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Synthesis of Arene-Soluble Dizirconium Nonaisopropoxide Lanthanide Cations Involving Divalent Ytterbium

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Introduction

Cationic metal complexes are currently of interest in polymerization and Lewis acid catalyzed reactions because of the enhanced electrophilicity conveyed on the complexes by the formal positive charge.[1] Although a variety of cationic complexes are known for the lanthanide metals, almost all of these involve trivalent metals. Cationic complexes of the divalent lanthanides are of interest because they have an additional avenue of reactivity via a redox process. However, to our knowledge the only cationic complexes of the divalent lanthanides in the literature are the following specialized examples: $[Yb(THF)_6][Sn(SePh)_3]_2$,[2] $[(DIME)_3Ln][M(CO)_x]_2$ (Ln = Sm, Yb, Eu; M = Co, $x = 4$; M = Mn, $x = 5$, DIME = diethylene glycol dimethyl ether),[3] $\{(DIME)_2Yb(NCMe)_2\}\{Hg[Fe(CO)_4]_2\}$,[3] $[(DIME)Yb(NCMe)_5][B_{12}H_{12}]$,[3] and $\{(C_5H_5N)_5Yb(NCMe)_2\}\{Hg[Fe(CO)_4]_2\}$[3]. These examples show that cations containing divalent lanthanides are accessible and tend to form in a highly solvated state. Unsolvated cations would be more desirable for high reactivity because coordination sites are not blocked. However, unsolvated cations are typically more difficult to isolate because they tend to be less soluble in noncoordinating solvents.[4]

In efforts to expand the range of well-characterized cationic complexes containing divalent lanthanides, to make more soluble cations, and to attempt to make an unsolvated divalent cation, we have examined the chemistry of cationic complexes involving the dizirconium nonaisopropoxide (dzni) ligand $\{Zr_2(O^iPr)_9\}^-$. Recent studies have shown that this tetradentate monoanionic ligand can replace cyclopentadienyl ligands in traditional types of organolanthanide metallocene complexes to form analogues with enhanced solubility in nonpolar solvents which are solvent-free.[5,6] We report here on studies originating with the readily available diamagnetic precursor $\{[Zr_2(O^iPr)_9]Yb(\mu\text{-}I)\}_2$.[6]

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.[7] $K\{N(SiMe_3)_2\}$ was purchased from Aldrich and sublimed before use. $[\{Zr_2(O^iPr)_9\}Yb(\mu\text{-}I)]_2$ was prepared as previously described.[6] NMR spectra were acquired, and magnetic moments were measured by the method of Evans[8] using a Bruker DRX400 or a General Electric QE500 spectrometer. Infrared spectra were obtained using a ReactIR (Applied Systems, Inc.) spectrometer fitted with a silicon probe. The spectra were obtained with the probe-head oriented up and fitted with a cross-shaped adapter. The bottom of the adapter made an airtight connection to the probe; one side was for an incoming stream of nitrogen connected to a Schlenk line, one side was for the exit stream of nitrogen, and the top part was fitted with a septum. After an inert atmosphere was established in the adapter system, a few drops of a concentrated solution were deposited on the tip of the probe and the solution was evaporated to leave a thin film. Elemental analyses were performed by Desert Analytics, Tuscon, Arizona.

$[\{Zr_2(O^iPr)_9\}Yb\{N(SiMe_3)_2\}]$, 1. Addition of $[\{Zr_2(O^iPr)_9\}Yb(\mu\text{-}I)]_2$ (0.520 g, 0.256 mmol) to $K[N\{Si(CH_3)_3\}_2]$ (0.103 g, 0.518 mmol) in 5 mL of toluene immediately formed a red-orange solution followed by precipitation of solids within 30 s. After 10 min, the reaction was cloudy and purple. The reaction was stirred for 45 min, and white solids were removed via centrifugation. The solvent was removed by rotary evaporation leaving $[\{Zr_2(O^iPr)_9\}Yb\{N(SiMe_3)_2\}]$, **1**, as a purple oily solid (0.438 g, 80%). Neither trituration with alkanes nor high-vacuum treatment converted **1** into a powder. ^1H NMR (C_6D_6, 20 °C): δ 4.57 (m, 5H, $OC\mathit{H}(CH_3)_2$), 4.38 (m, 4H, $OC\mathit{H}(CH_3)_2$), 1.68 (d, 12H, $OCH(C\mathit{H}_3)_2$), 1.53 (d, 12H, $OCH(C\mathit{H}_3)_2$), 1.37 (d, 6H, $OCH(C\mathit{H}_3)_2$), 1.24 (d, 24H, $OCH(C\mathit{H}_3)_2$), 0.49 (s, 18H, $Si(C\mathit{H}_3)_3$). ^{13}C NMR (C_6D_6, 20 °C): δ 71.95, 71.10, 70.63, 69.19, 68.12 ($O\mathit{C}H(CH_3)_2$), 27.40, 27.13, 26.94, 26.82, 22.97, ($OCH(\mathit{C}H_3)_2$), 2.57 ($N[Si(\mathit{C}H_3)_3]_2$). IR (neat film): 2958 s, 2925 s, 2861 s, 1605 w, 1580 w, 1567 w, 1461 m, 1378 m, 1252 m, 1177 m, 1162 m, 1136 m, 1009 m, 932 w, 841 m, 727 m cm^{-1}.

$[\{Zr_2(O^iPr)_9\}Yb(THF)_2][BPh_4]$, 2. Addition of **1** (0.139 g, 0.133 mmol) to a slight excess of $[NH_4][B(C_6H_5)_4]$ (0.042 g, 0.134 mmol) in 5 mL of THF immediately formed a slightly cloudy orange mixture. After the solution was stirred for 12 h, a small amount of white insoluble material was separated by centrifugation and the solvent was removed via rotary evaporation to leave an orange solid. The solid was extracted with toluene and dried under vacuum to give the mono-THF solvate $[\{Zr_2(O^iPr)_9\}Yb(THF)][BPh_4]$ as a yellow-orange powder (0.146 g, 84%). Anal. Calcd for $YbZr_2O_{10}C_{55}H_{91}$: C, 51.67; H, 7.17. Found: C, 51.32; H, 7.09. ^1H NMR (C_6D_6, 20 °C): δ 8.11 (broad s ($\nu_{1/2}$ 32 Hz), 8H, $B(C_6\mathit{H}_5)_4$), 7.38 (broad s ($\nu_{1/2}$ 40 Hz), 8H, $B(C_6\mathit{H}_5)_4$), 6.98 (s, 4H, $B(C_6\mathit{H}_5)_4$), 4.38 (m, 8H, $OC\mathit{H}(CH_3)_2$), 3.90 (m, 1H, $OC\mathit{H}(CH_3)_2$), 3.56 (s, THF), 1.41 (s, THF), 1.38 (d, 6H, $OCH(C\mathit{H}_3)_2$), 1.20 (overlapping d, 36H, $OCH(C\mathit{H}_3)_2$), 0.91 (d, 12H, $OCH(C\mathit{H}_3)_2$). ^{13}C NMR (C_6D_6, 20 °C): δ 69.1 ($O\mathit{C}H(CH_3)_2$), 67.8 (THF), 31.91 (THF), 27.1, 26.8, 25.8 ($OCH(\mathit{C}H_3)_2$). IR (neat film): 3217 s, 2966 s, 2929 m, 2861 m, 2626 w, 1958 w, 1904 w, 1578 w, 1463 m,. 1362 s, 1260 s, 1167 s, 1011 s, 833 m, 710 m cm^{-1}. Recrystallization of $\{[Zr_2(O^iPr)_9]Yb(THF)\}[BPh_4]$ from a concentrated toluene solution at −30 °C gave crystals of **2** suitable for X-ray analysis.

X-ray Data Collection, Structure Determination, and Refinement for 2. A yellow crystal of dimensions 0.20 mm × 0.33 mm × 0.40 mm was mounted on a glass fiber and transferred to a Siemens CCD platform diffractometer. The SMART[10] program package was used to determine the unit-cell parameters and for data collection (30 s/frame scan time for a hemisphere of diffraction data). The raw frame data

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Table 1. X-ray Data Collection Parameters for $[\{Zr_2(O^iPr)_9\}Yb(THF)_2][BPh_4]$, **2**

	2
formula	$C_{66}H_{107}BO_{11}YbZr_2$
fw	1442.81
temp (°C)	−115
space group	$P2_1/c$ (No. 14)
a (Å)	16.2654(7)
b (Å)	19.8330(9)
c (Å)	21.6504(10)
β (deg)	91.7330(10)
V (Å^3)	6980.9(5)
Z	4
λ (Å)	0.710 73
ρ_{calcd} (Mg/m^3)	1.373
diffractometer	Siemens CCD
μ (mm^{-1})	1.675
R1[a]	0.0254
wR2[b]	0.0588

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_o^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

was processed using SAINT[12] and SADABS[13] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[14] program. The diffraction symmetry was $2/m$, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$, which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. One equivalent of toluene cocrystallized with the title compound. The analytical scattering factors[10] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0588 and GOF = 1.033 for 1114 variables refined against 17 024 unique data (as a comparison for refinement on F, R1 = 0.0254 for those 14 772 data with [$I > 2.0\sigma(I)$]) (Table 1).

$[\{Zr_2(O^iPr)_9\}Yb][BPh_4]$, 3. Addition of **1** (0.370 g, 0.35 mmol) to a slight excess of $[NH_4][B(C_6H_5)_4]$ (0.110 g, 0.36 mmol) in 5 mL of toluene formed a red-orange solution after being stirred for 30 min. After 24 h, the reaction mixture was slightly cloudy. White insolubles were removed by centrifugation, and the solvent was removed via rotary evaporation to leave an orange, oily solid. Repeated trituration with hexanes gave $[\{Zr_2(O^iPr)_9\}Yb][BPh_4]$, **3**, as an orange powder (0.303 g, 64%). ^1H NMR (C_6D_6, 20 °C): δ 7.92 (broad s ($\nu_{1/2}$ 45 Hz), 8H, $B(C_6H_5)_4$), 7.39 (broad ($\nu_{1/2}$ 35 Hz) s, 8H, $B(C_6H_5)_4$), 7.16 (s, 4H, $B(C_6H_5)_4$), 4.24 (m, 8H, $OCH(CH_3)_2$), 4.10 (m, 1H, $OCH(CH_3)_2$), 1.35 (d, 6H, $OCH(CH_3)_2$), 1.22 (d, 12H, $OCH(CH_3)_2$), 1.19 (overlapping d, 24H, $OCH(CH_3)_2$), 1.12 (d, 12H, $OCH(CH_3)_2$). ^{13}C NMR (C_6D_6, 20 °C): δ 137.3, 127.9, 123.7 ($B(C_6H_5)$), 72.4, 69.3 ($OCH(CH_3)_2$), 27.3, 26.7, 26.5, 26.4 ($OCH(CH_3)_2$). IR (neat film): 3217 m, 2966 s, 2931 w, 2861 m, 1561 w, 1463 m, 1376 m, 1337 w, 1262 m, 1167 s, 1007 s, 960 m, 845 m, 806 w, 702 w, 675 w cm^{-1}. Addition of THF to **3** (0.124 g, 0.103 mmol) generated **2** (0.127 g, 95%).

Results and Discussion

The reaction of $[\{Zr_2(O^iPr)_9\}Yb(\mu\text{-}I)]_2$ with $AgBPh_4$ was examined as a possible route to a $\{(dzni)Yb\}^+$ moiety. Unfortunately, instead of halide abstraction, redox chemistry occurred and Ag metal and paramagnetic trivalent ytterbium products were formed.

An alternative approach based on work by Ephritikhine et al. with uranium systems involved removal of an NR_2 ligand with $[NH_4][BPh_4]$.[9] The necessary precursor, the heteroleptic dzni complex $[\{Zr_2(O^iPr)_9\}Yb\{N(SiMe_3)_2\}]$, **1**, can be prepared in good yield from the reaction of $[\{Zr_2(O^iPr)_9\}Yb(\mu\text{-}I)]_2$ and $K\{N(SiMe_3)_2\}$, according to

$$[\{Zr_2(O^iPr)_9\}Yb(\mu\text{-}I)]_2 + 2K\{N(SiMe_3)_2\} \xrightarrow{THF} 2[\{Zr_2(O^iPr)_9\}Yb\{N(SiMe_3)_2\}] + 2KI \quad (1)$$

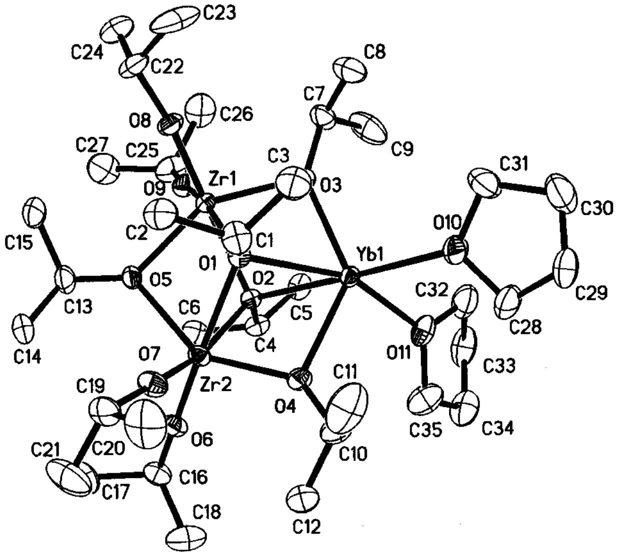

Figure 1. Thermal ellipsoid plot of the $[\{Zr_2(O^iPr)_9\}Yb(THF)_2]^+$ cation in $[\{Zr_2(O^iPr)_9\}Yb(THF)_2][BPh_4]$, **2**, with ellipsoids drawn at the 50% level.

Complex **1** is extremely soluble in arene and alkane solvents and is difficult to dry completely. Despite the oily nature of the product, no solvent was observed in the NMR spectra and the ^1H NMR spectrum showed only one 4:2:2:1 set of signals typical of the isopropoxide groups of a dzni complex.[5,6] The ^{13}C NMR spectrum also showed the expected several signals for a single type of dzni ligand.

Although **1** was resistant to crystallization, it could be converted in high yield to a divalent cationic complex $[\{Zr_2(O^iPr)_9\}Yb(THF)_2][BPh_4]$, **2**, using $[NH_4][BPh_4]$ in THF (Figure 1:

$$\underset{\mathbf{1}}{[\{Zr_2(O^iPr)_9\}Yb\{N(SiMe_3)_2\}]} + [NH_4][BPh_4] \xrightarrow[-NH_3 \atop -HN(SiMe_3)_2]{THF} \underset{\mathbf{2}}{[\{Zr_2(O^iPr)_9\}Yb(THF)_2][BPh_4]} \quad (2)$$

The ^1H NMR spectrum of **2** shows the presence of the $[BPh_4]^-$ anion and the dzni ligand in a 1:1 ratio overall as well as coordinated THF. Elemental analysis of **2** in powder form was consistent with the isolation of a monosolvate, but crystallographic analysis of single crystals revealed the presence of two coordinated THF solvent molecules per Yb (Figure 1). Complex **2** is the first solvated lanthanide $[Zr_2(O^iPr)_9]^-$ species to be crystallographically characterized; all other examples of divalent or trivalent lanthanide dzni complexes have been isolated as solvent-free species.[5,6]

By X-ray crystallography, **2** was found to crystallize in the solid state as a monomeric species containing six coordinate ytterbium and zirconium centers. The $\{Zr_2(O^iPr)_9\}^-$ ligand coordinates to the metal through four bridging isopropoxide groups, as observed in all other dzni lanthanide complexes structurally characterized to date.[5,6] The bond distances with the dzni unit are conventional. The Yb−O distances can be compared to the only other known divalent Yb(II) dnzi complex,

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$(C_5H_5)Yb\{Zr_2(O^iPr)_9\}$, **4**.[5] The 2.381(1)−2.475(1) Å range of Yb−O distances in **2** is similar to the 2.44(6)−2.46(4) Å range in $(C_5H_5)Yb\{Zr_2(O^iPr)_9\}$, **4**, within error limits. This is somewhat unusual because **2** is lower coordinate and carries a formal positive charge.

The fact that the dzni ligand does not break down in the presence of $K\{N(SiMe_3)_2\}$ or ammonium reagents is significant because it is being evaluated as a cyclopentadienyl replacement for lanthanide complexes. To be useful in this regard, it must be inert to the common reagents used in this field.

Compound **1** also reacts with 1 equiv of $[NH_4][BPh_4]$ *in arenes* to form the unsolvated cation $[\{Zr_2(O^iPr)_9\}Yb][BPh_4]$, **3**. The ^{1}H NMR signals for the phenyl peaks of the anion appear at 7.92, 7.36, and 7.19 ppm and integrate into an 8:8:4 ratio. The peaks for the tertiary protons of the dzni ligand appear at 4.24 and 4.10 ppm in an 8:1 ratio. Three sets of methyl protons were distinct in a 2:2:1 ratio. Two other sets of doublets were too close together to integrate separately but integrated to a relative intensity of 4 as expected for two doublets. The ^{13}C NMR spectrum shows only peaks associated with the dzni ligand and the $[BPh_4]^-$ anion; no peaks for THF were observed. Compound **3** can be quantitatively converted to **2** upon treatment with THF. The solubility of **3** in toluene at 20 °C is 0.21 g/mL.

Conclusion

The dzni ligand has proven to be effective in generating arene-soluble cationic complexes containing a divalent lanthanide center. As anticipated, the dzni group provides good solubility to this class of cationic complexes and both solvated and unsolvated complexes are stabilized by dzni. We are currently examining the reactivity of these compounds and exploring the generality of amide protonolysis as a route to new divalent and trivalent cationic lanthanide complexes.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of $[\{Zr_2(O^iPr)_9\}Yb(THF)_2][BPh_4]$, **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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