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Article

Lanthanide Metallocene Complexes of the 1,3,4,6,7,8-Hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinato Ligand, (hpp)$^{1-}$

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Reaction of the lanthanide metallocene allyl complexes, $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)(THF)$ (Ln = Ce, Sm, Y) with 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, Hhpp, forms a series of metallocene complexes, $(C_5Me_5)_2Ln(hpp)$ (Ln = Ce, Sm, Y) in which the (hpp)$^{1-}$ anion coordinates as a terminal bidentate ligand. Isomorphous structures were observed by X-ray crystallography regardless of the size of the metal. The acetonitrile adduct, $(C_5Me_5)_2Sm(hpp)(MeCN)$, was also crystallographically characterized to provide an unusual pair of eight- and nine-coordinate complexes. The coordination mode of the (hpp)$^{1-}$ anion in these complexes is compared with that in other heteroallylic metallocenes like the caprolactamate $(C_5Me_5)_2Y(ONC_6H_{10})$ and the dithiocarbamate $(C_5Me_5)_2Sm(S_2CNEt_2)$, which was also structurally characterized.

Introduction

The bicyclic guanidinate anion, (hpp)$^{1-}$, derived from 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, Hhpp, by deprotonation has been found to have an extensive chemistry with a wide range of transition metals.[1−7] This ligand can have a spectacular effect on redox chemistry as demonstrated by the tungsten complex $W_2(\mu\text{-}\eta^1{:}\eta^1\text{-hpp})_4$ which has a lower gas-phase ionization energy than cesium.[3] Although guanidinates[1,8] have been extensively studied with yttrium and the lanthanide metals,[9−19] the only example of an (hpp)$^{1-}$ complex of metals of this type is the complicated tetrametallic yttrium chlorooxide, $Y_4(\mu\text{-}\eta^2{:}\eta^2\text{-hpp})_4(\eta^2\text{-hpp})_4Cl_2(\mu_4\text{-O})$.[13] To examine the coordination chemistry of the (hpp)$^{1-}$ ligand with the lanthanides in a coordination environment suitable for comparison with other ligands, the synthesis of (hpp)$^{1-}$ complexes was examined using a lanthanide metallocene platform. Met-

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allocene chemistry has previously been shown to be an effective approach for examining new ligand systems for the f elements.[20]

We report here the synthesis and structural analysis of $(hpp)^{1-}$ complexes of Ce, Sm, and Y metallocenes. The variation of coordination mode with the size of the metal and with the addition of a Lewis base was examined. The structural data on the $(hpp)^{1-}$ complexes are compared with those of three other heteroallylic metallocene complexes, the previously reported caprolactamate $(C_5Me_5)_2Y(ONC_6H_{10})$[21] and thiocarbamate $(C_5Me_5)_2Sm(S_2CNMe_2)$,[22] as well as $(C_5Me_5)_2Sm(S_2CNEt_2)$ whose structure is reported here.

Experimental Section

The manipulations described below were conducted under argon or nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were dried over Q-5 and molecular sieves and saturated with UHP argon using GlassContour[23] columns. NMR solvents (Cambridge Isotope Laboratories) were dried over sodium−potassium alloy, degassed, and vacuum-transferred before use. $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)(THF)$[24−26] and $(C_5Me_5)_2Sm(THF)_2$[27] were prepared according to literature methods. Hhpp (Sigma-Aldrich) was purified by sublimation prior to use. Tetraethylthiuram disulfide (disulfiram) was obtained from Sigma-Aldrich and was placed under vacuum (10×10^{-3} Torr) for 12 h before use. Acetonitrile (Sigma-Aldrich) was dried over calcium hydride, distilled onto activated 4 Å molecular sieves, and degassed by three freeze−pump−thaw cycles before use. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer at 25 °C. Infrared spectra were recorded as KBr pellets on a Varian 1000 FTIR spectrophotometer at 25 °C. Elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany). Lanthanide metal analyses were carried out by complexometric titration.[28]

$(C_5Me_5)_2Ce(hpp)$, 1. A solution of Hhpp (44 mg, 0.31 mmol) in toluene (2 mL) was added dropwise to a stirred green solution of $(C_5Me_5)_2Ce(\eta^3\text{-}CH_2CHCH_2)(THF)$ (164 mg, 0.313 mmol) in toluene (8 mL). After the reaction mixture was stirred for 12 h, volatiles were removed under reduced pressure to yield **1** as a blue crystalline solid (167 mg, 97%). Blue X-ray quality crystals of **1** were grown from a concentrated benzene solution at 25 °C. Anal. Calcd for $CeC_{27}H_{42}N_3$: C, 59.09; H, 7.71; N, 7.66; Ce, 25.5. Found: C, 55.29; H, 7.61; N, 7.54; Ce, 25.1. Despite six attempts on single crystalline samples, the carbon analysis was consistently low. ^1H NMR (C_6D_6) δ 5.01 (br s, 4H, $C_7\mathit{H}_{12}N_3$, $\Delta\nu_{1/2} = 14$ Hz), 1.89 (br s, 30H, $C_5\mathit{Me}_5$, $\Delta\nu_{1/2} = 16$ Hz), 1.42 (br s, 4H, $C_7\mathit{H}_{12}N_3$, $\Delta\nu_{1/2} = 17$ Hz), −10.15 (br s, 4H, $C_7H_{12}N_3$, $\Delta\nu_{1/2} = 20$ Hz). ^{13}C NMR (C_6D_6) δ 189.6 ($\mathit{C}_7H_{12}N_3$), 116.5 (C_5Me_5), 52.4 ($\mathit{C}_7H_{12}N_3$), 27.4 ($\mathit{C}_7H_{12}N_3$), 22.1 ($\mathit{C}_7H_{12}N_3$), 8.6 ($C_5\mathit{Me}_5$). IR: 2941s, 2851m, 2723w, 1620m, 1528s, 1492s, 1467m, 1448s, 1381s, 1319s, 1289m, 1260m, 1197m, 1145m, 1109m, 1066m, 1024m, 878w, 801m, 718m, 689w cm^{-1}.

$(C_5Me_5)_2Sm(hpp)$, 2. As described for **1**, **2** was obtained as a yellow crystalline solid (94 mg, 97%) from a solution of Hhpp (25 mg, 0.18 mmol) in toluene (2 mL) and $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)(THF)$ (96 mg, 0.18 mmol) in toluene (8 mL). Yellow crystals of **2** suitable for X-ray diffraction were grown from a concentrated toluene solution at −35 °C. Anal. Calcd for $C_{27}H_{42}N_3Sm$: C, 58.01; H, 7.57; N, 7.52; Sm, 26.90. Found: C, 57.73; H, 7.53; N, 7.55; Sm, 27.20. ^1H NMR (C_6D_6) δ 4.63 (t, 4H, $C_7\mathit{H}_{12}N_3$), 2.20 (quintet, 4H, $C_7\mathit{H}_{12}N_3$), 1.16 (s, 30H, $C_5\mathit{Me}_5$), −2.86 (t, 4H, $C_7\mathit{H}_{12}N_3$). ^{13}C NMR (C_6D_6) δ 118.3 (C_5Me_{5s}), 50.9 ($\mathit{C}_7H_{12}N_3$), 39.4 ($\mathit{C}_7H_{12}N_3$), 22.7 ($\mathit{C}_7H_{12}N_3$), 18.1 ($C_5\mathit{Me}_5$). IR: 2921s, 2852s, 2722w, 1626m, 1531s, 1494s, 1467m, 1438s, 1382s, 1319s, 1293m, 1261m, 1209m, 1197m, 1148m, 1109m, 1068m, 1025m, 879w, 801w, 721m, 691w cm^{-1}.

$(C_5Me_5)_2Y(hpp)$, 3. As described for **1**, **3** was obtained as a pale yellow crystalline solid (216 mg, 96%) from a solution of Hhpp (63 mg, 0.45 mmol) in toluene (2 mL) and $(C_5Me_5)_2Y(\eta^3\text{-}CH_2CHCH_2)(THF)$ (213 mg, 0.452 mmol) in toluene (8 mL). Colorless X-ray quality crystals of **3** were grown from a concentrated benzene solution at 25 °C. Anal. Calcd for $YC_{27}H_{42}N_3$: C, 65.18; H, 8.51; N, 8.44; Y, 17.9. Found: C, 63.34; H, 8.48; N, 7.83; Y, 17.7. Despite six attempts on single crystalline samples, the carbon analysis was consistently low. ^1H NMR (C_6D_6) δ 3.07 (t, 4H, $C_7\mathit{H}_{12}N_3$), 2.62 (t, 4H, $C_7\mathit{H}_{12}N_3$), 2.02 (s, 30H, $C_5\mathit{Me}_5$), 1.56 (quintet, 4H, $C_7\mathit{H}_{12}N_3$). ^{13}C NMR (C_6D_6) δ 155.4 ($\mathit{C}_7H_{12}N_3$), 116.1 (C_5Me_5), 48.2 ($\mathit{C}_7H_{12}N_3$), 42.5 ($\mathit{C}_7H_{12}N_3$), 24.9 ($\mathit{C}_7H_{12}N_3$), 11.3 ($C_5\mathit{Me}_5$). IR: 2901s, 2854s, 2722w, 1634m, 1535s, 1499s, 1468m, 1438s, 1383s, 1319s, 1294m, 1263m, 1199m, 1151m, 1110m, 1071m, 1026m, 879w, 802w, 727m, 694w cm^{-1}.

$(C_5Me_5)_2Sm(hpp)(NCMe)$, 4. In an NMR tube, excess MeCN was added to a yellow solution of **1** (15 mg, 0.027 mmol) in 1 mL of C_6D_6. No color change was noticed upon the addition of MeCN. Yellow crystals of **4** suitable for X-ray diffraction were grown from this solution via slow evaporation of a C_6D_6 solution at 25 °C in an NMR tube. ^1H NMR (C_6D_6) δ 3.77 (t, 4H, $C_7\mathit{H}_{12}N_3$), 2.01 (quintet, 4H, $C_7\mathit{H}_{12}N_3$), 1.57 (s, 30H, $C_5\mathit{Me}_5$), 0.36 (t, 4H, $C_7\mathit{H}_{12}N_3$). ^{13}C NMR (C_6D_6) δ 112.1 (C_5Me_5), 49.7 ($\mathit{C}_7H_{12}N_3$), 40.8 ($\mathit{C}_7H_{12}N_3$), 23.5 ($\mathit{C}_7H_{12}N_3$), 16.2 ($C_5\mathit{Me}_5$). IR: 2941s, 2909s, 2852s, 2721w, 2271w, 1623w, 1531s, 1493s, 1468m, 1438s, 1381s, 1318s, 1291m, 1261 m, 1209m, 1198m, 1147m, 1110m, 1068m, 1025m, 879w, 801w, 751w, 720m, 691w, 677w, 613w cm^{-1}.

$(C_5Me_5)_2Sm(S_2CNEt_2)$, 5. A solution of tetraethylthiuram disulfide (54 mg, 0.18 mmol) in THF (2 mL) was added dropwise to a stirred dark purple solution of $(C_5Me_5)_2Sm(THF)_2$ (206 mg, 0.364 mmol) in THF (8 mL). The solution immediately turned light orange. After the reaction mixture was stirred for 12 h, solvent was removed under reduced pressure to yield **5** as a light orange solid (200 mg, 96%). Yellow X-ray quality crystals of **5** were grown from a concentrated toluene solution at −35 °C. Anal. Calcd for $C_{24}H_{41}NS_2Sm$: C, 52.76; H, 7.08; N, 2.46; Sm, 26.42. Found: C, 52.58; H, 7.01; N, 2.55; Sm, 26.08. ^1H NMR (C_6D_6) δ 4.35 (q, 4H, $S_2CN(C\mathit{H}_2CH_3)_2$), 1.76 (t, 6H, $S_2CN(CH_2C\mathit{H}_3)_2$), 1.08 (s, 30H, $C_5\mathit{Me}_5$). ^{13}C NMR (C_6D_6) δ 116.9 (C_5Me_5), 45.7 ($S_2CN(\mathit{C}H_2CH_3)_2$), 30.8 ($S_2\mathit{C}N(CH_2CH_3)_2$), 18.2 ($C_5\mathit{Me}_5$), 13.0 ($S_2CN(CH_2\mathit{C}H_3)_2$). IR: 2971s, 2930s, 2898s, 2856s, 2725w, 1486s, 1455m, 1422s, 1378m,

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Table 1. X-ray Data Collection Parameters for $(C_5Me_5)_2Ce(hpp)$, **1**, $(C_5Me_5)_2Sm(hpp)$, **2**, $(C_5Me_5)_2Y(hpp)$, **3**, $(C_5Me_5)_2Sm(hpp)(NCMe)$, **4**, and $(C_5Me_5)_2Sm(S_2CNEt_2)$, **5**

Empirical formula	$C_{27}H_{42}N_3Ce$ **1**	$C_{27}H_{42}N_3Sm$ **2**	$C_{27}H_{42}N_3Y$ **3**	$C_{32}H_{45}N_4Sm$ **4**	$C_{25}H_{40}NS_2Sm$ **5**
formula weight	548.76	558.99	497.55	636.07	569.05
temperature (K)	100(2)	163(2)	163(2)	481(2)	163(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	24.874(5)	24.738(2)	24.530(2)	20.221(10)	9.5414(12)
b (Å)	8.4450(15)	8.4809(7)	8.4910(8)	10.110(5)	10.2394(13)
c (Å)	25.131(5)	25.004(2)	24.829(3)	16.301(8)	14.1557(19)
α (deg)	90	90	90	90	101.258(2)
β (deg)	91.754(3)	91.439(2)	91.160(2)	109.752(9)	98.324(2)
γ (deg)	90	90	90	90	103.261(2)
volume (Å^3)	5276.6(18)	5244.3(8)	5170.4(9)	3136(3)	1293.9(3)
Z	8	8	8	4	2
ρ_{calcd} (Mg/m^3)	1.382	1.416	1.278	1.347	1.461
μ (mm^{-1})	1.743	2.257	2.274	1.897	2.442
R1^a ($I > 2.0\sigma(I)$)	0.0346	0.0312	0.0458	0.0359	0.0227
wR2^b (all data)	0.0859	0.0733	0.1173	0.0897	0.0594

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

1357m, 1302w, 1204m, 1140m, 1088m, 1065w, 1023w, 982m, 909m, 839m, 801w, 776w, 607w, 561m cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Ce(hpp)$, 1. A blue rod 0.25 × 0.10 × 0.10 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 5 s per frame using a scan width of 0.3°. Data collection was 99.9% complete to 25.00° in θ. A total of 61598 reflections were collected covering the indices, $-32 \le h \le 33$, $-10 \le k \le 10$, $-33 \le l \le 33$. 12280 reflections were found to be symmetry independent, with an R_{int} of 0.0303. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/n$ (No. 14). Solution by direct methods (SHELXS-97) produced a complete heavy-atom phasing model consistent with the proposed structure (Table 1).

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm(hpp)$, 2. A yellow crystal of approximate dimensions 0.12 × 0.19 × 0.28 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[29] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[30] and SADABS[31] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[32] program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[33] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were two molecules of the formula unit present ($Z = 8$). The pentamethylcyclopentadienyl ligands defined by atoms C(31)-C(40B) and C(41)-C(50B) were disordered and included using multiple components, partial site-occupancy-factors, and isotropic temperature parameters.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Y(hpp)$, 3. A colorless crystal of approximate dimensions 0.15 × 0.35 × 0.37 mm was handled as described for **2**. The SMART[29] program package was used to determine the unit-cell parameters and for data collection (45 s/frame scan time for a sphere of diffraction data). The structure was solved using the coordinates of the samarium analogue and refined on F^2 by full-matrix least-squares techniques. There were two molecules of the formula unit present ($Z = 8$). The pentamethylcyclopentadienyl ligands defined by atoms C(31)-C(40B) and C(41)-C(50B) were disordered and included using multiple components, partial site-occupancy-factors, and isotropic temperature parameters.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm(hpp)(NCMe)$, 4. A yellow plate 0.30 × 0.30 × 0.08 mm in size was was handled as described for **1**. Data were collected in a nitrogen gas stream at 208(2) K using phi and omega scans. Exposure time was 10 s per frame using a scan width of 0.3°. A total of 19026 reflections were collected covering the indices, $-24 \le h \le 23$, $-12 \le k \le 12$, $-20 \le l \le 19$. 6154 reflections were found to be symmetry independent, with an R_{int} of 0.0363. The space group was found to be $P2_1/c$ (No. 14).

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm(S_2CNEt_2)$, 5. A yellow crystal of approximate dimensions 0.22 × 0.23 × 0.40 mm was handled as described for **2**. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. Atoms N(1) and C(21)−C(25) were disordered and included using multiple components, partial site-occupancy-factors, and anisotropic thermal parameters.

Results

Synthesis. The $(hpp)^{1-}$ lanthanide metallocene complexes, $(C_5Me_5)_2Ln(hpp)$ (Ln = Ce, **1**; Sm, **2**; Y, **3**), were prepared by protonolysis of the corresponding $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)(THF)$ allyl complexes with Hhpp, eq 1. Complexes **1**−**3** were obtained in the same way that the heteroallylic caprolactamate $(C_5Me_5)_2Y(ONC_6H_{10})$, **6**, was prepared, as shown in eq 2.[21]

In the search of alternative routes for the synthesis of **2**, it was found that both divalent $(C_5Me_5)_2Sm(THF)_2$[27] and

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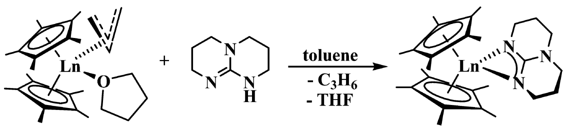
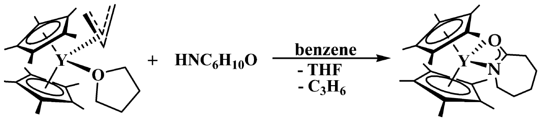


(1)

Ln = Ce, **1**; Sm, **2**; Y, **3**



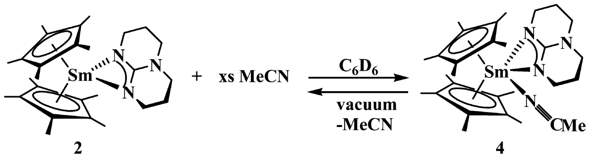
6

(2)

$(C_5Me_5)_2Sm$[34] react with Hhpp to produce **2**. A resonance consistent with the formation of H_2 was also observed in the ^{1}H NMR spectrum of the reaction products of both reactions. Other byproducts were formed, however, and eq 1 is a better synthesis.

Complexes **1**−**3** have analogous infrared spectra and contain C=N stretches at 1620, 1626, and 1634 cm^{-1} for **1**, **2**, and **3**, respectively.[35] The ^{1}H NMR resonances of the $(hpp)^{1-}$ ligand in diamagnetic **3** at 3.07, 2.62, and 1.56 are shifted to 5.01, 1.42, and −10.15 in **1** and 4.63, 2.20, and −2.86 in **2** because of the paramagnetism of Ce^{3+} and Sm^{3+}.

When complex **2** was treated with excess MeCN, the solvated product $(C_5Me_5)_2Sm(hpp)(NCMe)$, **4**, was crystallized by slow evaporation of C_6D_6 to provide an analogue of **2** with a higher coordination number, eq 3. The coordinated MeCN can be easily removed under vacuum at room temperature to regenerate complex **2**. The infrared spectrum of **4** is similar to that of **2** except that it also contains an absorption at 2272 cm^{-1} assignable to the C≡N stretch of the coordinated MeCN. This value is larger than the 2250 cm^{-1} υ_{CN} of free MeCN[36] as is typical in f-element complexes when the nitrile functions as a donor ligand.[36−38]



2 **4**

(3)

Structure. Complexes **1**−**3** are isomorphous and crystallize in the space group $P2_1/n$ with two molecules in the unit cell (Table 1). Each eight-coordinate Ln^{3+} center is ligated by two pentamethylcyclopentadienyl ligands and a chelating $(hpp)^{1-}$ ligand, Figure 1.

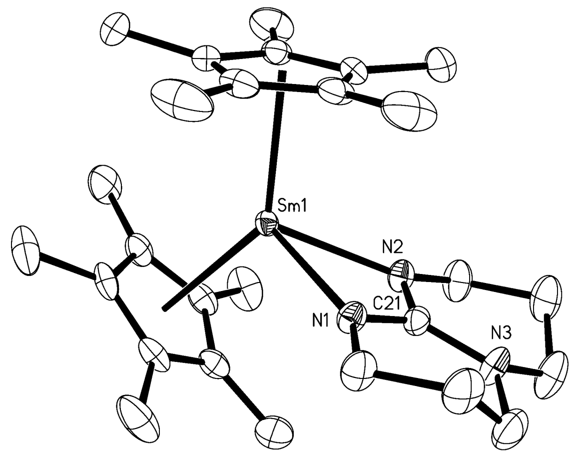


Figure 1. Thermal ellipsoid plot of $(C_5Me_5)_2Sm(hpp)$, **2**, with ellipsoids drawn at the 30% probability level. Hydrogen atoms and disorder in $(C_5Me_5)^{1-}$ ligands have been excluded for clarity.

The metallocene units in complexes **1**−**3** have crystallographic parameters that are normal for $[(C_5Me_5)_2M]^{1+}$ moieties containing an eight-coordinate lanthanide metal center[39] and follow the periodic trend for bond lengths, Table 2. For example, the 137.9−139.1° (C_5Me_5 ring centroid)-Ln-(C_5Me_5 ring centroid) angles are within the range of other eight-coordinate $[(C_5Me_5)_2M]^{1+}$ moieties and the 2.79(1), 2.72(1), and 2.66(1) Å Ln-C(C_5Me_5) average distances decrease in the order of decreasing eight coordinate ionic radii for Ce^{3+}, Sm^{3+}, and Y^{3+}, that is, 1.143, 1.079, and 1.019 Å, respectively.[40]

The $(hpp)^{1-}$ ligand interacts with the Ln^{3+} centers primarily through two nitrogen atoms. The 2.311(2) and 2.312(2) Å Y−N bond lengths in **3** are shorter than the 2.421(3)−2.687(3) Å distances in the bridging $(hpp)^{1-}$ ligands in $Y_4(\mu\text{-}\eta^2{:}\eta^2\text{-hpp})_4(\eta^2\text{-hpp})_4Cl_2(\mu_4\text{-O})$[13] as expected for terminal versus bridging ligands. However, they are also shorter than the 2.374(3) and 2.413(3) Å distances in the terminal $(hpp)^{1-}$ ligand in $Y_4(\mu\text{-}\eta^2{:}\eta^2\text{-hpp})_4(\eta^2\text{-hpp})_4Cl_2(\mu_4\text{-O})$.[13] The Y−N distances in **3** are similar to those in the guanidinate complex $(C_5H_5)_2Y[^iPrNC(N^iPr_2)N^iPr]$[11] [2.316(3) and 2.321(3) Å] and are slightly longer than the 2.274(5) and 2.253(5) Å Y−N distances in $(C_5Me_5)_2Y[N(SiMe_3)_2]$.[41] The Ln−N bond lengths in **1** and **2** are comparable to the corresponding distances in the lanthanide guanidinate complexes $(C_5H_5)_2Ln[^iPrNC(N^iPr_2)N^iPr]$[42] (Ln = Dy, Yb), when the differences in ionic radii are considered.[40] The 2.871(3), 2.803(3), and 2.741(3) Å Ln(1)−C(21) distances in **1**−**3**, respectively, are too long for a significant interaction. In comparison, $(C_5Me_5)_2Y(\eta^3\text{-}CH_2CHCH_2)$ has a 2.601(2) Å Y−C(allyl) distance to the central carbon of the allyl ligand with 2.582(2) Å distances to the end carbons and an average Y−C(C_5Me_5) distance of 2.660(7) Å.[25]

N(1), N(2), N(3), C(21), and Ln(1) in **1**−**3** are coplanar within 0.013, 0.006, and 0.005 Å, respectively. The nearly equivalent 1.338(4)−1.344(4) Å bond lengths observed for C(21)−N(1) and C(21)−N(2) in the N−C−N fragment are shorter than the average distance expected for a C−N single bond (1.469 Å) but longer than that expected for a C−N

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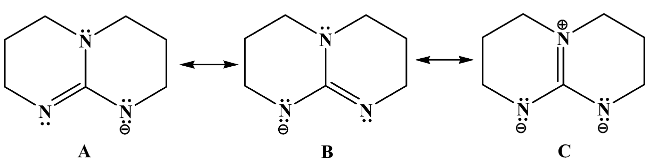
Table 2. Bond Distances (Å) and Angles (deg) in $(C_5Me_5)_2Ce(hpp)$, **1**, $(C_5Me_5)_2Sm(hpp)$, **2**, $(C_5Me_5)_2Y(hpp)$, **3**, and $(C_5Me_5)_2Sm(hpp)(NCMe)$, **4**

	1	**2**	**3**	**4**
n-coordinate ionic radius	1.143^a	1.079^a	1.019^a	1.132^b
Ln(1)−(C_5Me_5 ring centroid)	2.513/2.519	2.443/2.449	2.375/2.381	2.497/2.498
Ln(1)−C(C_5Me_5) avg	2.79(1)	2.72(1)	2.66(1)	2.77(1)
Ln(1)−N(1)	2.423(2)	2.367(3)	2.311(2)	2.405(4)
Ln(1)−N(2)	2.426(2)	2.371(3)	2.312(2)	2.426(4)
Ln(1)−C(21)	2.871(3)	2.803(3)	2.741(3)	2.860
N(1)−C(21)	1.341(4)	1.338(4)	1.339(4)	1.334(7)
N(2)−C(21)	1.344(4)	1.338(4)	1.343(4)	1.324(7)
N(3)−C(21)	1.361(4)	1.369(4)	1.372(4)	1.383(6)
Ln(1)−N(4)	N/A	N/A	N/A	2.592(4)
Cnt1−Ln(1)−Cnt2	139.10	138.4	137.9	137.13
N(1)−C(21)−N(2)	114.5(3)	114.9(3)	114.7(2)	114.4(4)
N(1)−Ln(1)−N(2)	55.53(8)	56.85(9)	58.47(8)	55.1(2)
Ln(1)−N(1)−C(21)	95.0(2)	94.2(2)	93.5(2)	95.5(3)
Ln(1)−N(2)−C(21)	94.8(2)	94.0(2)	93.4(2)	94.8(3)

^{a} $n = 8$. ^{b} $n = 9$.

Scheme 1



double bond (1.303 Å).[43] This indicates delocalization of the negative charge of the monoanionic (hpp)$^{1-}$ ligand over the N(1)−C(21)−N(2) moiety. The Δ_{CN} values,[44] that is, the difference in N(1)−C(21) and N(2)−C(21) bond lengths, are 0.003, 0.000, and 0.004 Å for **1**−**3**, respectively. These also support a delocalized bonding arrangement. Fully delocalized systems should have $\Delta_{CN} = 0$.[44]

The 1.361(4)−1.372(4) Å C(21)−N(3) bond lengths are slightly longer than the N(1)−C(21) and N(2)−C(21) bond lenghts. This pattern is similar to that in the $M_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-hpp})_4$ complexes (M = Cr, Mo, W) which have a range of 1.317−1.348 Å for the C(21)−N(1, 2) analogues and 1.375−1.389 Å for the C(21)−N(3) analogue.[45,46] The analogous distances in $Y_4(\mu\text{-}\eta^2\text{:}\eta^2\text{-hpp})_4(\eta^2\text{-hpp})_4Cl_2(\mu_4\text{-O})$ are 1.327(5)−1.348(4) Å and 1.361(5)−1.378(5) Å.[13] The Δ'_{CN} values, previously defined by Coles and Hitchcock[44] as the difference between the average C−N(amidine) and C−N(amide) bond lengths, for **1**−**3** are −0.0185, −0.031, and −0.031 Å, respectively, and indicate a small contribution of the zwitterionic resonance form **C** (Scheme 1) to the overall bonding. The larger the Δ'_{CN} value, the greater the contribution of **C**.

Complex **4** crystallizes in the space group $P2_1/c$ with a nine-coordinate Sm^{3+} center ligated by two pentamethylcyclopentadienyl ligands, a chelating (hpp)$^{1-}$ ligand, and the nitrogen of the coordinated MeCN, Figure 2. Selected bond lengths and angles for **4** are provided in Table 2.

The $[(C_5Me_5)_2Sm]^{1+}$ unit in complex **4** has crystallographic parameters that are normal for metallocene moieties containing a nine-coordinate Sm^{3+} ion.[39] As in **1**−**3** the chelating (hpp)$^{1-}$ ligand is bound to the Sm^{3+} center primarily by two Sm−N bonds. The 2.405(4) and 2.426(4) Å Sm−N bonds lengths in **4** are similar to those in **2**, taking into account the 0.053 Å difference in ionic radii between eight- and nine-coordinate Sm^{3+} ions. The C−N distances in the (hpp)$^{1-}$ ligand are also similar to those in **1**−**3**. The SmN_3C unit in **4** is planar within 0.02 Å.

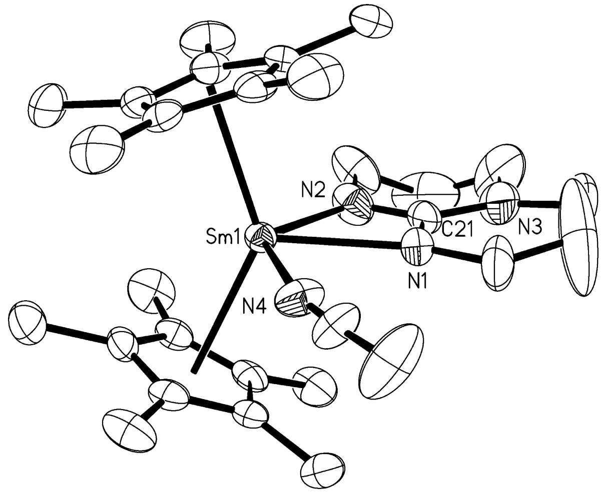


Figure 2. Thermal ellipsoid plot of $(C_5Me_5)_2Sm(hpp)(NCMe)$, **4**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

The 2.592(4) Å Sm−N(4) bond length of the coordinated acetonitrile in **4** is significantly longer than the Sm−N(hpp) distances as expected for a neutral versus ionic ligand. The Sm−N(MeCN) distance provides an internal comparison in **4** for what would be expected if the (hpp)$^{1-}$ ligand were not delocalized. If this were in fact the case, one of the Sm−N(hpp) distances could be as long as the Sm−N(4) bond length. The Sm−N(MeCN) distance in **4** is slightly longer than those found in $[Sm(MeCN)_9][AsF_6]_3 \cdot 3MeCN$,[36] 2.510(5)−2.546(5) Å, and in $(C_5Me_5)_2Ce(I)(NCMe)_2$,[38] 2.63(1) Å, when considering the 0.064 Å difference in ionic radii between Ce^{3+} and Sm^{3+} ions.[40]

Synthesis of $(C_5Me_5)_2Sm(S_2CNEt_2)$, 5. Reported along with the (hpp)$^{1-}$ complexes in this study are the synthesis and structure of another heteroallylic metallocene complex, $(C_5Me_5)_2Sm(S_2CNEt_2)$, **5**, made from tetraethylthiuram disulfide and divalent $(C_5Me_5)_2Sm(THF)_2$ according to eq 4, Figure 3. The analogous Yb and Nd complexes were

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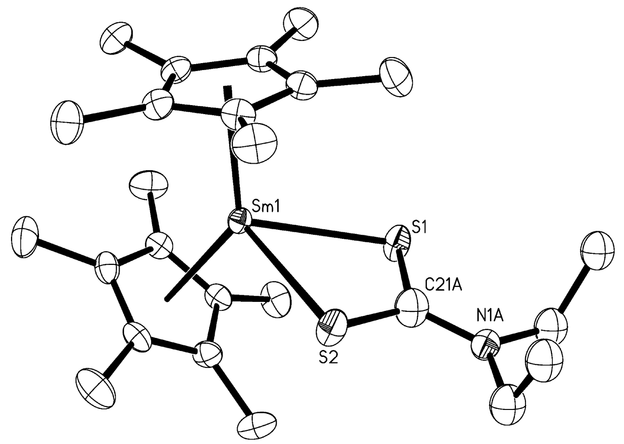


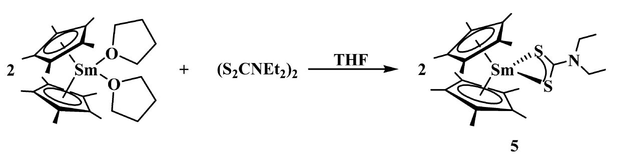
Figure 3. Thermal ellipsoid plot of $(C_5Me_5)_2Sm(S_2CNEt_2)$, **5**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

Table 3. Bond Distances (Å) and Angles (deg) in $(C_5Me_5)_2Sm(hpp)$, **2**, $(C_5Me_5)_2Sm(S_2CNEt_2)$, **5**, and $(C_5Me_5)_2Sm(S_2CNMe_2)$, **7**[a]

	2	**5**	**7**
Sm(1)−(C_5Me_5 ring centroid)	2.443/2.449	2.434/2.436	2.432/2.432
Sm(1)−C(C_5Me_5) avg	2.72(1)	2.72(2)	2.71(1)
Sm(1)−E(1)	2.367(3)	2.7964(6)	2.808
Sm(1)−E(2)	2.371(3)	2.7990(6)	2.808
Sm(1)−C(21)	2.803(3)	3.209	3.233
E(1)−C(21)	1.338(4)	1.731(5)	1.718
E(2)−C(21)	1.338(4)	1.714(5)	1.718
N(X)[b]−C(21)	1.369(4)	1.339(6)	1.323
Cnt1−Sm(1)−Cnt2	138.4	138.9	136.9
E(1)−C(21)−E(2)	114.9(3)	121.1(3)	120.5(7)
E(1)−Sm(1)−E(2)	56.85(9)	64.837(18)	64.1(1)
Sm(1)−E(1)−C(21)	94.2(2)	86.93(17)	87.73
Sm(1)−E(2)−C(21)	94.0(2)	87.17(17)	87.73

[a] E = N for **2**; E = S for **5** and **7**. [b] **2**, X = 3; **5** and **7**, X = 1.

previously synthesized by ionic metathesis between $(C_5Me_5)_2LnCl_2Na(Et_2O)_2$ and NaS_2CNEt_2.[47] The synthesis



(4)

5

of **5** is analogous to that of the closely related methyl analogue $(C_5Me_5)_2Sm(S_2CNMe_2)$, **7**.[22]

Heteroallylic Comparisons. Selected bond lengths and angles for the heteroallylic samarium metallocenes **2**, **5**, and **7** are compared in Table 3. Complexes **5** and **7** have Sm-(C_5Me_5 ring centroid) distances and (C_5Me_5 ring centroid)−Sm−(C_5Me_5 ring centroid) angles that are very close to those in **2** despite the larger sulfur donor atoms. Hence, the presence of the larger donor atoms leads to an adjustment in the angles between the metal and the heteroallylic ligand. Complexes **5** and **7** have larger (donor atom)−Sm−(donor atom) angles and smaller Sm−(donor atom)−(central allylic carbon) angles compared to **2**. As shown in Table 3, the two Sm−S distances in **5** are very similar. This is also the case for the two Sm−S distances in **7** and the two Sm−N distances in **2**.

Table 4. Bond Distances (Å) and Angles (deg) in $(C_5Me_5)_2Y(hpp)$, **3**, and $(C_5Me_5)_2Y(ONC_6H_{10})$, **6**

	3	**6**
Y(1)−(C_5Me_5 ring centroid)	2.375/2.381	2.358/2.361
Y(1)−C(C_5Me_5) avg	2.66(1)	2.67(2)
Y(1)−N(1)	2.311(2)	2.362(4)
Y(1)−O(1)[a]	2.312(2)	2.288(3)
Y(1)−C(21)	2.741(3)	2.684(5)
N(1)−C(21)	1.339(4)	1.280(6)
O(1)−C(21)[a]	1.343(4)	1.309(5)
Cnt1−Y(1)−Cnt2	137.9	140.0
N(1)−C(21)−O(1)[a]	114.7(2)	119.8(4)
N(1)−Y(1)−O(1)[a]	58.47(8)	57.56(12)
Y(1)−N(1)−C(21)	93.5(2)	89.9(3)
Y(1)−O(1)−C(21)[a]	93.4(2)	92.5(3)

[a] In **3**, the second donor atom is nitrogen not oxygen.

Selected bond lengths and angles for the previously characterized $(C_5Me_5)_2Y(ONC_6H_{10})$,[21] **6**, are compared with those of the yttrium complex **3** in Table 4. Complexes **6** and **3** also show similar Y−(C_5Me_5 ring centroid) distances and (C_5Me_5 ring centroid)−Y−(C_5Me_5 ring centroid) angles. However, with the O and N donor atom set in **6**, there is asymmetry in the coordination. The 2.288(3) Å Y−O and 2.362(4) Å Y−N distances show the difference in bond length that can occur in a heteroallylic ligand.

Conclusion

The $(hpp)^{1-}$ ligand can form monometallic lanthanide complexes and coordinate in a chelating mode in which both nitrogen donor atoms are equidistant from the metal. The $(hpp)^{1-}$ ligand coordinates similarly to both large and small metals in this series and can also accommodate addition of another Lewis base ligand without changing coordination mode. It appears that a variety of heteroallylic ligands can coordinate to $[(C_5Me_5)_2Ln]^{1+}$ fragments without perturbing the structural parameters of the metallocene. Large donor atom ligands can adopt larger angles to coordinate equivalently to smaller donor atom ligands.

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Supporting Information Available: X-ray diffraction data, atomic coordinates, thermal parameters, and complete bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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