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Divalent lanthanide complexes free of coordinating anions: facile synthesis of fully solvated dicationic $[LnL_x]^{2+}$ compounds

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Abstract

Fully-solvated, divalent lanthanide dication complexes free of coordinating anions, $[LnL_x]^{2+}$, in which L = MeCN, THF, have been synthesized by protonation of amide, indenyl, and pentamethylcyclopentadienyl precursors. The Sm(II) dication $[Sm(THF)_7]^{2+}$ was initially isolated as $[Sm(THF)_7][BPh_4]_2$, (**1**), by protonolysis of the indenyl complex $(C_9H_7)_2Sm(THF)_3$ with $[Et_3NH][BPh_4]$. Compound **1** can also be obtained from $(C_5Me_5)Sm[N(SiMe_3)_2](THF)_2$ and $[Et_3NH][BPh_4]$. The Yb analog, $[Yb(THF)_6][BPh_4]_2$, (**2**), was obtained from the reaction of the bimetallic $[(C_5Me_5)Yb(THF)]_2(C_8H_8)$ with $AgBPh_4$ and the reaction of $(C_5Me_5)Yb[N(SiMe_3)_2](THF)_2$ with $[Et_3NH][BPh_4]$, but $[YbL_x]^{2+}$ is best obtained from the reaction of $Yb[N(SiMe_3)_2]_2(THF)_2$ with $[Et_3NH][BPh_4]$. Reaction of $Yb[N(SiMe_3)_2]_2(THF)_2$ with $[Et_3NH][BPh_4]$ in THF followed by recrystallization from acetonitrile affords $[Yb(MeCN)_8][BPh_4]_2$, (**3**). The seven THF molecules in **1** form a pentagonal bipyramidal ligand environment around Sm^{2+}. Complex **2** has an octahedral Yb^{2+} coordination environment and **3** has a distorted square antiprismatic arrangement of MeCN ligands around Yb^{2+}.

Keywords: Lanthanides; Dications; Divalent; Cyclopentadienyl; Amide; Protonolysis

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1. Introduction

Recently, the chemistry of cationic metal complexes has received considerable attention due to the enhanced electrophilicity conveyed on such complexes by the formal positive charge and the effect this can have in polymerization and Lewis acid catalyzed reactions [1,2]. Several types of cationic complexes are known for the lanthanide metals, almost all of which involve the metals in their most common and stable +3 oxidation state [2,3]. Cationic complexes of divalent lanthanides are potentially more interesting since they also possess redox reactivity. To our knowledge the only crystallographically characterized cationic complexes of the divalent lanthanides in the literature are the following specialized examples: $[Yb(THF)_6][Sn(SePh)_3]_2$ [4], $[Sm(THF)_7][Zn_4(\mu^2\text{-}SePh)_6(SePh)_4]$ [4] $[(DIME)_3Ln][M(CO)_x]_2$ (Ln = Sm, Yb, Eu; M = Co, $x = 4$; M = Mn, $x = 5$, DIME = diethylene glycol dimethyl ether) [5], $\{(DIME)_2Yb(NCMe)_2\}\{Hg[Fe(CO)_4]_2\}$ [5], $[(DIME)Yb(NCMe)_5][B_{12}H_{12}]$ [5], $\{(C_5H_5N)_5Yb(NCMe)_2\}\{Hg[Fe(CO)_4]_2\}$ [5], $[\{Zr_2(O^iPr)_9\}Yb(THF)_2][BPh_4]$ [6] $\{[C_5H_3(SiMe_3)_2]Sm(18\text{-crown-}6)\}\{[C_5H_3(SiMe_3)_2]_3Sm\}$ [7] and $\{[C_5H_3(SiMe_3)_2]Yb(18\text{-crown-}6)\}[C_5H_3(SiMe_3)_2]$ [7]. The isolation of these specific compounds depends crucially on the choice of reaction solvent and counter-anion.

Some years ago in an effort to make cationic metallocene complexes from $(C_9H_7)_2Sm(THF)_3$ [8] by protonolysis with $[Et_3NH][BPh_4]$, a common route to make cationic f-element derivatives [2,9,10] the fully solvated $[Sm(THF)_7][BPh_4]_2$ (**1**), was isolated and crystallographically characterized [11]. The existence of this dication free of any coordinating anions stimulated our interest in this class of compounds in terms of their reactivity compared with that of the popular reagent $SmI_2(THF)_2$ [12]. An indirect route to an ytterbium

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analog, $[Yb(THF)_6][BPh_4]_2$ (**2**), was also discovered in the reaction of $[(C_5Me_5)Yb(THF)]_2(C_8H_8)$ [13] with 1 equiv. of $AgBPh_4$. Attempts to make the putative $[(C_5Me_5)Yb(THF)_x]^+$ intermediate in the latter reaction by protonolysis of $(C_5Me_5)Yb[N(SiMe_3)_2](THF)_2$ [14] provided a reliable route to **2**. Protonolysis of $(C_5Me_5)Sm[N(SiMe_3)_2](THF)_2$ likewise formed **1**. Although these syntheses were more reliable and they indicated that fully solvated lanthanide dication complexes could be obtained with simple counter-anions, the synthetic route was not optimal since it was not an efficient use of the C_5Me_5 ligand.

We report here that the reaction of the bis(trimethylsilyl)amide complexes, $Ln[N(SiMe_3)_2]_2(THF)_2$ (Ln = Sm [15] Yb [16]) with alkylammonium salts of $[BPh_4]^-$ constitutes a useful synthesis of divalent lanthanide complexes free of any coordinating anions. Dicationic $[LnL_x]^{2+}$ species are isolated in which L is a common solvent such as THF or MeCN and the anion is a non-coordinating tetraarylborate.

2. Experimental

2.1. General

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox techniques. $Ln[N(SiMe_3)_2]_2(THF)_2$, [14,15] $[(C_5Me_5)Yb(THF)]_2(C_8H_8)$, [13] $(C_9H_7)_2Sm(THF)_3$, [8] and $(C_5Me_5)Ln[N(SiMe_3)_2](THF)_2$ [14] were prepared by the literature method. Solvents were purified as previously described [17]. NMR spectra were recorded and magnetic moments were measured by the method of Evans [18] using a Bruker DRX400 or a General Electric GE500 spectrometer. Infrared spectra were recorded on a ReactIR system (Applied Systems Inc.) as thin films [6]. Complexometric analyses for Yb and Sm were performed as previously described [19]. C and H elemental analyses were carried out by Desert Analytics, Tucson, AZ.

2.2. $[Sm(THF)_7][BPh_4]_2$, (*1*). From $(C_9H_7)_2Sm(THF)_3$

In a glovebox, $(C_9H_7)_2Sm(THF)_3$ (27 mg, 0.055 mmol) and $[Et_3NH][BPh_4]$ (24 mg, 0.057 mmol) were stirred in 5 ml of THF for 20 h. The initially bright purple mixture became green–brown. Concentration of this THF solution at −35 °C for 48 h resulted in the isolation of **1** as purple crystals suitable for X-ray crystallographic analysis.

2.3. $[Sm(THF)_7][BPh_4]_2$ (*1*). From $(C_5Me_5)Sm[N(SiMe_3)_2](THF)_2$

In a glovebox, $(C_5Me_5)Sm[N(SiMe_3)_2](THF)_2$ (0.126 g, 0.21 mmol) was reacted with $[Et_3NH][BPh_4]$ (0.067 g, 0.22 mmol) in 4 ml of THF. The clear purple solution was stirred 12 h and then centrifuged to remove a small amount of white insoluble material. The solvent was removed from the deep purple–blue solution via rotary evaporation to leave purple solids. ^1H NMR spectroscopy in THF-d_8 was consistent with the presence of $(C_5Me_5)_2Sm(THF)_2$ [20] and two BPh_4 groups per two C_5Me_5 groups. Concentration of the solution at −30 °C resulted in the formation of purple crystals of **1** (0.103 g, 75%). The NMR spectra of the supernatant revealed only $(C_5Me_5)_2Sm(THF)_2$. ^1H NMR (THF-d_8, 20 °C): δ 7.14 (broad s, 2H), 6.85 (broad s, 3H), 3.57 (THF), 1.58 (THF). ^{13}C NMR (THF-d_8, 20 °C): δ 133.9, 122.7, 119.1 (phenyl), 67.5, 23.2 (THF). IR: 2968 w, 2361 m, 2327 w, 1620 m, 1477 w, 1426 w, 1270 m, 1157 w, 1031 m, 950 w, 871 m, 711 m cm^{-1}. *Anal.* Calc. for $SmB_2O_7C_{76}H_{96}$: C, 70.56; H, 7.42. Found: C, 69.80; H, 7.26%.

2.4. $[Yb(THF)_6][BPh_4]_2$ (*2*). From $[(C_5Me_5)Yb(THF)]_2(C_8H_8)$

Red $[(C_5Me_5)Yb(THF)]_2(C_8H_8)$ (0.072 g, 0.08 mmol) reacts with $AgBPh_4$ (0.036 g, 0.08 mmol) in 5 ml of THF to form a brown–yellow solution and black insoluble material over 8 h. Solids were removed by centrifugation and the resulting red–brown supernatant was dried via rotary evaporation to yield a purple–red solid. Extraction of this solid with 4 ml of toluene yielded a red–purple toluene solution and black insoluble material. The ^1H and ^{13}C NMR spectra of the toluene soluble product showed only the presence of $(C_5Me_5)Yb(C_8H_8)$ [13]. When the toluene insoluble material was treated with THF, a bright yellow solution formed from which **2** crystallizes from over the period of 48 h at room temperature (r.t.; 0.037 g, 36%). These crystals were suitable for X-ray analysis. The NMR spectrum of the supernatant revealed only $(C_5Me_5)_2Yb(THF)$ [21] (1.89 ppm). ^1H NMR (THF-d_8, 20 °C): δ 7.35 (m, C_6H_5), 6.91 (m, C_6H_5), 6.78 (m, C_6H_5), 3.65 (s, THF), 1.75 (s, THF) ^{13}C NMR: δ 137.7, 125.8, 121.9. (C_6H_5). IR: 3033 m, 2991 w, 2949 m, 2869 w, 2243 w, 1644 s, 1513 s, 1463 s, 1278 s, 1089 s, 1046 m, 940 s, 907 m, 837 w, 772 s, 683 m cm^{-1}. *Anal.* Calc. for $YbB_2O_6C_{72}H_{88}$: C, 69.51; H, 7.13. Found: C, 69.14; H, 6.71%. Addition of MeCN to **2** quantitatively generates **3**, as determined by NMR spectroscopy and by indexing the crystals of **3**, which formed.

2.5. *[Yb(THF)$_6$][BPh$_4$]$_2$ (**2**). From (C$_5$Me$_5$)Yb[N(SiMe$_3$)$_2$](THF)$_2$*

In a glovebox, $(C_5Me_5)Yb[N(SiMe_3)_2](THF)_2$ (0.267 g, 0.44 mmol) reacts with $[Et_3NH][B(C_6H_5)_4]$ (0.137 g, 0.46 mmol) in 4 ml of THF over 12 h to form a deep orange–yellow solution and a small amount of white insoluble material which was removed by centrifugation. The solvent was removed via rotary evaporation to leave a yellow solid. ^{1}H NMR data (THF-d_8) indicated the presence of $(C_5Me_5)_2Yb(THF)$ [21] and phenyl signals consistent with the presence of two BPh_4 groups per two C_5Me_5 groups. Concentration of the solution at −30 °C resulted in the formation of yellow crystals of **2** (0.210 g, 77%), while the NMR spectrum of the supernatant showed only peaks for $(C_5Me_5)_2Yb(THF)$.

2.6. *[Yb(MeCN)$_8$][BPh$_4$]$_2$, (**3**)*

In a glovebox, red $Yb[N(SiMe_3)_2]_2(THF)_2$ (71 mg, 0.11 mmol) reacts with $[Et_3NH][BPh_4]$ (94 mg, 0.23 mmol) in THF over 12 h to form a pale yellow supernatant which was separated from yellow insoluble material via centrifugation. Addition of 5 ml of MeCN to the insoluble product generates a bright orange solution. Concentration of this solution at −30 °C resulted in the isolation of **3** (86 mg, 68%). ^{1}H NMR (CD_3CN, 20 °C): δ 7.25 (m, 2H, C_6H_5), 6.98 (m, 2H, C_6H_5), 6.82 (m, 1H, C_6H_5), 1.96 (MeCN). ^{13}C NMR: δ 136.8, 126.6, 122.8 (C_6H_5). IR: 3057 m, 3003 w, 2930 s, 2304 m, 2274 m, 1583 w, 1482 w, 1268 m, 1185 m, 1067 m, 1031 s, 988 m, 926 s, 849 m, 737 s, 706 s cm^{-1}. *Anal.* Calc. for $C_{64}H_{64}N_8B_2Yb$: C, 67.43; H, 5.66. Found: C, 68.09; H, 5.63%. Crystals suitable for X-ray analysis were obtained from a concentrated solution of **3** at r.t.

2.7. *X-ray data collection, structure determination and refinement for [Sm(THF)$_7$][BPh$_4$]$_2$·THF*

A dark red crystal of approximate dimensions 0.13 × 0.23 × 0.30 mm was mounted in a thin-walled capillary under nitrogen and transferred to a Siemens P4 rotating-anode diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by standard procedures [22]. Intensity data were collected at 296 K using a θ–2θ scan technique with Mo Kα radiation under the conditions described in Table 1. All 5176 data were corrected for absorption [23] and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences hkl for $h+k=2n+1$ and $h0l$ for $h+l=2n+1$. The two possible monoclinic space groups are the noncentrosymmetric Cc or the centrosymmetric $C2/c$. It was later determined that space group $C2/c$ was correct.

Table 1
X-ray collection parameters for $[Sm(THF)_7][BPh_4]_2\cdot THF$ (**1**) THF, $[Yb(THF)_6][BPh_4]_2\cdot THF$ (**2**) THF, and $[Yb(MeCN)_8][BPh_4]_2\cdot 2MeCN$ (**3**) 2MeCN

Compound	**1** THF	**2** THF	**3** 2MeCN
Formula	$C_{80}H_{114}O_8B_2Sm$	$C_{76}H_{96}B_2O_7Yb$	$C_{68}H_{70}B_2N_{10}Yb$
Fw	1356.6	1316.18	1222.00
Temperature (K)	296	163	158
Crystal system	monoclinic	monoclinic	tetragonal
Space group	$C2/c$	$P2_1/n$	$I4_1cd$
a (Å)	20.742(3)	11.9661(6)	18.3318(6)
b (Å)	19.319(3)	13.3457(7)	18.3318(6)
c (Å)	18.556(3)	21.0776(10)	39.9872(17)
α (°)	90	90	90
β (°)	95.085(11)	94.580(1)	90
γ (°)	90	90	90
V (Å^3)	7406(2)	3355.3(3)	13 437.9(8)
Z	4	2	8
ρ_{calc} (Mg m^{-3})	1.225	1.303	1.208
Diffractometer	Siemens P4 RA	Siemens CCD	Siemens CCD
μ (mm^{-1})	0.846	1.447	1.437
Final R indicies	0.080	0.1558	0.1307
$R1[I>2\sigma(I)]$	0.072	0.0693	0.0470

Crystallographic calculations were carried out using either a locally modified version of the UCLA Crystallographic Computing Package [24] or the SHELXTL PLUS program set [25]. The analytical scattering factors for neutral atoms were used throughout the analysis; [26] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The structure was solved via an automated Patterson routine (SHELXTL) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d(C–H) = 0.96$ Å and $U_{iso} = 0.08$ Å^2. The molecule is located about a twofold rotation axis. Atoms Sm(1) and O(2) lie directly on the twofold axis and were each assigned site-occupancy-factors of 1/2. There are two molecules of tetraphenylborate and one molecule of THF per formula unit. The THF molecule is located about the twofold rotation axis and is disordered. The five atoms that define the THF are disordered over six positions as a result of the molecule lying about the twofold. Each of the three symmetry-independent atoms (C(39), C(40), C(41)) were refined as carbon atoms with site-occupancy-factors of 0.88889 to account for an equal disorder of the oxygen and carbon atoms over the six sites. The hydrogen atoms associated with the disordered THF were not included in the refinement. Refinement of positional and thermal parameters led to convergence with $R_F = 7.2\%$; $R_{wF} = 8.0\%$ and GOF = 1.20 for 416 variables refined against those 3439 data with $F > 3.0\sigma(F)$. A final difference-Fourier synthesis yielded $\rho(\max) = 0.90$ e Å^{-3}. Selected bond distances and angles are given in Table 2.

2.8. *X-ray data collection, structure determination, and refinement for [Yb(THF)$_6$][BPh$_4$]$_2$·THF*

A yellow crystal of dimensions 0.33 × 0.11 × 0.11 mm was mounted on a glass fiber and transferred to a Siemens CCD platform diffractometer. The SMART [27] program package was used to determine the unit-cell parameters and for data collection (30 s per frame scan time for a hemisphere of diffraction data). The raw frame data were processed using SAINT [28] and SADABS [29] to yield the reflection data files. Subsequent calculations were carried out using the SHELXTL [30] program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ 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 molecule of THF co-crystallized with the ytterbium complex. Disorder in the BPh$_4$ and THF groups was modeled by assigning partial occupancy to disordered components. The analytical scattering factors [26] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, $wR_2 = 0.1558$ and GOF = 1.151 for 355 variables refined against 8004 unique data. Selected bond distances are given in Table 2.

2.9. *X-ray data collection, structure determination, and refinement for [Yb(MeCN)$_8$][BPh$_4$]$_2$·2MeCN*

A yellow crystal of dimensions 0.40 × 0.27 × 0.30 mm was handled as described in the previous paragraph. The diffraction symmetry was $4/mmm$ and the systematic absences were consistent with the tetragonal space group $I4_1cd$ which was later determined to be correct. The structure was solved as described in the previous paragraph. Two molecules of acetonitrile co-crystallized with the compound. Disorder in the acetonitrile was modeled by assigning partial occupancy to disordered components. At convergence, $wR_2 = 0.1307$ and GOF = 1.188 for 363 variables refined against 7426 unique data. Selected bond distances are given in Table 3.

Table 2
Selected bond lengths and angles for [Sm(THF)$_7$][BPh$_4$]$_2$ (**1**), and [Yb(THF)$_6$][BPh$_4$]$_2$ (**2**)

[Sm(THF)$_7$][BPh$_4$]$_2$		[Yb(THF)$_6$][BPh$_4$]$_2$	
Bond lengths			
Sm–O(1)	2.646(10)	Yb–O(1)	2.388(4)
Sm–O(2)	2.555(8)	Yb–O(2)	2.392(4)
Sm–O(3)	2.569(8)	Yb–O(3)	2.350(4)
Sm–O(4)	2.621(8)		
Bond angles			
O(1)–Sm–O(2)	87.8(2)	O(1)–Yb–O(2)	88.14(15)
O(2)–Sm–O(4)	77.1(3)	O(1)–Yb–O(3)	88.13(15)
O(4)–Sm–O(2′)	106.6(3)	O(2)–Yb–O(3)	89.50(16)
O(1)–Sm–O(3)	75.3(2)	O(1)–Yb–O(1′)	180.0(30
O(4)–Sm–O(4′)	72.9(4)	O(3′)–Yb–O(1)	91.87(15)
O(2)–Sm–O(3)	99.0(3)	O(1′)–Yb–O(2′)	91.86(15)
O(3′)–Sm–O(2)	79.9(3)	O(3)–Yb–O(2′)	90.50(16)
O(2)–Sm–O(2′)	175.5(4)		
O(3)–Sm–O(4)	74.6(3)		

Table 3
Selected bond lengths and angles for [Yb(MeCN)$_8$][BPh$_4$]$_2$ (**3**)

Bond lengths	
Yb–N(1)	2.566(10)
Yb–N(2)	2.537(10)
Yb–N(3)	2.552(10)
Yb–N(4)	2.570(9)
Bond angles	
N(1)–Yb–N(2)	73.6(3)
N(1)–Yb–N(3)	74.1(3)
N(1)–Yb–N(4)	86.44(17)
N(2)–Yb–N(3)	119.51(18)
N(2)–Yb–N(4)	149.4(4)
N(3)–Yb–N(4)	74.9(3)
N(2′)–Yb–N(2)	82.1(4)
N(2′)–Yb–N(3)	132.42(16)
N(3′)–Yb–N(1′)	150.0(4)
N(2)–Yb–N(4′)	69.8(3)

3. Results

3.1. *Synthetic results. Initial isolation of [Sm(THF)$_7$]$^{2+}$ (1), and [Yb(THF)$_6$]$^{2+}$ (2)*

As part of a study of the reaction chemistry of the bis(indenyl) Sm(II) metallocene, (C$_9$H$_7$)$_2$Sm(THF)$_3$ [8] this complex was treated with [Et$_3$NH][BPh$_4$] to see if Sm(II) reduction or ligand protonation would occur first. Surprisingly, the only isolated product was [Sm(THF)$_7$][BPh$_4$]$_2$ (**1**), Fig. 1, which contained a fully solvated Sm(II) dication free of any coordinating anions. Although this reaction provided material suitable for crystallographic studies and demonstrated the existence of this dication, it had neither the yield nor the reliability to be useful synthetically.

An ytterbium analog of **1** was also obtained in an indirect manner. In this case, the synthesis arose from efforts to prepare a mixed valent bimetallic species such as {[(C$_5$Me$_5$)Yb$^{\rm III}$(THF)$_x$](μ-C$_8$H$_8$)[(C$_5$Me$_5$)-Yb$^{\rm II}$(THF)$_x$]}$^+$ from the reaction of [(C$_5$Me$_5$)Yb-(THF)]$_2$(C$_8$H$_8$) with 1 equiv. of AgBPh$_4$. As shown in Eq. (1), the

$$[(\mathrm{C_5Me_5})\mathrm{Yb(THF)}]_2(\mathrm{C_8H_8}) + \mathrm{AgBPh_4} \xrightarrow[-\mathrm{Ag}]{\mathrm{THF\ \ toulene}} (\mathrm{C_5Me_5})\mathrm{Yb}(\mathrm{C_8H_8}) + \mathbf{A} \qquad (1)$$

reaction, initially led to the formation of toluene soluble (C$_5$Me$_5$)Yb(C$_8$H$_8$) and a black toluene insoluble mate-

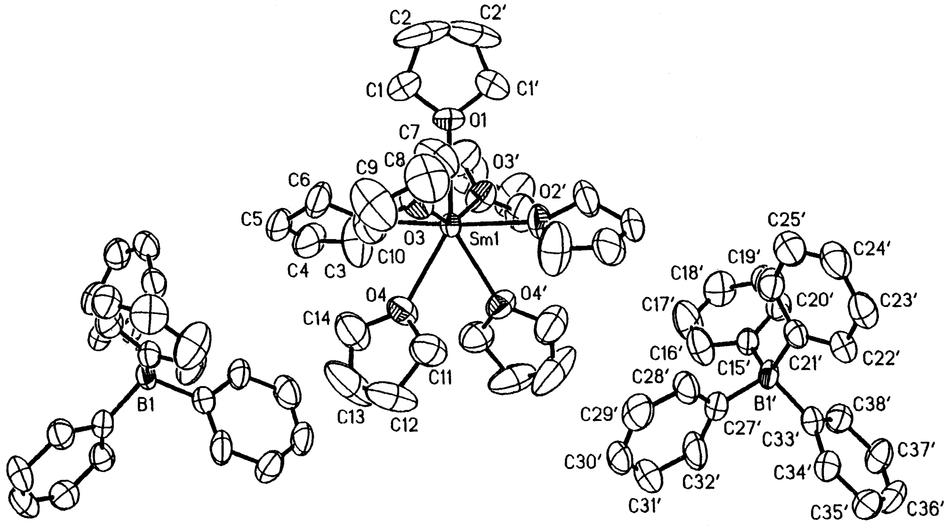

Fig. 1. Thermal ellipsoid plot of $[Sm(THF)_7][BPh_4]_2$ (**1**), with ellipsoids drawn at the 50% probability level.

rial, **A**. Subsequent treatment of **A** with THF gave a mixture from which $[Yb(THF)_6][BPh_4]_2$, (**2**), preferentially crystallized leaving $(C_5Me_5)_2Yb(THF)$ [21] in the mother liquor according to Eq. (2).

$$\mathbf{A} \xrightarrow{\mathrm{THF}} [Yb(THF)_6][BPh_4]_2 + (C_5Me_5)_2Yb(THF) \qquad (2)$$

Compound **2** was characterized by NMR, IR, elemental analysis and X-ray crystallography, Fig. 2. The ^1H NMR spectrum of **2** shows only resonances for the tetraphenylborate groups at 7.35, 6.91, and 6.78 ppm and coordinated THF appears at 3.65 and 1.75 ppm. The ^{13}C NMR spectrum has tetraphenylborate peaks at 137.7, 125.8, and 121.9 ppm as well as peaks for the associated THF molecules.

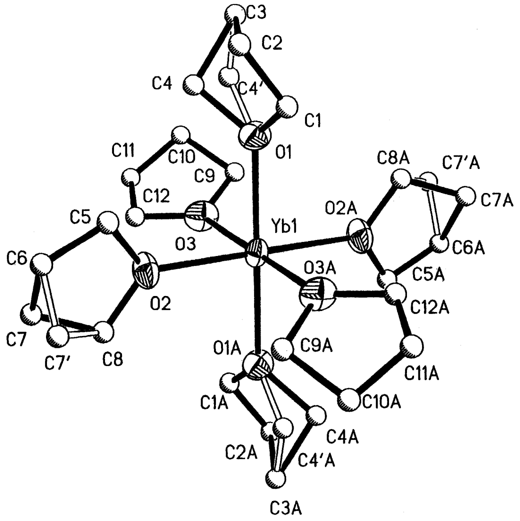

Fig. 2. Thermal ellipsoid plot of the $[Yb(THF)_6]^{2+}$ dication in **2**, drawn at the 50% probability level.

3.2. *Improved synthesis of $[Yb(THF)_6]^{2+}$*

The products of Eq. (2) suggested that the black insoluble **A** contained a mono(pentamethylcyclopentadienyl) Yb(II) cation, $[(C_5Me_5)Yb(THF)_x]^+$. In efforts to make such a complex directly, $(C_5Me_5)Yb[N(SiMe_3)_2](THF)_2$ [14] was treated with 1 equiv. of $[Et_3NH][BPh_4]$ in THF. This resulted in the formation of a yellow solution which had a ^1H NMR spectrum containing a resonance at 1.93 ppm in THF-d_8 different from $(C_5Me_5)_2Yb(THF)$ or starting materials. Attempts to crystallize this product again generated $[Yb(THF)_6][BPh_4]_2$ and $(C_5Me_5)_2Yb(THF)$ in a combined yield of 77% based on Yb, according to Eq. (3).

$$(C_5Me_5)Yb[N(SiMe_3)_2](THF)_2 + [Et_3NH][BPh_4] \xrightarrow{\mathrm{THF}} [Yb(THF)_6][BPh_4]_2 + (C_5Me_5)_2Yb(THF) \qquad (3)$$

The $[Sm(THF)_7]^{2+}$ dication, **1**, could also be generated in good yield (75%) by an analogous route, Eq. (4).

$$(C_5Me_5)Sm[N(SiMe_3)_2](THF)_2 + [Et_3NH][BPh_4] \xrightarrow{\mathrm{THF}} [Sm(THF)_7][BPh_4]_2 + (C_5Me_5)_2Sm(THF)_2 \qquad (4)$$

3.3. *Reactions of $Ln[N(SiMe_3)_2]_2(THF)_2$ with ammonium reagents*

Since Eqs. (1)–(4) were neither intended as routes to $[LnL_x]^{2+}$ cations nor were they efficient routes since the cyclopentadienyl and cyclooctatetraenyl byproducts were not the primary synthetic targets, a more direct route to the fully solvated cations was pursued. Eq. (3) suggested that protonolysis of $Yb[N(SiMe_3)_2]_2(THF)_2$ would be a good route to **2**. Surprisingly, protonolysis of $Yb[N(SiMe_3)_2]_2(THF)_2$ in THF gave a yellow powder which was insoluble. This material analyzed for

$[Yb(THF)_6][BPh_4]_2$, but could not be recrystallized for full structural and spectroscopic confirmation of its composition. Further evidence supporting the analytical data was the fact that addition of a small amount of MeCN generated $[Yb(MeCN)_8][BPh_4]_2$ (**3**), quantitatively. Similar results were obtained with the reaction of $Sm[N(SiMe_3)_2]_2(THF)_2$ with ammonium reagents.

Since **3** could be readily isolated and crystallized from MeCN, the direct reaction of $Yb[N(SiMe_3)_2]_2(THF)_2$ with 2 equiv. of $[Et_3NH][BPh_4]$ in MeCN was examined. This formed **3** in 68%, Eq. (5).

$$Yb[N(SiMe_3)_2]_2(THF)_2 + 2Et_3NHBPh_4 \xrightarrow{THF} [Yb(MeCN)_8][BPh_4]_2 \quad (5)$$

Compound **3** was characterized by NMR and IR spectroscopy, elemental analysis, and X-ray crystallography. The ^1H NMR and ^{13}C spectra of **3** contained only the resonances of the anion and MeCN. Complex **3** displayed a ν_{CN} stretch at 2274 cm^{-1} in the infrared spectrum which can be compared with the 2260 cm^{-1} absorption in free MeCN. Higher ν_{CN} stretching frequencies for MeCN solvated to lanthanides are common [3a,3b,31].

3.4. Structural results

3.4.1. Structure of $[Sm(THF)_7][BPh_4]_2$ (*1*)

As shown in Fig. 1, the seven THF molecules adopt a distorted pentagonal bipyramidal geometry around Sm(II). This geometry is the same as is found in other divalent, seven coordinate Sm structures, such as $SmI_2(THF)_5$, [32] $SmI_2(DME)(THF)_3$, [32] and $SmI_2(DME)_2(THF)$ [32]. The irregularity of the structure can be seen from the O(2)–Sm–O(2′) angle in **1**, 175.5(4)°, which is not quite linear, and the 77.1(3)°–106.6(3)° O(axial)–Sm–O(equatorial) angles, which would be 90° in an idealized pentagonal bipyramid. The O(equatorial)–Sm–O(equatorial) angles in **1**, which should be 72° in an idealized pentagonal bipyramid, range from 72.9(4)° to 75.3(2)°. The equatorial THF ligands do not line up in a regular canted arrangement. The same samarium dication in $[Sm(THF)_7][Zn_4(\mu^2\text{-}SePh)_6(SePh)_4]$ [4] has a pentagonal bipyramidal geometry even more distorted than that in **1**. The O(axial)–Sm–O(axial) angle is 166.6(7)° with the O(axial)–Sm–O(equatorial) angles ranging from 77.2(7)° to 115.3(6)°. The axial (2.55(5) Å) and equatorial (2.60(6) Å) Sm–O(THF) bond lengths in **1** are similar to those in $SmI_2(DME)_2(THF)$ (2.530(5) Å), [32] $SmI_2(DME)(THF)_3$ (2.578(4) Å), [32] $(C_{13}H_9)_2Sm(THF)_2$ (2.550(6) Å), [8] $(C_5Me_5)_2Sm(THF)$ (2.569(3) Å), [33] and $(C_5Me_5)_2Sm(THF)_2$ (2.62(1) Å) [20].

3.4.2. $[Yb(THF)_6][BPh_4]_2$ (*2*)

As shown in Fig. 2, the dication $[Yb(THF)_6]^{2+}$ has a well-defined octahedral geometry of oxygen atoms around the Yb center. The *cis* O(THF)–Yb–O(THF) angles range from 88.13(15)° to 91.87(13)° while the *trans* O–Yb–O angles have an average of 180.03(10)°. In this structure, the O(1) and O(3) THF rings were disordered and were modeled with partial occupancy. The Yb–O(THF) distances range from 2.350(4) to 2.392(2) Å. In comparison, the ytterbium dication $[Yb(THF)_6][Sn(SePh)_3]_2$ [4] has 2.354(11)–2.402(11) Å Yb–O(THF) distances and similar O(THF)–Yb–O(THF) angles.

3.4.3. $[Yb(MeCN)_8][BPh_4]_2$ (*3*)

The eight acetonitrile ligands coordinated to Yb^{2+} in **3** define a distorted square antiprismatic structure, Fig. 3. The dihedral angle between the N(1), N(2), N(3), N(4a) plane and the N(1a), N(2a), N(3a), and N(4a) plane is 179.2(1)°. The Yb–N(MeCN) bond lengths range from 2.537(10) to 2.570(9) Å. These distances can be compared the analogous 2.44(2) and 2.46(3) Å distances in the seven coordinate $[(py)_5Yb(MeCN)_2]^{2+}$ [5] and a range of 2.513(6)–2.597(7) Å Yb–N(MeCN) distances in the eight coordinate $[(DIME)Yb(MeCN)_5]^{2+}$ [5].

4. Discussion

The formation of fully solvated divalent lanthanide dications free of anionic ligands appears to be facile via a number of synthetic pathways. Initial attempts to make the cyclopentadienyl-ligated cations $[(C_9H_{11})Sm(THF)_x]^+$ and $[(C_5Me_5)Yb(THF)_x](\mu\text{-}C_8H_8)[Yb(C_5Me_5)(THF)_x]^+$ generated the dications, $[Sm(THF)_7]^{2+}$ and $[Yb(THF)_6]^{2+}$ instead. Likewise, in the deliberate reaction of $(C_5Me_5)Yb[N(SiMe_3)_2](THF)_2$ and

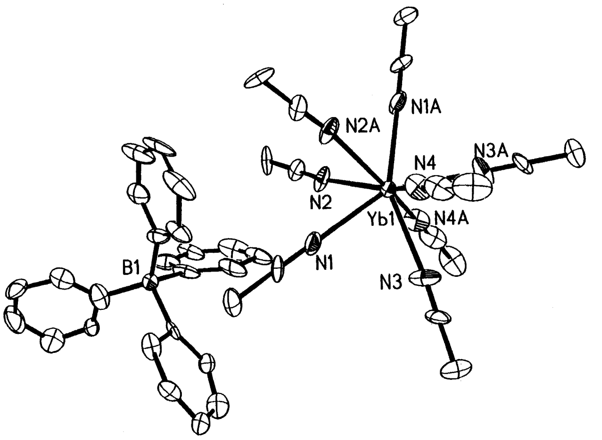

Fig. 3. Thermal ellipsoid plot of the dication $[Yb(MeCN)_8]^{2+}$ and one $[BPh_4]^-$ anion in **3** with ellipsoids drawn at the 50% probability level.

$[Et_3NH][BPh_4]$ to make $[(C_5Me_5)Yb(THF)_x]^+$, the dicationic $[Yb(THF)_6]^{2+}$ species was isolated preferentially. This situation does not arise from any inherent incompatibility of cyclopentadienyl rings with cationic complexes as evidenced by the many types of metallocene cations, $[(C_5R_5)_2ML_x]^+$ and $[(C_5R_5)_2MRL]^+$, in the literature [1] and the isolation of $\{[C_5H_3(SiMe_3)_2]Sm(18\text{-crown-}6)\}\{[C_5H_3(SiMe_3)_2]_3Sm\}$, [7] and $\{[C_5H_3(SiMe_3)_2]Yb(18\text{-crown-}6)\}[C_5H_3(SiMe_3)_2]$ [7].

The $[(C_5Me_5)Yb(THF)]_2(C_8H_8)$–$AgBPh_4$ reaction suggests that a divalent cyclopentadienyl intermediate such as $[(C_5Me_5)Yb^{II}(THF)](\mu\text{-}C_8H_8)[Yb^{III}(C_5Me_5)(THF)_x]$ is formed, but its stability is marginal. The formation of the $(C_5Me_5)Yb(C_8H_8)$ product is the usual result from reactions of $[(C_5Me_5)Ln]_2(C_8H_8)$ with reducible substrates [13]. This leaves the $[(C_5Me_5)Yb]^+$ monocation, which is usually oxidized further and trapped by the oxidant. Clearly, this $[(C_5Me_5)Yb]^+$ is a reactive species since only $(C_5Me_5)_2Yb(THF)_x$ and $[YbL_x]^{2+}$ were isolated from this system. Further evidence on this disproportionation was obtained from the reaction of $(C_5Me_5)Yb[N(SiMe_3)_2](THF)_2$ with 1 equiv. of $[Et_3NH][BPh_4]$ in THF. In this case, a new C_5Me_5 NMR resonance was observed consistent with the presence of $[(C_5Me_5)Yb(THF)_x]^+$, but only $[YbL_x]^{2+}$ and $(C_5Me_5)_2Yb(THF)$ were isolable. This '$[(C_5Me_5)Yb]^+$' system does have the advantage that it can provide $[YbL_x]^{2+}$ in soluble form which could be useful synthetically in further reactions.

Further study will be required before the reasons for the instability of $[(C_5Me_5)Yb(THF)_x](\mu\text{-}C_8H_8)[Yb(C_5Me_5)(THF)_x]^+$ and the tendency of $[(C_5Me_5)YbL_x]^+$ to disproportionate to $(C_5Me_5)_2Yb(THF)$ and $[YbL_x]^{2+}$ are fully understood. Since the examples of the more stable metallocene cations typically involve metals with +3 and +4 formal charges, this may be important. However, divalent lanthanide cations have been isolated with the $C_5H_3(SiMe_3)_2$ ligand in $\{[C_5H_3(SiMe_3)_2]Sm(18\text{-crown-}6)\}\{[C_5H_3(SiMe_3)_2]_3Sm\}$, and $\{[C_5H_3(SiMe_3)_2]Yb(18\text{-crown-}6)\}[C_5H_3(SiMe_3)_2]$ [7] and with the cyclopentadienyl analog, the di-zirconium-nona-isopropoxide (dzni) ligand, in $\{[Zr_2(O^i\text{-}Pr)_9]Yb(THF)_2\}[BPh_4]$ [6]. Further information on the factors affecting the disproportionations observed for the $[(C_5Me_5)Yb]^+$ cations is desirable since the formation of such cations could be useful synthetically to provide soluble forms of cations of transient stability.

The most reliable and atom efficient route to fully solvated divalent lanthanide dications free of coordinating anions is the reaction of the $Ln[N(SiMe_3)_2]_2(THF)_2$ with $[Et_3NH]^+$ salts. Protonolysis with ammonium salts has been commonly used in f-element chemistry to make cationic species [2,9,10] and in this study it successfully accomplishes the transformation with several types of divalent precursors without oxidizing the metal. These reactions involve careful selection of the solvent/anion if soluble species are to be obtained. Hence, acetonitrile provides a soluble complex with tetraphenylborate, $[Yb(MeCN)_8][BPh_4]_2$, (**3**), but in THF, the $[BPh_4]^-$ salt, $[Yb(THF)_6][BPh_4]_2$, (**2**), is formed as an insoluble powder.

5. Conclusion

These studies show that $[Ln(solvent)_x]^{2+}[anion]_2^-$ are often the end products in reactions of divalent lanthanide species with protic reagents. In the presence of the appropriate solvent, soluble dications free of coordinating anions are accessible in high yields. The chemistry of these divalent dicationic species is currently under investigation.

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