2$), 1.56 d (12H, $OCH(CH_3)_2$), 1.33 d (6H, $OCH(CH_3)_2$), 1.14 d (24H, $OCH(CH_3)_2$); ^{13}C, δ 73.1, 71.3 ($OCH(CH_3)_2$), 26.9, 26.5, 26.1 ($OCH(CH_3)_2$). IR (thin film): 2968 s, 2930 m, 2864 m, 2629 w, 1741 w, 1463 m, 1366 s, 1339 w, 1166 s, 1131 s, 1007 s, 953 m, 849 m, 802 w, 702 m cm^{-1}. Melting point: 245 °C.

$[Zr_2(O^iPr)_9]ErCl_2$, 4. A solution of $KZr_2(O^iPr)_9$ (923 mg, 1.23 mmol) in 5 mL of THF was added to a gently heated suspension of $ErCl_3$ (356 mg, 1.30 mmol) in 3 mL of THF. The resultant pink solution was further stirred for 24 h and then centrifuged to remove a white precipitate. The supernatant was dried using a rotary evaporator, and the remaining solid was recrystallized from 2 mL of toluene at −20 °C to afford pink crystals suitable for X-ray diffraction (730 mg, 63%). Anal. Calcd for $C_{27}H_{63}O_9Cl_2Zr_2Er$: C, 34.00; H, 6.70. Found: C, 34.05; H, 6.78. IR (thin film): 2964 s, 2926 m, 2860 m, 2629 w, 1463 m, 1363 s, 1339 m, 1262 w, 1166 s, 1015 s, 953 s, 845 m, 802 s, 702 cm^{-1}. Magnetic susceptibility: $\chi_g^{298\ K} = 3.52 \times 10^{-6}$, $\mu_{eff}^{298\ K} = 9.0\ \mu_B$. Melting point: 241 °C.

$[Zr_2(O^iPr)_9]YbCl_2$, 5. A solution of $KZr_2(O^iPr)_9$ (902 mg, 1.20 mmol) in 5 mL of THF was added to a gently heated suspension of $YbCl_3$ (335 mg, 1.20 mmol) in 3 mL of THF. The resultant cloudy white solution was further stirred for 24 h and then centrifuged to remove a white precipitate. The supernatant was dried using a rotary evaporator, and the remaining solid was recrystallized from 2 mL of toluene at −20 °C to afford colorless crystals suitable for X-ray diffraction (770 mg, 67%). Anal. Calcd for $C_{27}H_{63}O_9Cl_2Zr_2Yb$: C, 33.85; H, 6.63. Found: C, 32.41; H, 6.08. IR (KBr): 2963 s, 2930 m, 2864 m, 2620 w, 1462 m, 1370 s, 1337 m, 1166 s, 1127 s, 1020 s 1002 s, 953 s, 923 s, 846 m, 830 m, 807 m cm^{-1}. Magnetic susceptibility: $\chi_g^{298\ K} = 7.66 \times 10^{-6}$, $\mu_{eff}^{298\ K} = 4.2\ \mu_B$.

$[Zr_2(O^iPr)_9]TmI_2$, 6. A light-sensitive green solution of $TmI_2(DME)_3$ (764 mg, 1.35 mmol) in 3 mL of DME was added to a stirred solution of $Zr_2(O^iPr)_8(^iPrOH)_2$ (1.05 g, 1.36 mmol) in 4 mL of toluene and 2 mL of DME. Upon addition the green color immediately disappeared and bubbles were noted. The solution was stirred for 30 min, and the volume was reduced to 0.5 mL by rotary evaporation. Crystals were formed slowly in a freezer at −20 °C. Alternatively, the reaction of TmI_3 (757 mg, 1.38 mmol) with $K[Zr_2(O^iPr)_9]$ (1039 mg, 1.38 mmol) in 3 mL of toluene overnight followed by centrifugation to remove the precipitate, reduction of solution volume to 0.5 mL, and addition of 2 mL of hexanes afforded **4** as a white precipitate (620 mg, 40%). Anal. Calcd for $C_{27}H_{63}O_9I_2Zr_2Tm$: C, 28.5; H, 5.6; I, 22.3; Zr, 16.0. Found: C, 28.5; H, 5.8; I, 22.5; Zr, 16.3. IR (KBr): 2966 m, 2925 w, 2862 w, 1470 w, 1459 m, 1453 m, 1381 s, 1366 s, 1339 w, 1169 s, 1129 s, 1022 s, 1002 s, 948 s, 917 m, 850 m, 832 m, 796 m, 577 w, 559 m cm^{-1}. Magnetic susceptibility: $\chi_g^{298\ K} = 1.93 \times 10^{-5}$, $\mu_{eff}^{298\ K} = 7.3\ \mu_B$.

X-ray Data Collection, Structure Determination, and Refinement for 1−6. All crystals were coated with Paratone oil, mounted on glass fibers, and transferred to the Bruker CCD platform diffractometer under a cold stream. The SMART[12] program package was used to determine the unit-cell parameters and for data collection. The raw frame data were processed using SAINT[13] and SADABS[14] to yield the reflection data files. Subsequent calculations were carried out using the SHELX-TL[15] program. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. Disorder in the isopropyl groups was modeled by assigning partial occupancy to the disordered components. There were two solvent molecules of THF present per formula unit in **1**. Experimental parameters for the data collection and structure refinement of **1**−**6** are given in Table 1. Important bond distances and angles for **1**−**6** are given in Table 2.

Results

Synthesis. The dzni potassium salt, $KZr_2(O^iPr)_9$, readily prepared from $Zr_2(O^iPr)_8(^iPrOH)_2$ and K,[1b] reacts with yttrium and lanthanide trihalides in THF to form complexes of formula $\{[Zr_2(O^iPr)_9]LnCl_2\}_n$, eq 1. Mixed-metal Zr/Ce and Zr/Y

$$LnCl_3 + [KZr_2(O^iPr)_9] \rightarrow \{[Zr_2(O^iPr)_9]LnCl_2\}_n + KCl \quad (1)$$

$$Ln = Ce,\ \mathbf{1};\ Ho,\ \mathbf{2};\ Y,\ \mathbf{3};\ Er,\ \mathbf{4};\ Yb,\ \mathbf{5}$$

complexes were readily prepared in this way. Complexes **1**, **3**, and **5** are colorless compounds, while **2** and **4** are light pink. **1**−**5** were fully characterized by elemental analysis, magnetic susceptibility, IR spectroscopy, and X-ray diffraction. The NMR spectra of **1**, **2**, **4**, and **5** were uninformative due to the paramagnetism of the metals. In the ^1H NMR spectrum of **3**, the methyl groups of the isopropoxide ligands display four separate chemical shifts in a ratio of 4:2:2:1.

A second method of synthesis involved the reduction of $Zr_2(O^iPr)_8(^iPrOH)_2$ by the Tm(II) complex, $TmI_2(DME)_3$ (DME = $CH_3OCH_2CH_2OCH_3$). $[Zr_2(O^iPr)_9]TmI_2$, **6**, is formed as shown in eq 2.

$$TmI_2(DME)_3 + Zr_2(O^iPr)_8(^iPrOH)_2 \rightarrow \underset{\mathbf{6}}{[Zr_2(O^iPr)_9]TmI_2} + H_2 \quad (2)$$

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Table 1. Data Collection Parameters[a] for $\{[Zr_2(O^iPr)_9]LnCl_2\}_2$ (Ln = Ce, **1**; Ho, **2**; Y, **3**), $[Zr_2(O^iPr)_9]LnCl_2$ (Ln = Er, **4**; Yb, **5**), and $[Zr_2(O^iPr)_9]TmI_2$, **6**

	1	**3**	**2**	**4**	**5**	**6**
formula	$C_{62}H_{142}Ce_2Cl_4O_{20}Zr_4$	$C_{61}H_{134}Cl_4O_{18}Y_2Zr_4$	$C_{54}H_{126}Cl_4Ho_2O_{18}Zr_4$	$C_{27}H_{63}Cl_2ErO_9Zr_2$	$C_{27}H_{63}Cl_2O_9YbZr_2$	$C_{27}H_{63}I_2O_9TmZr_2$
fw	1870.71	1840.18	1900.09	952.37	958.15	1136.94
temp (K)	158	158	158	158	158	158
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P\bar{1}$	$C2/c$	$C2/c$	$Pca2_1$	$Pca2_1$	$P2_1/m$
a (Å)	12.4147(6)	25.1194(13)	25.1290(12)	24.3874(12)	24.4339(12)	10.0764(5)
b (Å)	19.0034(9)	21.4503(11)	21.4085(10)	17.0759(8)	17.0538(8)	23.4626(11)
c (Å)	19.4922(9)	17.9466(9)	17.9501(9)	19.0537(9)	19.0967(9)	10.3053(5)
α (deg)	103.8160(10)	90	90	90	90	90
β (deg)	93.9810(10)	119.2770	119.3880(10)	90	90	103.8880(10)
γ (deg)	92.8480(10)	90	90	90	90	90
V (Å^3)	4444.4	8434.8(7)	8414.0(7)	7934.7(7)	7957.4(7)	2365.1(2)
Z	2	4	4	8	8	2
ρ_{calcd} (Mg/m^3)	1.398	1.449	1.500	1.594	1.600	1.596
μ (mm^{-1})	1.618	2.018	2.514	2.787	3.020	3.631
R1	0.0576	0.0780	0.0492	0.1089	0.0548	0.0772
wR2 [$I > 2\sigma(I)$]	0.1190	0.1025	0.1399	0.2027	0.0776	0.1486

[a] Radiation: Mo Kα (μ = 0.71073 Å). Monochromator: highly oriented graphite. $R1 = \sum||F_o| - |F_c||/\sum|F_c|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2. Summary of Relevant Ln−O and Ln−Cl Bond Distances (Å) and Angles (deg) for $\{[Zr_2(O^iPr)_9]LnCl(\mu\text{-}Cl)\}$ Structures, Ln = Ce (**1**), Ho (**2**), Y (**3**)

distance/angle	1	2	3
Ln−Cl(terminal)	2.688(1)	2.558(1)	2.564(1)
Ln−Cl (bridging)	2.873(1)	2.729(1)	2.735(1)
Ln−μ^2-O	2.456(3)	2.329(4)	2.327(3)
Ln−μ^2-O	2.481(3)	2.338(4)	2.335(3)
Ln−μ^3-O	2.529(3)	2.382(4)	2.379(3)
Ln−μ^3-O	2.544(3)	2.452(4)	2.451(3)
Ln−Cl−Ln	105.66(3)	107.31(4)	107.44(3)

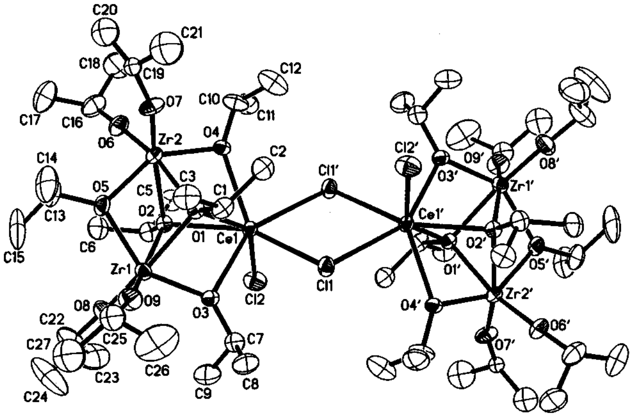

Figure 1. Plot of $\{[Zr_2(O^iPr)_9]CeCl_2\}_2$, **1**, with thermal ellipsoids drawn at 50% probability.

Gas evolution was observed, and magnetic moment data on **6** confirm that the thulium is indeed trivalent. These data are consistent with reduction of a coordinated alcohol from $Zr_2(O^iPr)_8(^iPrOH)_2$ as typically occurs with strong reducing agents such as potassium.

Structure. Since the NMR data on the paramagnetic complexes were not structurally definitive, X-ray crystallography was used for full characterization. Not surprisingly, $\{[Zr_2(O^iPr)_9]CeCl_2\}_2$, **1**, Figure 1, was found to have a dimeric structure in the solid state like the previously characterized $\{[Zr_2(O^iPr)_9]NdCl_2\}_2$, **7**.[2] In fact, **1** and **7** are isostructural. Interestingly, the yttrium complex, $\{[Zr_2(O^iPr)_9]YCl_2\}_2$, **3**, also had an analogous chloride-bridged structure, despite the significantly smaller size of the metal.[16] These structures have seven-coordinate Ce, Nd, and Y atoms due to the four oxygen donor atoms of dzni and one terminal and two bridging chloride ligands.

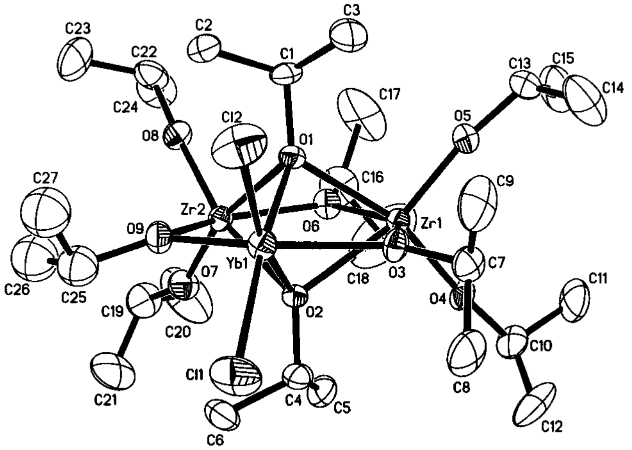

Figure 2. Plot of $[Zr_2(O^iPr)_9]YbCl_2$, **5**, with thermal ellipsoids drawn at 50% probability.

Crystallographic analysis of the ytterbium complex revealed a monomeric solid state structure, $[Zr_2(O^iPr)_9]YbCl_2$, **5**, Figure 2, in which the ytterbium ion is unsolvated and six coordinate. A reduction of coordination number is common for lanthanides as the size of the metal is decreased.[17] To determine the exact point of the cutoff between the seven-coordinate bridged structures and six-coordinate monomeric structures in the $\{[Zr_2(O^iPr)_9]LnCl_2\}_n$ series, structures of complexes of metals with radii between Y and Yb were sought. Fortunately, crystallographic data could be obtained on both Ho and Er compounds. This allowed a comparison of these metals, Ho, Y, and Er, which are usually thought to have very similar coordination chemistry.[18,19] $\{[Zr_2(O^iPr)_9]HoCl_2\}_2$, **2**, crystallized as a dimer, like the yttrium complex, **3**, but Er crystallized as a monomer, $[Zr_2(O^iPr)_9]ErCl_2$, **4**, isomorphous with the Yb complex **5**.

The structure of the Tm iodide derivative, $[Zr_2(O^iPr)_9]TmI_2$, **6**, was also determined, and, as expected on the basis of the larger size of the iodide ligands, it was monomeric, Figure 3.

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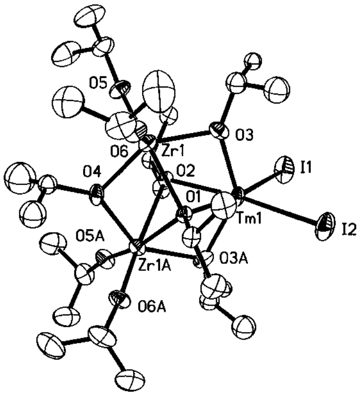

Figure 3. Plot of $[Zr_2(O^iPr)_9]TmI_2$, **6**, with thermal ellipsoids drawn at 50% probability.

Table 3. Relevant Bond Lengths and Angles for $[Zr_2(O^iPr)_9]LnCl_2$, Ln = Er (**4**), Yb (**5**)

distance/angle	**4**	**5**
Ln−Cl(1)	2.523(6)	2.499(2)
Ln−Cl(2)	2.526(5)	2.505(2)
Ln−μ^2-O	2.279(11)	2.240(4)
Ln−μ^2-O	2.298(11)	2.270(5)
Ln−μ^3-O	2.336(9)	2.297(4)
Ln−μ^3-O	2.419(11)	2.398(4)
Cl−Ln−Cl	95.2(2)	94.87(7)

Table 4. Table of Relevant Bond Lengths and Angles for $[Zr_2(O^iPr)_9]TmI_2$, **6**

distance/angle	**6**
Tm−I(1)	2.907(1)
Tm−I(2)	2.925(1)
Tm−O(3)	2.236(6)
Tm−O(1)	2.300(7)
Tm−O(2)	2.310(6)
I(1)−Tm−I(2)	89.71(3)

A summary of bond distances and angles is given in Tables 2−4. In all of the structures reported, the $[Zr_2(O^iPr)_9]^-$ unit coordinates to the metal with two triply bridging and two doubly bridging isopropoxide oxygen atoms with bond distances that are similar to those of previously reported dzni examples.[2] The dzni unit apparently is rather invariant in these structures. The lanthanide and yttrium chloride distances are also similar to analogous distances in the literature,[20,21] and bridging chloride distances are longer than the terminal distances, as is the usual case.

It is appropriate to compare the halide distances in **1**−**5** to similar distances in related cyclopentadienyl complexes since dzni, like a cyclopentadienyl ligand, is a polydentate monoanionic ligand and is potentially useful as a cyclopentadienyl replacement. No directly analogous unsolvated monocyclopentadienyl lanthanide halides are known,[5] but some comparisons with $(C_5H_5)LnCl_2(THF)_3$ complexes are made in Table 5.[23,24,25] As expected, the lower coordinate dzni ligated complexes have smaller Ln−Cl distances and the six-coordinate **4** and **5** display a greater difference from eight-coordinate $(C_5H_5)LnCl_2(THF)_3$ than seven-coordinate **2** and **3**.

Table 5. Comparison of $\{[Zr_2(O^iPr)_9LnCl(\mu\text{-}Cl)\}_2$ Structures (Ln = Ho (**2**), Y (**3**)) and $[Zr_2(O^iPr)_9]LnCl_2$ (Ln = Er (**4**), Yb (**5**)) with $(C_5H_5)LnX_2(THF)_3$ Analogues

compd	Ln−Cl(1) (Å)	Ln−Cl(2) (Å)	Cp analogue	Ln−Cl$_{av}$ (Å)
2	2.564(1)	2.729(1)	$CpHoCl_2(THF)_3$[23]	2.621(5)
3	2.564(1)	2.735(1)	$CpYCl_2(THF)_3$[24]	2.627(8)
4	2.523(6)	2.526(5)	$CpErCl_2(THF)_3$[25]	2.617(1)
5	2.499(2)	2.505(2)	$CpYbCl_2(THF)_3$[26]	2.595(5)

Discussion

Synthesis. The reaction of $K[Zr_2(O^iPr)_9]$ with cerium and yttrium trichlorides provides a convenient way to make arene-soluble mixed Zr/Ce and Zr/Y compounds, according to eq 1. This reaction also provides a general synthesis of unsolvated dzni lanthanide dihalides with both large and small lanthanides. Since this route has also been successfully employed in the synthesis of divalent lanthanide complexes $\{[Zr_2(O^iPr)_9]LnI\}_2$ (Ln = Eu, Sm, Yb) from $K[Zr_2(O^iPr)_9]$ and $LnI_2(THF)_2$,[2] ionic metathesis with $K[Zr_2(O^iPr)_9]$ appears to be a generally applicable synthetic approach to mixed-metal dzni containing electropositive metals. This is consistent with previous studies of dzni chemistry.[1]

The reaction of $TmI_2(DME)_3$ with $Zr_2(O^iPr)_8(^iPrOH)_2$ is unique to divalent thulium. $SmI_2(THF)_2$, the next most reducing divalent lanthanide diiodide, does not appear to react with $Zr_2(O^iPr)_8(^iPrOH)_2$, even after heating for several days. The reactivity of $TmI_2(DME)_3$[7] is so high that it has been difficult in the past to get clean reactivity to make isolable complexes from this reagent,[8] but in the case of eq 2, this was successful. As expected $[Zr_2(O^iPr)_9]TmI_2$, **6**, can also be made from TmI_3 and $K[Zr_2(O^iPr)_9]$, and this is the preferable synthetic route.

Structure. The most unusual structural aspect of the results reported here is that complexes **1**−**6** are routinely isolated *from THF* in solvate-free form. In the case in which dimers are formed, it is clear that the need for extra coordination around the lanthanide metal is fulfilled by a bridging halide ligand. However, in comparable cyclopentadienyl lanthanide halide systems, crystallization *from noncoordinating solvents* would be necessary to obtain solvent-free dimers: crystallization from THF would form a THF adduct.[5,21] In this regard, the dzni ligand differs from cyclopentadienyl ligands. It apparently has the ability to stabilize solvate-free dimeric systems.

This trend is even more evident in the monomeric $[Zr_2(O^iPr)_9]LnCl_2$ complexes **4** and **5**, since there are no cyclopentadienyl analogues. In fact, to our knowledge there are no other arene-soluble unsolvated $ZLnX_2$ complexes, where Z is a monoanionic ligand and X is a halide, in the literature. Since THF can diminish reactivity by blocking coordination sites, the opportunity to make solvate-free complexes is highly desirable.

The structural crossover from dimeric $n = 2$ complexes to monomeric $n = 1$ in the $\{[Zr_2(O^iPr)_9]LnCl_2\}_n$ series occurs between yttrium and erbium, two metals that generally are similar in their coordination chemistry.[19] The structural data

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obtained here suggest that Y is closer to Ho in size than to Er, and this is consistent with the Shannon radii for these ions.[16] It is possible that the structural difference may be the result of small differences in crystallization procedures and, hence, monomeric yttrium and dimeric erbium complexes may be discovered in the future. This has been observed previously with other $LnCl_3(solvate)_x$ systems,[22] but different crystallization procedures were used. In this study, attempts to get other structural types by varying crystallization conditions resulted in either no formation of crystals or the same monomer/dimer preferences described above.

Conclusions

Ionic metathesis with $K[Zr_2(O^iPr)_9]$ provides a convenient route to mixed-metal Zr/Ce and Zr/Y compounds. It also provides a route to soluble unsolvated monomeric lanthanide dihalides, a class of compounds, $(ligand)LnX_2$, for which there is no analogue in lanthanide chemistry with polydentate ligands, not even the ubiquitous cyclopentadienyl systems. Since solvate-free compounds may have enhanced reactivity, the dzni system may be very useful in lanthanide chemistry in providing arene-soluble unsolvated halide precursors.

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Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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