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Unsolvated Lanthanide Metallocene Cations $[(C_5Me_5)_2Ln][BPh_4]$: Multiple Syntheses, Structural Characterization, and Reactivity Including the Formation of $(C_5Me_5)_3Nd$[1]

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Abstract: Divalent $(C_5Me_5)_2Sm$ reacts with $AgBPh_4$ in toluene to form $[(C_5Me_5)_2Sm][BPh_4]$, **1**, in ca. 60% yield. The solid-state structure of **1** consists of a trivalent $(C_5Me_5)_2Sm$ bent metallocene unit with a 2.702(3) Å average Sm−C(C_5Me_5) distance that is oriented toward two of the phenyl rings of the $[BPh_4]^-$ anion with 2.825(3) and 2.917(3) Å Sm−C(*o*-Ph) distances. **1** can also be obtained from reactions of Et_3NHBPh_4 in arene solvents with the trivalent samarium precursors $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$ (>50% yield) and $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (**2**) (>95% yield). **1** reacts with $LiCH(SiMe_3)_2$ in benzene to produce $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$ in over 95% yield. The reaction of **1** with KC_5Me_5 in benzene constitutes a new synthesis of the sterically crowded complex $(C_5Me_5)_3Sm$, which is formed in over 90% yield. This reaction provides a convenient way to make $(C_5Me_5)_3Ln$ complexes with lanthanides which do not have a reactive divalent oxidation state. To enhance the ease of preparing $(C_5Me_5)_3Ln$ complexes from $LnCl_3$, an improved synthesis of the allyl precursors $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$ (Ln = Sm (**2**), Nd (**3**), Tm (**4**)) is reported. **2**−**4** can be prepared in 60−90% yield from $(C_5Me_5)_2LnCl_2K(THF)_2$ and $ClMg(CH_2CHCH_2)$ followed by desolvation of the solids between 55 and 70 °C for 4−16 h. **2**−**4** react with Et_3NHBPh_4 in benzene to produce $[(C_5Me_5)_2Ln][BPh_4]$ (Ln = Sm (**1**), Nd (**5**), Tm (**6**)). **5** has a solid-state structure identical to that of **1** and similarly reacts with $LiCH(SiMe_3)_2$ and KC_5Me_5 in benzene to produce $(C_5Me_5)_2Nd[CH(SiMe_3)_2]$ and $(C_5Me_5)_3Nd$ (**7**), respectively, in high yield. **7** was characterized by X-ray crystallography and shown to have an $(\eta^5\text{-}C_5Me_5)_3Nd$ structure with a 2.86(6) Å Nd−C(C_5Me_5) distance. Since the allyl complexes $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$ are readily converted to the hydrides $[(C_5Me_5)_2LnH]_n$ by hydrogen, the improved synthesis of the allyl complexes also provides an improved route to these hydrides as demonstrated by the reaction of $(C_5Me_5)_2Nd(\eta^3\text{-}CH_2CHCH_2)$ with H_2 to form $[(C_5Me_5)_2NdH]_2$ in 75% yield.

Introduction

Recent research in metallocene chemistry has shown that metallocene cations can play an important role in organometallic chemistry.[2−5] The enhanced electrophilicity of a metallocene bearing a formal positive charge can have an important influence on reactivity. This is especially important in olefin polymerizations and transformations.[2−5]

Despite the importance of metallocene cations, relatively few examples of lanthanide metallocene cations have been reported to date. In organosamarium chemistry, the first metallocene cation to be crystallographically characterized was $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$.[6] This complex can be conveniently made by oxidizing the divalent precursor $(C_5Me_5)_2Sm(THF)_2$[7] with

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$AgBPh_4$, eq 1. Bruno demonstrated that lanthanocene cations

$$(C_5Me_5)_2Sm(THF)_2 + AgBPh_4 \xrightarrow{THF} [(C_5Me_5)_2Sm(THF)_2][BPh_4] + Ag \quad (1)$$

of cerium and lanthanum could be prepared via abstraction of iodide from trivalent $[1,3\text{-}C_5H_3(SiMe_3)_2]_2LnI(NCMe)_2$ with $AgBF_4$ or $AgBPh_4$ to produce $\{[1,3\text{-}C_5H_3(SiMe_3)_2]_2Ln(NCMe)_2\}\{BF_4\}$ and $\{[1,3\text{-}C_5H_3(SiMe_3)_2]_2Ln(NCMe)(DME)\}[BPh_4]$ (Ln = Ce, La).[8] Teuben prepared $[(C_5Me_5)_2CeL_2][BPh_4]$ [L = THF, tetrahydrothiophene (THT)] by protonoylsis of $(C_5Me_5)_2Ce[CH(SiMe_3)_2]$ with Et_3NHBPh_4 in THF or THT.[9] Schaverien used the same protonolysis methodology to prepare the monocyclopentadienyl cation $\{(C_5Me_5)La[CH(SiMe_3)_2]\}[BPh_4]$ from $(C_5Me_5)La[CH(SiMe_3)_2]_2$ and $[PhNMe_2H]BPh_4$.[10] Very recently the ytterbium complex $[(Me_3CC_5H_4)_2Yb(THF)][BPh_4]$[11] has been prepared from the reduction of $AgBPh_4$ with divalent $(Me_3CC_5H_4)_2Yb(THF)_2$ in a synthesis analogous to that of $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$. Cationic lanthanide complexes based on polypyrazolylborate ligands have also been described.[12]

Although many metallocene cations are more reactive due to their increased electrophilicity, in the case of the solvated complex $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ this led to tight binding of the THF ligands which made the overall complex rather unreactive.[6] The solvated THF molecules were difficult to displace, even in refluxing pyridine, and they blocked access to the metal center, which resulted in limited reactivity. However, the stability of $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ suggested that the unsolvated $[(C_5Me_5)_2Ln]^+$ lanthanocene cations should be highly reactive.

Initial attempts to make a solvent free cationic species from unsolvated decamethylsamarocene, $(C_5Me_5)_2Sm$,[13] and $AgBPh_4$ in toluene in a THF-free reaction analogous to eq 1 led to insoluble materials. However, we now report that with the proper procedures the soluble unsolvated cation complex, $[(C_5Me_5)_2Sm][BPh_4]$ (**1**), can be isolated, and structurally characterized.

As anticipated, **1** is highly reactive and has proven to be a good precursor to other trivalent samarium complexes. Among its reactions is a new synthesis of $(C_5Me_5)_3Sm$,[14] a molecule originally thought to be too sterically crowded to exist. The synthetic utility of **1** indicated that this type of unsolvated lanthanocene cation should be a valuable starting material for other lanthanides. However, since the synthesis of **1** depended on the divalent precursor, $(C_5Me_5)_2Sm$, cations of lanthanides which did not have a reactive divalent state could not be made by this route. Accordingly, we sought to develop new synthetic routes to $[(C_5Me_5)_2Ln][BPh_4]$ which did not depend on divalent $(C_5Me_5)_2Ln$ precursors. We report here some new routes which were developed with samarium and then applied to neodymium and thulium. The reactivity of the neodymium analogue, $[(C_5Me_5)_2Nd][BPh_4]$, was subsequently examined, and it was found to provide the best synthesis to date for $(C_5Me_5)_3Nd$.

Experimental Section

The complexes described below are extremely air and moisture sensitive. Therefore, both the syntheses and manipulations of these compounds were conducted under nitrogen or argon with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. The argon glovebox used in these experiments was free of coordinating solvents. The preparation of $(C_5Me_5)_2Sm$,[13] $(C_5Me_5)_2LnCl_2K(THF)_2$,[15,16] and $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$[17] (Ln = Sm, Nd, Tm) and methods for drying solvents and taking physical measurements have been described previously.[18,19] $LiCH(SiMe_3)_2$ was prepared according to literature procedure.[20] Allylmagnesium chloride (2.0 M in THF, Aldrich) was used as received. ^1H and ^{13}C NMR analyses were carried out on DRX 500 and 400 spectrometers. Infrared analyses were carried out on KBr pellets with a Perkin-Elmer 1600 series FTIR. All C and H elemental analyses were conducted on a Carlo Erba instrument. All metal analyses were determined by complexometric titration.[19]

Synthesis of $[(C_5Me_5)_2Sm][BPh_4]$ (1) from $(C_5Me_5)_2Sm$. In an argon-filled glovebox, a green solution of $(C_5Me_5)_2Sm$ (124 mg, 0.295 mmol) in ca. 10 mL of toluene was added to a slurry of $AgBPh_4$ (426 mg, 0.298 mmol) in ca. 5 mL of toluene. The solution developed a brown-red color in under 10 min. After the mixture was stirred for 12 h, a pale brown toluene solution was separated from dark solids by centrifugation and discarded. The solids were extracted with ca. 20 mL of benzene to form a crimson red solution. Benzene was removed by rotary evaporation and the solids were recrystallized from hot toluene leaving red needles. The needles were dissolved in benzene and the solvent was removed to give pure **1** as a rose-colored solid (137 mg, 63%). ^1H NMR (C_6D_6) δ 8.4 (s, $\Delta\nu_{1/2}$ = 52 Hz, 8 H), −0.34 (s, C_5Me_5, 30H). ^{13}C NMR (C_6D_6) δ 138, 131, 129, 124 (*Ph*) 120 (C_5Me$_5$), 21.9 (C_5Me_5). IR 3050 s, 2900 s, 1954 w, 1882 w, 1820 w, 1717 w, 1578 m, 1472 s, 1429 s, 1379 m, 1263 m, 1155 m, 1062 m, 1027 s, 959 m, 923 w, 872 m, 850 m, 805 w, 739 s, 707 s, 682 s, 610 m cm^{-1}. Anal. Calcd for $SmC_{44}H_{50}B$: Sm, 20.32; C, 71.41; H, 6.81. Found: Sm 20.0; C, 70.5; H, 6.98. Addition of THF to **1** generated $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ in quantitative yield, as observed by ^1H NMR spectroscopy in THF-d_8.[6] X-ray quality crystals of **1** were grown from a concentrated benzene solution as red cubes.

Synthesis of 1 from $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$ and Et_3NHBPh_4. In an argon-filled glovebox, $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$ (20 mg, 0.034 mmol), Et_3NHBPh_4 (15 mg, 0.036 mmol), ca. 15 mL of toluene, and a stir bar were placed in a flask fitted with a high-vacuum greaseless stopcock. The flask was attached to a Schlenk line via a water-cooled condenser. The flask was placed under nitrogen and heated to reflux and stirred for ca. 20 min. In that time the color of the solution turned from orange to red. The solvent was removed leaving red solids. The flask was returned to the argon glovebox, solids were extracted with benzene, and solvent was removed to give **1** (23 mg, 90%). No evidence for Et_3N was observed in the ^1H NMR spectrum on **1**. Attempts to increase the scale of the reaction to >100 mg resulted in yields as low as 50%.

Synthesis of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (2) from $ClMg(CH_2CHCH_2)$. In a nitrogen-filled glovebox, a 2.0 M THF solution

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of $ClMg(CH_2CHCH_2)$ (1.5 mL, 3.0 mmol) was added to a stirring suspension of $(C_5Me_5)_2SmCl_2K(THF)_2$ (1.93 g, 2.86 mmol) in ca. 60 mL of toluene. The solution immediately turned deep red. After 30 min the solvent was removed by rotary evaporation leaving deep red solids and a deep red viscous oil. A solution of dioxanes (ca. <1 vol %) in hexanes was added, the mixture was stirred for ca. 30 min, and the solution was filtered to remove white solids which were discarded. Evaporation of solvent left red solids which were placed in a glass tube fitted with a greaseless Teflon stopcock and heated at 60 °C at 10^{-7} Torr for ca. 12 h. The red/orange solids were transferred to an argon-filled glovebox free of coordinating solvents and extracted with hexanes. Removal of solvent by rotary evaporation left $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (**2**) (1.32 g, 87%), which was identified by ^1H NMR spectroscopy in benzene-d_6.[21]

Synthesis of 1 from 2 and Et_3NHBPh_4. In an argon-filled glovebox, $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (77 mg, 0.16 mmol) and Et_3NHBPh_4 (72 mg, 0.17 mmol) were combined with ca. 4−6 mL of benzene and a stir bar. The light red solution was stirred at room temperature. After 5 min, excess unreacted Et_3NHBPh_4 was removed by centrifugation from the dark red solution. Rotary evaporation of solvent left **1** (118 mg, 96%).

Synthesis of $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$ from 1 and $LiCH(SiMe_3)_2$. In an argon-filled glovebox, $LiCH(SiMe_3)_2$ (7 mg, 0.04 mmol) in ca. 3 mL of benzene was added to a red solution of **1** (30 mg, 0.041 mmol) in ca. 5 mL of benzene. The solution turned orange in less than 10 min and white solids precipitated. The solids were removed by centrifugation, and evaporation of solvent left $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$ (22 mg, 94%) identified by ^1H NMR spectroscopy.[17]

Synthesis of $(C_5Me_5)_2Sm$ from 1 and Na. In an argon-filled glovebox, **1** (62 mg, 0.084 mmol) and ca. a 10 M excess of Na were combined along with a stir bar in ca. 10 mL of benzene. The color of the solution changed from red to green over a period of 12 h. White solids (presumed to be $NaBPh_4$), along with excess Na, were removed by filtration, and the solvent was removed by rotary evaporation to give $(C_5Me_5)_2Sm$ as a forest green solid (30 mg, 85% yield). The identity of $(C_5Me_5)_2Sm$ was confirmed by ^1H and ^{13}C NMR spectroscopy.[13]

Synthesis of $(C_5Me_5)_3Sm$ from 1 and KC_5Me_5. In an argon-filled glovebox, KC_5Me_5 (29 mg, 0.16 mmol) and **1** (120 mg, 0.162 mmol) were combined along with a stir bar in ca. 10 mL of benzene and the reaction was stirred for ca. 12 h, during which time the color of the solution turned from red to red/brown. White solids were removed from the solution by centrifugation. Rotary evaporation of solvent left $(C_5Me_5)_3Sm$ and a small amount of C_5Me_5H identified by ^1H NMR spectroscopy. Recrystallization from toluene left $(C_5Me_5)_3Sm$ (89 mg, 91%).[14]

Synthesis of $(C_5Me_5)_2Nd(\eta^3\text{-}CH_2CHCH_2)$ (3) from $ClMg(CH_2CHCH_2)$. As described above for **2**, $(C_5Me_5)_2NdCl_2K(THF)_2$ (1.97 g, 2.95 mmol) was reacted with a slight excess of 2 M $ClMg(CH_2CHCH_2)$ in THF (1.5 mL, 3.0 mmol) and a lime green toluene solution resulted. $(C_5Me_5)_2Nd(\eta^3\text{-}CH_2CHCH_2)$ (1.13 g, 84%) was isolated as described above for **2** and identified by ^1H NMR spectroscopy in toluene-d_8.[17]

Synthesis of $(C_5Me_5)_2Tm(\eta^3\text{-}CH_2CHCH_2)$ (4) from $ClMg(CH_2CHCH_2)$. As described above for **2**, $(C_5Me_5)_2TmCl_2K(THF)$ (618 mg, 0.995 mmol) was reacted with a slight excess of 2 M $ClMg(CH_2CHCH_2)$ in THF (0.5 mL, 1.0 mmol) and a light yellow toluene solution resulted. Solvent was removed leaving white solids which were handled as described above for **2**, leaving $(C_5Me_5)_2Tm(\eta^3\text{-}CH_2CHCH_2)$ (**4**) (302 mg, 63%) as a bright yellow powder. Anal. Calcd for $TmC_{23}H_{35}$: Tm, 35.16; C, 57.5; H, 7.34. Found: Tm 35.0; C, 57.2; H, 7.14. IR 2906 vs, 2856 vs, 1538 s, 1435 m, 1377 s, 1246 m, 1094 m, 1020 m, 773 s, 679 s cm^{-1}.

Synthesis of $[(C_5Me_5)_2Nd(\mu\text{-}H)]_2$ from 3 and H_2. In an argon-filled glovebox, **3** (117 mg, 0.257 mmol) in ca. 15 mL of hexanes and a stir bar were placed in a flask fitted with a high-vacuum greaseless stopcock. The flask was attached to a vacuum line and evacuated to the solvent vapor pressure. Excess H_2 at 1 atm was admitted to the flask and the solution was stirred. Solids started to precipitate in less than 10 min. The flask was stirred for 4 h, degassed, and transferred to a glovebox where the solids were separated from the solvent by centrifugation. The light blue/green solid was washed twice with small amounts of hexanes then dried under vacuum leaving $[(C_5Me_5)_2Nd(\mu\text{-}H)]_2$ (82 mg, 75%), which was identified by ^1H NMR spectroscopy in benzene-d_6.[17]

Synthesis of $[(C_5Me_5)_2Nd][BPh_4]$ (5). In an argon-filled glovebox, **3** (135 mg, 0.296 mmol) was reacted with Et_3NHBPh_4 (127 mg, 0.301 mmol) as described above for **1**. A mint green benzene solution resulted and **5** was isolated as a light green solid (211 mg, 97%) following the procedure for **1**. X-ray quality crystals of **5** were grown from a hot toluene solution as green needles. ^1H NMR (C_6D_6) δ 14.3 (s, $\Delta\nu_{1/2}$ = 130 Hz). IR 3046 s, 2907 s, 1944 w, 1882 w, 1820 w, 1713 w, 1605 m, 1472 s, 1429 s, 1380 m, 1260 m, 1154 m, 1072 m, 1025 s, 949 w, 851 m, 805 w, 740 s, 706 s, 610 m cm^{-1}. Anal. Calcd for $NdC_{44}H_{50}B$: Nd, 19.65; C, 72.01; H, 6.87. Found: Nd, 19.9; C, 71.5; H, 6.56.

Synthesis of $(C_5Me_5)_2Nd[CH(SiMe_3)_2]$ from 5 and $LiCH(SiMe_3)_2$. In an argon-filled glovebox, $LiCH(SiMe_3)_2$ (7 mg, 0.04 mmol) in ca. 3 mL of benzene was added to a blue-green solution of **5** (32 mg, 0.043 mmol) in ca. 5 mL of benzene. The solution turned blue in less than 10 min and white solids were deposited. The solids were removed by centrifugation and evaporation of solvent left $(C_5Me_5)_2Nd[CH(SiMe_3)_2]$ (24 mg, 96%) identified by ^1H NMR spectroscopy in C_6D_6.[17]

Synthesis of $[(C_5Me_5)_2Tm][BPh_4]$ (6). In an argon-filled glovebox, **4** (302 mg, 0.629 mmol) was reacted with Et_3NHBPh_4 (266 mg, 0.632 mmol) as described above for **1**. An orange/yellow benzene solution resulted. Evaporation of the solvent left an orange solid (467 mg). Recrystallization from hot toluene left pale yellow needles and a pale yellow solution. The crystals were removed by centrifugation and washed with hexanes. The crystals were then dissolved in benzene and evaporation of the solvent left $[(C_5Me_5)_2Tm][BPh_4]$ (**6**) (298 mg, 63%) as an orange solid. IR 3049 s, 2898 s, 1945 w, 1871 w, 1825 w, 1713 w, 1578 m, 1473 s, 1429 s, 1384 m, 1265 m, 1155 m, 1071 m, 1027 s, 950 w, 913 w, 852 m, 848 m, 803 w, 738 s, 703 s, 677 s, 610 m cm.$^{-1}$ Anal. Calcd for $TmC_{44}H_{50}B$: Tm, 22.3; C, 69.7; H, 6.64. Found: Tm 21.4; C, 69.3; H, 6.42.

Synthesis of $(C_5Me_5)_3Nd$ (7). In an argon-filled glovebox, KC_5Me_5 (84 mg, 0.48 mmol) was reacted with **5** (323 mg, 0.44 mmol) as described above for $(C_5Me_5)_3Sm$, yielding $(C_5Me_5)_3Nd$ (**7**) (241 mg, 95%) as a mustard green solid. ^1H NMR (C_6D_6) δ 8.88 (C_5Me_5). ^{13}C NMR (C_6D_6) δ 253 (C_5Me_5), δ −15.8 (C_5Me_5). IR 2904 vs, 1436 s, 1380 s, 1261 m, 1018 m br, 802 m, 597 m cm^{-1}. Anal. Calcd for $NdC_{30}H_{45}$: Nd, 26.23; C, 65.52; H, 8.25. Found: Nd, 26.0; C, 65.8; H, 8.46. Dark orange X-ray quality crystals of **7** were grown from a hot toluene solution.

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)_2Sm][BPh_4]$ (1). A red crystal of approximate dimensions 0.20 × 0.23 × 0.24 mm was mounted on a glass fiber and transferred to a Siemens P4 diffractometer. The determination of Laue symmetry, crystal cell, unit cell parameters, and the crystal's orientation matrix was carried out according to standard procedures.[22] Intensity data were collected at 158 K by using a $2\theta/\omega$ scan technique with Mo Kα radiation. The raw data were processed with a local version of CARESS,[23] which employs a modified version of the Lehman−Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. Subsequent calculations were carried out with the SHELXTL program.[24] All 8635 data were corrected for decay (5%), absorption, and Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The centrosymmetric monoclinic space group $P21/c$ [C_{2h}^5; No. 14] is therefore uniquely defined.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors

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[21] Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314.

[22] XSCANS Software Users Guide, Version 2.1, Siemens Industrial Automation, Inc.; Madison, WI, 1994.

[23] Broach, R. W.; Argonne National Laboratory, Illinois, 1978.

[24] Sheldrick, G. M.; Siemens Analytical X-ray Instruments, Inc.; Madison, WI, 1994.

for neutral atoms were used throughout the analysis.[25] Hydrogen atoms were located from a series of difference Fourier maps and refined (x,y,z and U_{iso}). At convergence, wR2 = 0.0551 and GOF = 1.032 for 615 variables refined against all 8330 unique data (as a comparison for refinement on F, R1 = 0.0261 for those 6587 data with $F > 4.0\sigma(F)$).

X-ray Data Collection for [$(C_5Me_5)_2Nd$][BPh_4] (5). A pale green crystal of approximate dimensions 0.20 × 0.18 × 0.06 mm was mounted on a glass fiber and transferred to a Siemens P4 diffractometer. The data on crystals of **5** were sufficient to provide atom connectivity, but not high precision metrical information due to the poor quality of the data collected.

X-ray Data Collection, Structure Determination, and Refinement for ($C_5Me_5)_3Nd$ (7). An orange crystal of approximate dimensions 0.30 × 0.23 × 0.23 mm was mounted on a glass fiber and transferred to a Siemens CCD platform diffractometer. The determination of Laue symmetry, crystal class, and unit cell parameters was carried out according to standard procedures.[26] Intensity data were collected at 158 K with Mo Kα radiation. The raw frame data were processed with SAINT[27] and SADABS[28] to yield the reflection data file. Subsequent calculations were carried out with the SHELXTL program.[24] The diffraction symmetry was $6/m$ and the systematic absences are consistent with the hexagonal space groups $P6_3$ or $P6_3/m$. It was later determined that the centrosymmetric space group $P6_3/m$ was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis.[25] Hydrogen atoms were located from a difference Fourier map and refined (x,y,z and U_{iso}). At convergence, wR2 = 0.0339 and GOF = 1.170 for 87 variables refined against 1164 unique data (as a comparison for refinement on F, R1 = 0.0136 for those 1138 data with $F > 4.0\sigma(F)$).

Results

Synthesis of [$(C_5Me_5)_2Sm$][BPh_4] (1) from Divalent $(C_5Me_5)_2Sm$. In a reaction that parallels the formation of the solvated cation, [$(C_5Me_5)_2Sm(THF)_2$][BPh_4], from $(C_5Me_5)_2Sm(THF)_2$ and $AgBPh_4$ in THF,[6] eq 1, the THF-free samarium(II) complex $(C_5Me_5)_2Sm$ reacts with $AgBPh_4$ in toluene over a 12 h period according to eq 2. Although the initially formed

$$(C_5Me_5)_2Sm + AgBPh_4 \xrightarrow{\text{toluene}} \text{black toluene insoluble solids} \xrightarrow{\text{benzene}} [(C_5Me_5)_2Sm][BPh_4] + \text{black solids} \quad (2)$$

black product is not noticeably soluble in toluene at room temperature, extraction with benzene provided a crimson red solution (ca. 18 mg/mL) of [$(C_5Me_5)_2Sm$][BPh_4] (**1**). Yields of 60−65% were obtained in toluene at room temperature. Reactions conducted in benzene at room temperature and at reflux and reactions in toluene at reflux and −78 °C did not give higher yields of **1**.

It is crucial that the starting materials be meticulously free of any coordinating solvents, since **1** readily adds Lewis bases. The purity of $AgBPh_4$, which requires an aqueous synthesis, is especially important. Since **1** is soluble in hot toluene and forms red needles upon cooling, hot toluene extraction provides a convenient purification method. Unfortunately, these crystals were of insufficient quality for X-ray diffraction analysis. Recrystallization from benzene, on the other hand, provided **1** as red cubes suitable for X-ray diffraction.

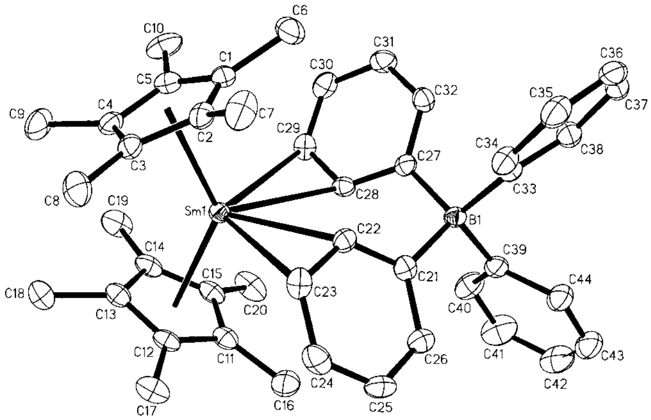

Figure 1. Thermal ellipsoid plot of [$(C_5Me_5)_2Sm$][BPh_4] (**1**) with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been excluded for clarity.

Table 1. Experimental Data for the X-ray Diffraction Studies of [$(C_5Me_5)_2Sm$][BPh_4] (**1**), [$(C_5Me_5)_2Nd$][BPh_4] (**5**), and $(C_5Me_5)_3Nd$ (**7**)

	1	5	7
formula	$C_{44}H_{50}BSm$	$C_{51}H_{58}BNd$	$C_{30}H_{45}Nd$
fw	740.00	826.02	549.90
temp (K)	158	158	158
crystal system	monoclinic	monoclinic	hexagonal
space group	$P2_1/c$	$P2_1$	$P6_3/m$
a (Å)	15.248(2)	11.200(3)	10.0178(4)
b (Å)	14.2576(12)	28.144(7)	10.0178(4)
c (Å)	17.804(2)	13.277(3)	15.5251(8)
β (deg)	110.717(7)	98.54(2)	120
V (Å^3)	3620.4(6)	4139(2)	1349.30(10)
Z	4	4	2
D_{calcd} (Mg/m^3)	1.358	1.326	1.938
diffractometer	Siemens P4	Siemens P4	Siemens CCD
μ(Mo Kα) (mm^{-1})	1.651	1.288	1.938
refinement[b] wR_2 (all data)	0.0551	0.1193	0.0339

[a] Radiation: Mo Kα (λ = 0.710730 Å). Monochromator: highly oriented graphite. [b] $R1 = [\sum[w(F_o^2 - F_c^2)^2]/\sum(w(F_o^2)^2)]^{1/2}$.

Characterization of [$(C_5Me_5)_2Sm$][BPh_4]. **1** was characterized by IR and NMR spectroscopy, elemental analysis, and addition of THF to produce the previously reported solvated complex [$(C_5Me_5)_2Sm(THF)_2$][BPh_4][6] in quantitative yield. The structure of **1** was determined by crystal structure analysis and found to have the solid state arrangement shown in Figure 1.

The ^1H NMR spectrum of paramagnetic **1** in C_6D_6 was not structurally definitive. The spectrum contained a singlet at δ −0.34, assigned as the methyl protons on the C_5Me_5 rings, and a broad signal at δ 8.4 that integrated for 7 to 8 protons compared to 30 for the signal at δ −0.34. Low-temperature NMR studies were precluded by the low solubility of **1** in toluene-d_8 and the freezing point of C_6D_6. Both high-temperature and spin−lattice (T_1)[29] experiments produced spectra identical to the room-temperature spectrum. The shifts of the C_5Me_5 carbon atoms in the ^{13}C NMR spectrum of **1** were consistent with the presence of Sm(III),[30] while the four remaining signals could be assigned to phenyl carbons.

In the X-ray crystal structure of **1,** the [$(C_5Me_5)_2Sm$]$^+$ cation is oriented toward two of the phenyl rings of the [BPh_4]$^-$ counteranion. Selected bond angles and distances are shown in Table 2. The 2.70(2) Å average Sm−C(C_5Me_5) distance is indistinguishable from the 2.69(2) Å average in [$(C_5Me_5)_2Sm$-

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[25] *International Tables of X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C.

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[27] *SAINT Software Users Guide*, Version 4.05; Siemens Industrial Automation, Inc.; Madison, WI, 1996.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2Sm][BPh_4]$ (**1**) and $(C_5Me_5)_3Nd$ (**7**)

1		**7**	
Sm(1)−C(1)	2.704(3)	Nd(1)−C(1)	2.8146(13)
Sm(1)−C(2)	2.740(3)	Nd(1)−C(2)	2.8421(14)
Sm(1)−C(3)	2.721(3)	Nd(1)−C(3)	2.927(2)
Sm(1)−C(4)	2.696(3)	Nd(1)−C(C_5Me_5)[d]	2.86(6)
Sm(1)−C(5)	2.670(3)	Nd(1)−Cent[e]	2.582
Sm(1)−C(11)	2.722(3)		
Sm(1)−C(12)	2.675(2)	Cnt−Nd(1)−Cnt	120
Sm(1)−C(13)	2.686(3)	C(2)−C(1)−C(4)	122.7(2)
Sm(1)−C(14)	2.703(3)	C(1)−C(2)−C(5)	123.7(2)
Sm(1)−C(15)	2.735(3)	C(2)−C(3)−C(6)	124.64(9)
Sm(1)−C(C_5Me_5)[a]	2.70(2)		
Sm(1)−C(22)	2.825(3)		
Sm(1)−C(28)	2.917(3)		
Sm(1)−C(23)	3.059(3)		
Sm(1)−C(29)	3.175(3)		
Cnt(1)[b]−Sm(1)−Cnt(2)[c]	134.4(2)		

[a] Sm(1)−C(C_5Me_5) is the average bond distance between Sm(1) and C(1) to C(5) and C(11) to C(15). [b] Cnt(1) is the centroid of the C(1)−C(5) ring. [c] Cnt(2) is the centroid of the C(11)−C(15) ring. [d] Nd(1)−C(C_5Me_5) is the average bond distance between Nd(1) and C(1) to C(3). [e] Cnt is the centroid of the C(1), C(2), C(3), C(1C), C(2C) ring.

$(THF)_2][BPh_4]$.[6] Both of these averages are on the low end of the range of distances found in trivalent $(C_5Me_5)_2Sm$-containing complexes,[31] as might be expected for a complex with a net positive charge and enhanced electrophilicity. The 134.4° (ring centroid)−Sm−(ring centroid) angle is normal and matches the 134.2° angle in $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$.[6] **1** and $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ differ in that the rings are staggered in **1** and eclipsed in the solvated analogue. This latter orientation may be due to the steric crowding caused by the closely located and tightly held THF ligands (Sm−O(THF) = 2.46(1) Å).[6]

The closest approach of the $[BPh_4]^-$ anion to samarium is through the *o*-carbon atoms C(22) and C(28) at distances of 2.825(3) and 2.917(3) Å, respectively. *m*-Carbon atoms C(23) and C(29) are located 3.059(3) and 3.175(3) Å from Sm, respectively. In comparison, the Sm−C(phenyl) single bond distance in $(C_5Me_5)_2Sm(C_6H_5)(THF)$[32] is 2.511(8) Å and the Sm−C(methyl) single bond distance in $(C_5Me_5)_2Sm(CH_3)(THF)$[19] is 2.484(14) Å. Since the Sm−C(*o*-phenyl) distances in **1** are longer than Sm−C single bonds and the Sm−C(ring) distances, they represent weaker interactions than these normal connections. Similar "long range" interactions have been found in other organosamarium complexes such as $[(C_5Me_5)_2Sm(C{\equiv}CCMe_3)]_2$, $[(C_5Me_5)_2Sm][\mu\text{-}\eta^2{:}\eta^2\text{-}Ph(CH_2)_2C{=}C{=}C{=}C(CH_2)_2Ph]$,[15] and $(C_5Me_4Et)_3Sm$,[33] and a wealth of agostic interactions have been reported for electrophilic organolanthanides[17,34] and actinides.[35] Comparison of these distances can also be made with the structure of $[(C_5Me_5)_2ThMe][B(C_6F_5)_4]$,[5a] which has 2.675(5) and 2.757(4) Å Th···F, 2.754(3) Å Th−C(C_5Me_5), and 2.399(8) Å Th−C(Me) distances (7-coordinate Th^{4+} is 0.037 Å larger than 6-coordinate Sm^{3+} based on Shannon radii[36]).

The orientations of the planes of the two phenyl rings closest to the samarium metal center were evaluated by measuring the dihedral angles between the Sm, C(22), C(23) plane and the C(22), C(23), phenyl ring centroid plane (124°) and the Sm, C(28), C(29) plane and the C(28), C(29), phenyl ring centroid plane (127°). These angles show that the rings interact at an angle with the metal rather than with the edge or face of the ring.

The interactions of the phenyl rings with the samarium cation do not change the tetrahedral nature of the phenyl rings around boron: the six C−B−C angles are in the narrow range of 107.5(2)−110.9(2)°. The C(phenyl)−C(phenyl) bond distances within the two closest phenyl rings have a narrow range, 1.381(4)−1.404(2) Å, similar to that in the other two phenyl rings, 1.375(4)−1.405(4) Å, and no localization is observed.

Reactivity of $[(C_5Me_5)_2Sm][BPh_4]$. The reactivity of **1** was initially compared to that of the solvated analogue $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$.[6] $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ can be reduced with sodium to form the divalent solvated metallocene $(C_5Me_5)_2Sm(THF)_2$ as shown in eq 3. **1** is similarly reduced, except that the unsolvated divalent metallocene, $(C_5Me_5)_2Sm$,[13] is isolated instead, eq 4.

$$[(C_5Me_5)_2Sm(THF)_2][BPh_4] + Na \xrightarrow{THF} (C_5Me_5)_2Sm(THF)_2 + NaBPh_4 \quad (3)$$

$$[(C_5Me_5)_2Sm][BPh_4] + Na \xrightarrow{benzene} (C_5Me_5)_2Sm + NaBPh_4 \quad (4)$$

1 and $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ also have similar reactivity with $LiCH(SiMe_3)_2$: both produce $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$ in quantitative yields,[37] eq 5. In this case, since the product is

$$\left.\begin{array}{l}[(C_5Me_5)_2Sm(THF)_2][BPh_4] + LiCH(SiMe_3)_2 \xrightarrow{THF} \\ [(C_5Me_5)_2Sm][BPh_4] + LiCH(SiMe_3)_2 \xrightarrow{benzene}\end{array}\right\} (C_5Me_5)_2Sm\{CH(SiMe_3)_2\} + LiBPh_4 \quad (5)$$

THF free, the same result is obtained with both cations. This type of reaction between **1** and alkali metal anion, MZ (M = alkali metal, Z = anion), is likely to be a convenient route to many types of $(C_5Me_5)_2SmZ$ complexes.

A reaction that would necessarily be very different for **1** and $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ is the reaction with KC_5Me_5. In the solvated case, this reaction does not give the $(C_5Me_5)_2SmZ$ product, which would be $(C_5Me_5)_3Sm$, but instead produces the THF ring-opened product, $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5]$, eq 6.[6] Since **1** is THF free, this reaction is not possible and the reaction

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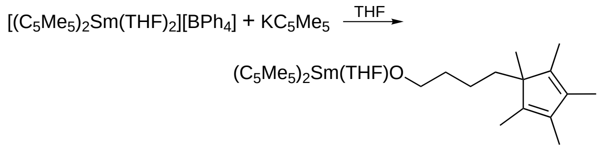
[36] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

[37] $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$ has previously been prepared by other routes, but in low yields (45%).[17]



(6)

with KC_5Me_5 provides a new route to $(C_5Me_5)_3Sm$. This reaction occurs in ca. 90% yield as shown in eq 7.

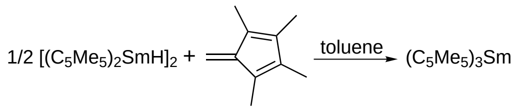
$$[(C_5Me_5)_2Sm][BPh_4] + KC_5Me_5 \xrightarrow{\text{benzene}} (C_5Me_5)_3Sm + KBPh_4 \quad (7)$$

The formation of $(C_5Me_5)_3Sm$ from **1** is an important synthetic breakthrough in the chemistry of the sterically crowded $(C_5Me_5)_3Ln$ complexes. The first two syntheses reported for $(C_5Me_5)_3Sm$, eqs 8[19] and 9,[33] required divalent starting materials,

$$2(C_5Me_5)_2Sm + C_8H_8 \xrightarrow{\text{toluene}} (C_5Me_5)_3Sm + (C_5Me_5)Sm(C_8H_8) \quad (8)$$

$$2(C_5Me_5)_2Sm(OEt)_2 + (C_5Me_5)_2Pb \xrightarrow{\text{toluene}} 2(C_5Me_5)_3Sm + Pb \quad (9)$$

$(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(OEt_2)_2$.[38] This precluded extension of these synthetic methods to the other lanthanides, since none have a divalent metallocene as reactive as $(C_5Me_5)_2Sm$. $(C_5Me_5)_3Sm$ can also be made from the trivalent precursor $[(C_5Me_5)_2SmH]_2$,[39] eq 10,[40] which is readily made from the divalent



(10)

$(C_5Me_5)_2Sm(THF)_2$, but analogous syntheses of $(C_5Me_5)_3Ln$ complexes require the preparation of $[(C_5Me_5)_2LnH]_2$ from trivalent precursors, which is neither an easy nor a high-yield process.[17] Since the unsolvated cations, $[(C_5Me_5)_2Ln][BPh_4]$, would be much better precursors to $(C_5Me_5)_3Ln$ complexes than any other currently known precursors, syntheses of $[(C_5Me_5)_2Ln][BPh_4]$ complexes which did not depend on divalent $(C_5Me_5)_2Ln$ were sought. Initial studies used samarium since there is more NMR data available on $(C_5Me_5)_2Ln$-containing complexes of samarium than for any other lanthanide.

Synthesis of $[(C_5Me_5)_2Sm][BPh_4]$ from Trivalent $(C_5Me_5)_2SmR$ Precursors. The formation of **1** by protonolysis of $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$ was first investigated because this precursor has been fully characterized[17] and can be readily isolated without coordinated solvent from trivalent starting materials. It was expected that $CH(SiMe_3)_2$ could be selectively protonated over C_5Me_5 based on the preparation of $\{(C_5Me_5)La[CH(SiMe_3)_2]\}[BPh_4]$ from $(C_5Me_5)La[CH(SiMe_3)_2]_2$.[10] Indeed, **1** can be prepared from the reaction of $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$ with Et_3NHBPh_4 in refluxing toluene in yields from 50 to 90% depending on scale of reaction, eq 11. Unfortunately, the yield is lower for the larger scale reactions.

$$(C_5Me_5)_2Sm[CH(SiMe_3)_2] + Et_3NHBPh_4 \xrightarrow[\text{reflux}]{\text{toluene}} Et_3N + H_2C(SiMe_3)_2 + [(C_5Me_5)_2Sm][BPh_4] \quad (11)$$

In these cases, dark solids, which proved to be insoluble even in THF, were formed. The typical decomposition products C_5Me_5H or $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$[41] were not observed in the ^1H NMR spectra of these reactions and could not explain the low yields. One important observation from these reactions was that the Et_3N byproduct was easily removed with solvent during evaporation leaving amine free **1**.

An attractive alternative to $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$ was the allyl complex $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (**2**), since (a) it is also free of coordinating solvents, (b) the byproduct of the reaction, propylene, could be easily removed from the reaction *in situ*, and (c) it can be easily purified by extraction with hexanes. As shown in eq 12, **1** can be prepared in quantitative

$$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2) + Et_3NHBPh_4 \xrightarrow{\text{benzene}} Et_3N + CH_3CH{=}CH_2 + [(C_5Me_5)_2Sm][BPh_4] \quad (12)$$

yield from **2** and Et_3NHBPh_4 in benzene at ambient temperatures. The reaction can be carried out with excess Et_3NHBPh_4 with no decomposition due to protonation of C_5Me_5 ligands. The synthesis of **1** from **2** is much more efficient in time, yield, and cost when compared to the $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$-based synthesis and the reaction can be conducted successfully on a large scale.

New Syntheses of $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$ from Trivalent Lanthanide Precursors. Although **2** proved to be a good precursor to **1**, the best route to **2** is from divalent $(C_5Me_5)_2Sm$, eq 13.[42] $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$ complexes, including

$$2(C_5Me_5)_2Sm + 3CH_3CH{=}CH_2 \rightarrow CH_3CH_2CH_3 + 2(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2) \quad (13)$$

the samarium complex, can be made from trivalent precursors, but this requires $[(C_5Me_5)_2LnH]_n$,[17,42] eq 14. Since the trivalent

$$^1/_2[(C_5Me_5)_2SmH]_2 + 2CH_3CH{=}CH_2 \rightarrow CH_3CH_2CH_3 + (C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2) \quad (14)$$

route to prepare these hydrides comes from $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$, allyl complexes prepared from $[(C_5Me_5)_2LnH]_n$ offer no synthetic advantage. Accordingly, a simpler and more direct route to THF-free $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$ complexes had to be developed. Again, this was investigated first with samarium.

Since it had been reported that the simple cyclopentadienyl complex $(C_5H_5)_2Sm(CH_2CHCH_2)(THF)_x$ could be prepared from a reaction of $(C_5H_5)_2SmCl$ with allylmagnesium bromide in THF,[43] a similar route was examined with allylmagnesium chloride and $(C_5Me_5)_2SmCl_2K(THF)_2$, which is directly obtainable from $SmCl_3$ and 2 equiv of KC_5Me_5.[15] A toluene suspension of $(C_5Me_5)_2SmCl_2K(THF)_2$ reacts instantly with a solution of $ClMgCH_2CHCH_2$ in THF. Unfortunately, initial attempts to extract the products in hexanes failed to produce any soluble materials. However, the addition of ca. 1 vol % of dioxane in hexanes produced a dark red solution along with

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Scheme 1

$$SmCl_3 + 2\,KC_5Me_5 \xrightarrow{THF} (C_5Me_5)_2SmCl_2K(THF)_2 + KCl$$

$$(C_5Me_5)_2SmCl_2K(THF)_2 + ClMgCH_2CHCH_2 \xrightarrow[\text{2) hexanes/dioxane}]{\text{1) toluene}} (C_5Me_5)_2Sm(CH_2CHCH_2)L + KCl + MgCl_2$$

$$(C_5Me_5)_2Sm(CH_2CHCH_2)L \xrightarrow[\text{4 - 16 hours}]{55\text{-}65\ ^\circ C,\ 10^{-7}\ \text{torr}} \underset{\mathbf{2}}{(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)}$$

L = dioxane, THF

white solids, presumed to be dioxane solvates of $MgCl_2$ as well as KCl, which were removable by filtration. Removal of the dioxane/hexanes solvent at room temperature left the solvated complex $(C_5Me_5)_2Sm(CH_2CHCH_2)(THF)_n$,[21] along with traces of dioxane. Heating the solids between 55 and 70 °C at 10^{-7} Torr over a 4−20 h period (depending on the amount of material) followed by extraction in hexanes left pure **2** in yields over 80% with no trace of dioxane or THF, Scheme 1. The neodymium and thulium analogues, $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$ (Ln = Nd (**3**), Tm (**4**)), were prepared analogously and both **2** and **3** have been prepared on a gram scale with this procedure.

Synthesis of $[(C_5Me_5)_2Nd][BPh_4]$ and $[(C_5Me_5)_2Tm][BPh_4]$ from $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$. $(C_5Me_5)_2Nd(\eta^3\text{-}CH_2CHCH_2)$ (**3**) reacts with Et_3NHBPh_4 in benzene to produce $[(C_5Me_5)_2Nd][BPh_4]$ (**5**) in quantitative yield, eq 15. As in the

$$(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2) + Et_3NHBPh_4 \xrightarrow{\text{benzene}} Et_3N + CH_3CH{=}CH_2 + [(C_5Me_5)_2Ln][BPh_4] \quad (15)$$
$$Ln = Nd\ (\mathbf{5}),\ Tm\ (\mathbf{6})$$

synthesis of **1**, excess Et_3NHBPh_4 could be used with no observable decomposition of **5**. Likewise, the reaction of **4** with Et_3NHBPh_4 in benzene produces $[(C_5Me_5)_2Tm][BPh_4]$ (**6**). However, a more modest yield, 63%, was observed for this smaller metal.

Characterization of $[(C_5Me_5)_2Nd][BPh_4]$ (5) and $[(C_5Me_5)_2Tm][BPh_4]$ (6). Both **5** and **6** were characterized with use of analytical methods as well as IR spectroscopy. **5** was further characterized by NMR spectroscopy and a crystal structure determination. The IR spectra of **5** and **6** were nearly identical to that of **1**, while the NMR spectra of **5** were less informative due to the larger magnetic moment of Nd(III) (3.5−3.6 μ_B).[44] Unlike **1** and **5**, characterization of **6** by NMR spectroscopy was precluded by the large magnetic moment of trivalent thulium (7.1−7.4 μ_B).[44] The similar solubility properties of **5** and **6** compared to **1** again allowed for purification by recrystallization from hot toluene. In contrast to **1**, crystals of **5** or **6** suitable for X-ray diffraction were not obtained from benzene. However, needles of **5** produced from recrystallization in hot toluene were examined by X-ray diffraction and found to be isostructural with **1**.

Reactivity of $[(C_5Me_5)_2Nd][BPh_4]$. Complex **5**, like **1**, reacts with $LiCH(SiMe_3)_2$ in benzene to produce the known complex $(C_5Me_5)_2Nd[CH(SiMe_3)_2]$[17] in quantitative yield, eq 16. **5** reacts slowly with KC_5Me_5 in benzene to produce $(C_5Me_5)_3Nd$, **7**, in yields over 90%, eq 17. **7** was characterized by NMR and IR

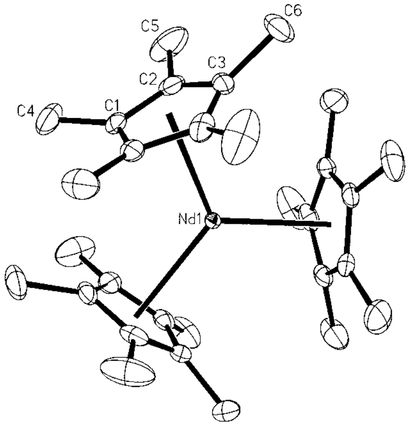

Figure 2. Thermal ellipsoid plot of $(C_5Me_5)_3Nd$ (**7**) with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been excluded for clarity.

$$\underset{\mathbf{5}}{[(C_5Me_5)_2Nd][BPh_4]} + LiCH(SiMe_3)_2 \xrightarrow{\text{benzene}} (C_5Me_5)_2Nd\{CH(SiMe_3)_2\} + LiBPh_4 \quad (16)$$

$$\underset{\mathbf{5}}{[(C_5Me_5)_2Nd][BPh_4]} + KC_5Me_5 \xrightarrow{\text{benzene}} \underset{\mathbf{7}}{(C_5Me_5)_3Nd} + KBPh_4 \quad (17)$$

spectroscopy as well as by a crystal structure determination to unequivocally confirm that it is the third fully characterized example of a $(C_5Me_5)_3M$ complex, Figure 2.

Complex **7** was found to be isostructural and isomorphous with $(C_5Me_5)_3Sm$.[14] The differences in the three individual Ln−C bond distances in the two complexes are consistent with the 0.031 Å difference in ionic radii of the two metals:[36] the differences are 0.017(5) Å for Ln−C(1), 0.025(4) Å for Ln−C(2), and 0.033(4) Å for Ln−C(3).

The ^1H NMR spectrum of **7** contains a singlet at δ 8.88 while the ^{13}C NMR spectrum contains singlets at δ 253 and −15.8 ppm for the ring and methyl carbons, respectively. **7** was first prepared from a reaction of $[(C_5Me_5)_2NdH]_2$ with tetramethylfulvalene, but was not obtained in sufficient yield for full characterization.[45]

Attempts to reduce **7** with either Na or K to form a divalent complex in analogy to eq 4 were conducted due to the reported preparation of a divalent neodymium complex, $[K(THF)_n][(C_5Me_5)_2NdCl_2]$.[46] No new Nd(II) products were isolated and mostly starting material was recovered.

Reaction of $[(C_5Me_5)_2Tm][BPh_4]$ with Potassium. Attempts to form $(C_5Me_5)_2Tm$ from **6** by reduction with potassium in analogy to eq 4 produced dark toluene insoluble products which formed green/blue solutions in dimethoxyethane. Although these dark colors are similar to that of the crystallographically characterized Tm(II) complex $TmI_2(DME)_3$,[47] crystallographic data on a new Tm(II) complex were not obtained.

Efficient Synthesis of $[(C_5Me_5)_2LnH]_n$ from $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$. It was previously shown that the allyl

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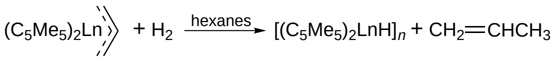
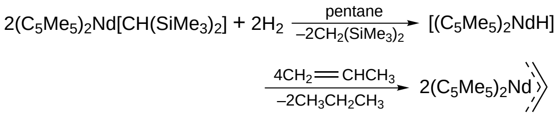
complex $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ could be hydrogenolyzed to $[(C_5Me_5)_2SmH]_2$, eq 18.[42] Likewise, $(C_5Me_5)_2Nd(\eta^3\text{-}CH_2CHCH_2)$ reacts with H_2 in hexanes to make $[(C_5Me_5)_2NdH]_2$[17] in 75% yield, eq 18. In the past, $(C_5Me_5)_2Nd(\eta^3\text{-}CH_2CHCH_2)$ was made *from* the hydride, which was made from $(C_5Me_5)_2Nd[CH(SiMe_3)_2]$, eq 19.[17] Hence, the improved synthesis of these allyl complexes also provides an improved synthesis of the hydrides.



(18)



(19)

Discussion

As anticipated, the unsolvated cation, $[(C_5Me_5)_2Sm]^+$, is highly electrophilic. Fortunately, the electrophilicity of the metal center can be satisfied by a single $[BPh_4]^-$ unit, which interacts strongly enough to generate a soluble zwitterion $[(C_5Me_5)_2Sm][BPh_4]$ (**1**) rather than an insoluble, intermolecularly connected oligomer involving bridging C_5Me_5 or BPh_4 groups.

It is also fortunate that the $[BPh_4]^-$ moiety can be easily displaced by other reagents. Facile loss of $[BPh_4]^-$ effectively provides a soluble form of the highly electrophilic $[(C_5Me_5)_2Sm]^+$ cation. In this regard, complex **1** should become a generally useful starting material in organosamarium chemistry. This was best demonstrated by the fact that it can provide a route to sterically crowded $(C_5Me_5)_3Sm$, a molecule that in the past has been difficult to prepare.

Although the synthesis of $(C_5Me_5)_3Sm$ from **1** is now the fourth synthesis of $(C_5Me_5)_3Sm$, it is the one that is best for generalization to the other lanthanides. This is typical of the development of organolanthanide metallocene chemistry. The high reactivities of divalent reagents $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ often provide the first examples of new types of lanthanide metallocene derivatives and hence organosamarium chemistry develops faster than that of the other elements. Once a particular type of new complex is discovered, one can devise routes to the analogous complexes of the other metals using trivalent chemistry.

To use $[(C_5Me_5)_2Ln][BPh_4]$ complexes as precursors to $(C_5Me_5)_3Ln$ and other compounds where Ln ≠ Sm, it was necessary to develop a synthesis that did not rely on Ln(II). The general synthesis of $[(C_5Me_5)_2Ln][BPh_4]$ from trivalent $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$ provides this route and emphasizes the importance of these allyl complexes as precursors. To use the $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$ complexes as precursors in cases in which Ln ≠ Sm, a synthesis of the allyl compounds that did not depend on Ln(II) was needed. In addition, it was desirable to have a synthesis of the allyl complexes that did not depend on $[(C_5Me_5)_2LnH]_n$ and its precursor $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$. Since these unsolvated allyl species can now be conveniently made directly from $LnCl_3$, KC_5Me_5, and $ClMg(CH_2CHCH_2)$ in high yield for samarium, neodymium, and thulium, it is likely that these $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$ complexes will be more heavily utilized as pseudo-alkyl starting materials in the future not only to make cationic metallocenes, but also to make other lanthanide metallocene derivatives. The allyl complexes are cheaper and easier to prepare than the commonly used $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$[17] and have been shown to readily form $(C_5Me_5)_2Sm(\eta^1\text{-}CH_2CH{=}CH_2)$ intermediates.[21,48,49] As shown for neodymium, the improved synthesis now makes these allyl complexes the best precursors to the $[(C_5Me_5)_2LnH]_n$ hydrides which, in the past, were the precursors to the allyl complexes for Ln ≠ Sm.

The development of the $(C_5Me_5)_2NdCl_2K(THF)_2$ to $(C_5Me_5)_2Nd(\eta^3\text{-}CH_2CHCH_2)$ to $[(C_5Me_5)_2Nd][BPh_4]$ route for neodymium, which made it possible to prepare $(C_5Me_5)_3Nd$ for definitive characterization, shows the utility of these results for the synthesis of new complexes as well. Other $(C_5Me_5)_3Ln$ complexes should be accessible by this route, and this should extend the unusual chemistry of $(C_5Me_5)_3Sm$[14,50] to the other lanthanide metals.

Conclusion

The unsolvated decamethylsamarocenium cation complex $[(C_5Me_5)_2Sm][BPh_4]$ was synthesized, structurally characterized, and used to develop a general convenient synthetic route to unsolvated $[(C_5Me_5)_2Ln][BPh_4]$ cations of other lanthanides. These cations should have wide applicability as precursors in organolanthanide chemistry, since the tetraphenylborate anion can be displaced by a variety of ligands. The $[(C_5Me_5)_2Ln][BPh_4]$ complexes currently are the best starting material for the syntheses of $(C_5Me_5)_3Ln$ complexes via Ln(III) routes. In connection with the development of the synthesis of these lanthanocene cations, a convenient synthesis was also found for the allyl complexes $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$, which should make these complexes easily obtainable metallocene pseudo-alkyl alternatives to the commonly used alkyls $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$.

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Supporting Information Available: Atomic coordinates, thermal parameters, and complete bond distances and angles for compounds **1**, **5**, and **7** (37 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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