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1,2,4-Diazaphospholide Complexes of Samarium(III)

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A series of 1,2,4-diazaphospholide (dp$^-$) samarium complexes with a variety of coordination modes were prepared via the metathesis reaction of $SmCl_3(THF)_3$ and potassium 3,5-disubstituted 1,2,4-diazaphospholide or by the reaction of $Sm[N(SiMe_3)_2]_3$ and 3,5-diphenyl-1,2,4-diazaphosphole.

While trivalent lanthanide complexes bearing cyclopentadienyl ligands (Cp$^-$) are interesting because of their structural variability as well as to their catalytic potential,[1] the design and use of alternatives to the Cp$^-$(Cp*$^-$) ligand have become an area of active investigation.[2] The deprotonated 1*H*-1,2,4-diazaphosphole group (dp$^-$),[3] a mixed nitrogen−phosphorus ($\sigma^2\lambda^3$) analogue of Cp$^-$, may be viewed as a combination of phospholyl[4] and pyrazolato (pz)[5] ions. Given the differences in electronegativity as well as in the radii between the concerned heteroatoms (N vs P), the 1,2,4-diazaphospholides are expected to exhibit a remarkable variability in their coordination sphere.[6] We have been interested in the chemistry of 1,2,4-diazaphosphole[7] and 1,2,4-diazaphospholide complexes[8,9] as well as their applications.[10] Of particular interest to us are the bulky 1,2,4-diazaphospholides, which have proven to be excellent ancillary ligands with specific coordination ability to metal ions.[8,9] Notably, because the phosphorus atoms ($\sigma^2\lambda^3$) of the resulting complex have donor lone pairs available, they might provide additional binding sites to act as significant π acceptors,[2a] allowing for a more varied coordination chemistry.[10,11] While the lanthanide complexes incorporating Cp$^-$(Cp*$^-$) and five-membered heterocyclic ligands have been extensively investigated,[1,2] the 1,2,4-diazaphospholide lanthanide complexes have never been reported. Therefore, it seemed interesting to assess the potential of 1,2,4-diazaphospholides with lanthanides. We hereafter report the synthesis and crystal structures of the first 1,2,4-diazaphospholide samarium(III) complexes.

Reactions of potassium 3,5-diphenyl-1,2,4-diazaphospholide $[(\eta^2{:}\eta^4\text{-}3,5\text{-}Ph_2dp)K(Et_2O)]_n$ (**1a**)[8] and potassium 3,5-di-*tert*-butyl-1,2,4-diazaphospholide $[K\{3,5\text{-}t\text{-}Bu_2dp\}]_n$ (**1b**)[9] with $SmCl_3(THF)_3$[12] in THF afforded the two heteroleptic compounds, $[(\eta^2(N,N)\text{-}3,5\text{-}Ph_2dp)_3Sm(THF)_3]$ (**2a**) and $[(\eta^2(N,N)\text{-}3,5\text{-}t\text{-}Bu_2dp)_3Sm(THF)_2]$ (**2b**), respectively.[13] Both of the complexes are soluble in toluene, THF, and benzene but sparingly soluble in *n*-hexane. Structure elucidation of **2a** evidenced a monomeric compound containing three 3,5-Ph_2dp ligands and three THF molecules (Figure 1).[13] The coordination sphere about the samarium ion possesses a distorted octahedral geometry, assuming that the centers of the N−N bonds of the 3,5-Ph_2dp ligands are treated as monodentate donors. The three coplanar oxygen atoms of the THF molecules are arranged in the O−Sm−O angles of 151.69(9)°, 79.88(8)°, and 127.75(9)°, respectively [the sum of the angles is 359.32(9)°]. The X-ray crystal structure analysis revealed that complex **2b** is a monomeric species and has a distorted trigonal-bipyramidal geometry with three

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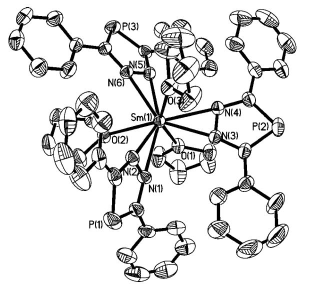


Figure 1. Molecular structure of **2a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sm(1)−N(1) 2.431(3), Sm(1)−N(3) 2.432(3), Sm(1)−N(5) 2.447(3), Sm(1)−N(4) 2.445(4), Sm(1)−N(6) 2.454(3), Sm(1)−N(2) 2.473(4), Sm(1)−O(1) 2.498(3), Sm(1)−O(3) 2.531(3), Sm(1)−O(2) 2.670(3); O(1)−Sm(1)−O(3) 151.75(11), O(1)−Sm(1)−O(2) 79.78(10), O(3)−Sm(1)−O(2) 127.80(10), N(3)−Sm(1)−N(4) 32.31(11).

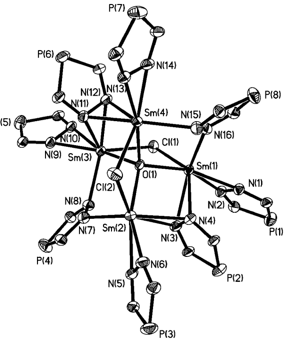
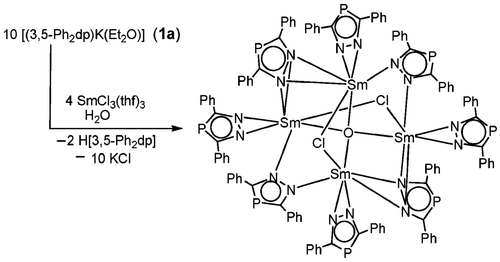


Figure 2. (a) Molecular structure of **3** with thermal ellipsoids at the 30% probability level. Phenyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sm(1)−O(1) 2.355(3), Sm(1)−N(1) 2.371(4), Sm(1)−N(2) 2.400(5), Sm(1)−N(16) 2.460(5), Sm(1)−N(3) 2.489(4), Sm(1)−N(4) 2.604(4), Sm(1)−Cl(1) 2.7436(15); N(1)−Sm(1)−N(2) 33.36(14), N(3)−Sm(1)−N(4) 31.60(13).

Scheme 1. Preparation of Complex **3**



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3,5-*t*-Bu$_2$dp ligands and two solvated THF molecules.[14] Coordination with an additional THF molecule in **2a** relative to that in **2b** likely reflects both the less steric and electronic demand of the phenyl groups. The bond lengths of Sm−N [Sm(1)−N(1) 2.431(3) Å; Sm(1)−N(2) 2.473(4) Å] in **2a** suggest an η^2-bonding mode. In the ^{31}P{^{1}H} NMR (C$_6$D$_6$) spectrum, only one resonance is observed at 110.75 (s) ppm for **2a** (vs 67.19 ppm of **1a**) and at 105.78 (s) ppm for **2b** (vs 50.65 ppm of **1b**), indicating that the structures of **2a** and **2b** are maintained in solution. The ^{1}H NMR (C$_6$D$_6$, 23 °C) spectrum of **2a** (**2b**) displays multiple resonances at 7.12, 7.23, and 7.38 [2.10 (s)] ppm for phenyl rings (*t*-Bu groups) and two broad upfield resonances at 0.13 (−1.03) and 1.45 (−1.73) ppm for the coordinated THF molecules, likely due to the paramagnetism of **2a** (**2b**).

Hydroxo- and oxolanthanide complexes with a multifunctional organic group are structurally interesting[1b] and have potential technological applications.[15,16] By treatment of **1a**[8] with SmCl$_3$(THF)$_3$[12] and small traces of water in THF, an unusual complex [(μ-η^1(*N*):η^1(*N*)-3,5-Ph$_2$dp)$_2$(η^2(*N*,*N*)-3,5-Ph$_2$dp)$_4$(μ-Cl)$_2$(μ_4-O)(μ-η^2(*N*,*N*):η^2(*N*,*N*)-3,5-Ph$_2$dp)$_2$Sm$_4$] (**3**), after workup, was isolated as THF (DMSO)-soluble, yellow crystals (Scheme 1).[13] The ^{1}H NMR (DMSO-*d*$_6$, 23 °C) spectrum of **3** displays two broad resonances at about 7.24 and 7.97 ppm assigned to the overlap of phenyl groups and a sharp resonance at 2.31 ppm (−C*H*$_3$ of toluene). The resonances of ^{31}P{^{1}H} NMR (DMSO-*d*$_6$, 23 °C) are observed at 95.12 (s), 92.93, and 65.48 (s) ppm for phosphorus($\sigma^2\lambda^3$) atoms, respectively [vs 110.75 (s) ppm of **2a** in C$_6$D$_6$]. To obtain an oxo complex bearing exclusive dp ligands, we initially tried to hydrolyze **2a** (**2b**) but were unable to isolate the reaction product. The reaction of SmCl$_3$(THF)$_3$ and **1a** with water in situ, however, led to the formation of **3**. The approach to **3** was evidenced to be readily accessible and reproducible. The mechanism of the formation for **3** is likely via hydrolysis of an intermediate species [η^2(*N*,*N*)-3,5-Ph$_2$dp)$_2$Sm(μ_2-Cl)(μ-η^1(*N*):η^1(*N*)-3,5-Ph$_2$dp)Sm(η^2(*N*,*N*)-3,5-Ph$_2$dp)$_2$(THF)$_x$].[13]

The monomeric complex **3** contains eight 3,5-Ph$_2$dp ligands, one oxygen, two chlorine, and four samarium atoms, as established by X-ray crystallography (Figure 2).[13] The four Sm ions are arranged in a core of tetrahedron and have a common center [O(1)] to which the distance of each samarium is about 2.371(3) Å (average). Each samarium is seven-coordinate, being bound to three 1,2,4-diazaphospholides [η^2-(*N*1,*N*2)-, μ_2-η^2:η^2-(*N*3,*N*4)-, and μ-η^1:η^1-(*N*16)-bridged], to one chlorine atom (μ-bridged), and to one oxygen atom (μ_4-bridged), thus forming an oxygen-centered tetrasamarium octadiazaphospholido cluster. Eight phosphorus atoms are located on the sphere of the molecule of **3**, which thus renders the potential to bind further species.[2a,10,11] The bond length of Sm−Cl is 2.7436(15) Å, slightly longer than that found in [(Tmp)$_6$Sm$_2$(KCl)$_2$(C$_7$H$_8$)$_3$]$_n$ [Sm−Cl 2.632(3) Å, Tmp = 2,3,4,5-tetramethylphospholyl].[17] The terminal 1,2,4-diazaphospholides show perfect η^2 interaction with the samarium [Sm(1)−N(1) 2.371(4) Å; Sm(1)−N(2) 2.400(5) Å], with one Sm−N distance being about 0.029 Å shorter than the other. To the best of our knowledge, the 1,2,4-diazaphospholides with the coordination types of μ-η^2:η^2-(*N*3,*N*4) and μ-η^1:η^1-(*N*15,*N*16) have not been reported before. The bond lengths of Sm1−N3 [2.489(4) Å] and Sm1−N4 [μ-η^2; 2.604(4) Å] are slightly slipped, while the distance of Sm1−N16 (μ-η^1) is 2.460(5) Å, slightly shorter than that of Sm(1)−N(4) [2.604(4) Å].

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(14) The crystallographic data quality of **2b** is not warranted for publication in this case because of the disorder of *t*-Bu groups, but the structural connections are clear [C$_{38}$H$_{70}$N$_6$O$_2$P$_3$Sm, M_r = 886.26, monoclinic, space group *C2/c*, a = 18.82(6) Å, b = 12.99(4) Å, c = 20.37(7) Å, $\alpha = \gamma$ = 90.00°, β = 102.05(4)°].

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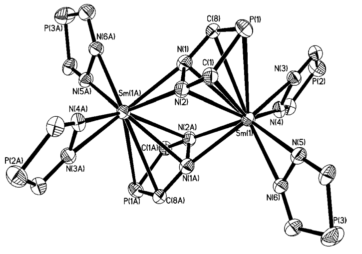
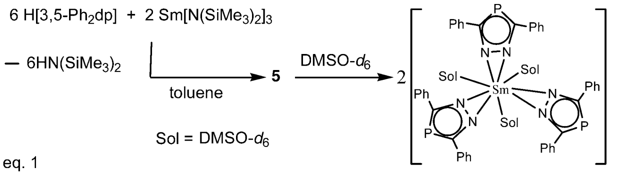


Figure 3. Molecular structure of **5** with thermal ellipsoids at the 30% probability level. Phenyl groups are not shown for clarity. Selected bond lengths (Å) and angles (deg): Sm(1)−N(1) 2.695(4), Sm(1)−N(2) 2.710(4), Sm(1)−N(3) 2.384(4), Sm(1)−N(4) 2.333(4), Sm(1)−N(5) 2.381(5), Sm(1)−N(6) 2.371(5), Sm(1)−N(1A) 2.517(5), Sm(1)−N(2A) 2.530(5), Sm(1)−C(1) 3.014(5), Sm(1)−C(8) 2.992(5), Sm(1)−P(1) 3.352(2); N(6)−Sm(1)−N(5) 33.67(16), N(4)−Sm(1)−N(3) 33.93(16), N(1A)−Sm(1)−N(2A) 31.83(14), Sm(1A)−N(1)−Sm(1) 100.31(16), Sm(1A)−N(2)−Sm(1) 99.58(15), N(1A)−Sm(1)−N(2) 71.73(14), N(2A)−Sm(1)−N(2) 80.42(15). Symbol A ≡ symmetry code $-x + 2$, $-y + 1$, $-z + 1$.

The preparation of a homoleptic 1,2,4-diazaphospholide samarium complex is one of our goals, which may present some interesting structure features. As shown in the structure of **2a**, the THF molecules bonded to the samarium atom are functioned as coligands because of the open coordination site of the metal ion. While unsolvated homoleptic complexes are expected in a neutral donor-free system, the reaction of H[3,5-Ph_2dp] (**4**)[7] and Sm[N($SiMe_3$)$_2$]$_3$[18] was thus carried out in toluene. After workup, compound [(μ_2-η^2(*N*,*N*):η^5-3,5-Ph_2dp)(η^2(*N*,*N*)-3,5-Ph_2dp)$_2$Sm]$_2$ (**5**) was isolated as yellow crystals (eq 1).[13] **5** is well-soluble in aprotic polar solvents such as THF, DMSO, and hot toluene but insoluble in *n*-hexane and benzene.



eq. 1

6

The X-ray structure analysis of **5** revealed a remarkable dimeric species containing six 3,5-Ph_2dp ligands (Figure 3).[13] Each Sm is 11-coordinate, being bound to four 1,2,4-diazaphospholides [μ-η^2(*N*1,*N*2):η^5-(*N*1,*N*2,*C*1,*C*8,*P*1), η^2-(*N*3,*N*4), and η^2-(*N*5,*N*6)]. The simplified representation clearly shows the head-to-tail arrangement of two π-bonding 1,2,4-diazaphospholides with a dihedral angle of 81.7° between the plane defined by the atoms N(1), N(2), and Sm(1) and the plane of the heterocyclic core [N(1), N(2), C(1), C(8), and P(1)]. The samarium is thus located below the plane of the ligand with an η^5 interaction (slipped π bonding) and also has two terminal η^2-1,2,4-diazaphospholide ligands with a dihedral angle of 173.1° between the plane defined by the atoms N(1A), N(2A), and Sm(1) and the plane of the heterocyclic core [N(1A), N(2A), C(1A), C(8A), and P(1A)]. The samarium ion is set beside the N−N bond of the ligand, suggesting σ donation of the in-plane nitrogen atom lone pairs to samarium. The ligands bind μ-η^2:η^5 to samarium atoms, demonstrating a new type of 1,2,4-diazaphospholide coordination (a type of μ-η^2:η^4 coordination mode was previously observed in **1a**[8]). The distances of Sm−C [Sm(1)−C(1) 3.014(5) Å; Sm(1)−C(8) 2.992(5) Å] are longer than the corresponding values found in the bowed trinuclear pyrazolato complex [μ-η^5:η^2-Nd_3(3,5-Ph_2pz)$_9$] [Nd−C 2.945(5) Å (average)],[19] even without considering the differences of metal ion radii,[20] and in the complex [(η^5-C_5Me_5)$_2$Sm(η^5-2,5-di-*tert*-butylphospholyl)] [Sm−C 2.862(3) Å],[21] likely due to the larger radius of the phosphorus center in the ligand as well as the slipped η^5 interactions (toward the nitrogen centers) demonstrated in the space-filling picture.[13] The bond lengths of Sm−N with π bonding [Sm(1)−N(1) 2.695(4) Å; Sm(1)−N(2) 2.710(4) Å] are comparable to those found in complex [μ-η^5:η^2-Nd_3(3,5-Ph_2pz)$_9$] [Nd−N 2.639(4) Å],[19] while the distances of Sm−N with σ bonding [Sm(1)−N(1A) (N(2A)) 2.517(5) Å,; Sm(1)−N(3) (N(4)) 2.384(4) Å; Sm(1)−N(5) (N(6)) 2.381(5) Å] are slightly shorter than that found in **2a** [2.431(3) Å]. The Sm(1)−P(1A) distance of each η^5 interaction (slipped) is 3.352(2) Å, which is only 0.078 Å longer than that found in the (η^5-C_5Me_5)$_2$Sm(η^5-phospholyl) complex [Sm−P 3.274(1) Å],[21] supporting the Sm−P π interaction because the Sm(1) ion is tilted toward the N−N bonds of the 1,2,4-diazaphospholide ligand, where the plane defined by the atoms N(1)−N(2)−Sm(1) (η^5 interaction) is nearly normal to the ring plane of the 1,2,4-diazaphospholide ligands (81.7°). In the $^{31}P\{^1H\}$ NMR (DMSO-d_6, 23 °C) spectrum, only one resonance is observed at 96.08 (s) ppm, probably indicating that **5** undergoes dissociation into solvated monomeric species **6** in the solution (eq 1).

In conclusion, we prepared several samarium complexes that are the first examples of lanthanide complexes bearing 1,2,4-diazaphospholide ligands. The structures of **2a**, **3**, and **5** have evidenced that 1,2,4-diazaphospholide is a versatile ligand that stabilize novel coordination environments of samarium. Particularly, with the lone pairs of the phosphorus atoms ($\sigma^2\lambda^3$) available, the 1,2,4-diazaphospholide samarium complexes seem to present additional binding sites on the sphere of the molecules. The study on the coordination behavior and application in catalysis of 1,2,4-diazaphospholide samarium complexes is in progress.

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Supporting Information Available: Synthetic procedures, analytical and spectroscopic data for **2a**, **2b**, **3**, and **5**, and X-ray crystallographic files for **2a**, **3**, and **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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