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1,2,4-Diazaphospholide Complexes of Yttrium(III), Dysprosium(III), Erbium(III), and Europium(II, III): Synthesis, X-Ray Structural Characterization, and EPR Analysis

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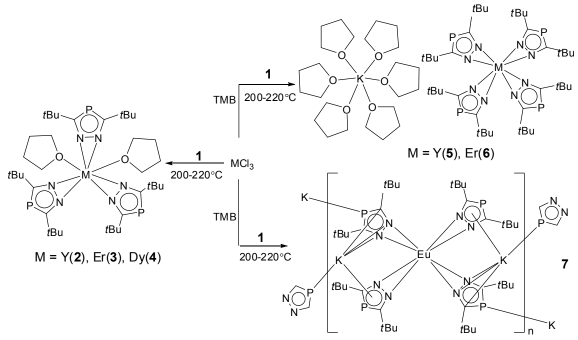
Several structurally characterized heteroleptic, charge-separated heterobimetallic, and polymeric alkali metal ate complexes of 1,2,4-diazaphospholide Y(III), Dy(III), Er(III), Eu(III), and Eu(II) were prepared via the reaction of MCl_3 and K[3,5-R_2dp] in a varied ratio at 200–220°C (M = Y, Dy, Er, Eu; R = *t*Bu, Ph).

While lanthanide complexes bearing cyclopentadienyl ligands (Cp^-) are interesting owing to their structural variability as well as to the catalytic potential,[1] the design and use of alternatives to the Cp^- (Cp^{*-}) ligand have become an area of active investigation.[2] Although the isolobal N(P)/CH and diagonal P/C relationship[3] has suggested that the 1,2,4-diazaphospholides should behave like the corresponding cyclopentadienyl-substituted analogues,[4,5] the work has shown that this mixed low-coordinated phosphorus ($\sigma^2\lambda^3$)- and nitrogen-containing system exhibited subtle differences in both bonding and reactivity due to the unique electronic structure.[6] We have been interesting in the chemistry of 1,2,4-diazaphosphole derivatives,[7] 1,2,4-diazaphospholide complexes[6–9] as well as in their applications.[10] Recently, we demonstrated that the 1,2,4-diazaphospholides are with a nature of non-innocence to be oxidized by hypervalent metal ions.[6e,f] This result prompted us to set out to prepare rare earth metal complexes such as terminal charge-separated heterobimetallic, or alkali metal ate complexes bearing 1,2,4-diazaphospholide ligands because charge-separated heterobimetallic and alkali metal ate lanthanide complexes[11a–b] have proven to be effective catalysts in organic transformations.[11c–f] On the other hand, even though the lone pairs at the phosphorus atoms ($\sigma^2\lambda^3$), which features a significant amount of 3s character, is only weakly basic,[3] the phosphorus atoms of the resultant complexes with donor lone pairs available on the periphery of the molecule thus provide additional binding sites to act as significant π-acceptors for later transition metals,[2a] allowing for a more-varied coordination chemistry[3,10] Curiously, however, 1,2,4-diazaphospholide lanthanide chemistry has yet been well-developed so far and only several 1,2,4-diazaphospholide samarium(III) complexes are known.[8,12] We hereafter report the synthesis and crystal structures of a few heteroleptic, heterobimetallic charge-separated, and alkali metal ate complexes of 1,2,4-diazaphospholide yttrium(III), dysprosium(III), erbium(III), and europium(III,II).

Reactions of 3,5-di-*tert*-butyl-1,2,4-diazaphospholide potassium [(3,5-*t*Bu_2dp)K] (**1**)[6a,b] with MCl_3[13] (M = Y, Er, Dy) in a ratio of 3:1 in the presence of 1,2,4,5-tetramethylbenzene (TMB) in a sealed Carius tube at 200–220°C[14,15] smoothly afforded, after workup, three THF-solvated heteroleptic compounds [(η^2(*N*,*N*)-3,5-*t*Bu_2dp)$_3$M(THF)$_2$] (M = Y(**2**), Er(**3**), Dy(**4**)) as colorless or pink crystals (Scheme 1).[‡,16] Complexes **2–4** are well-soluble in THF and hot toluene, but not soluble in *n*-hexane.



Scheme 1. The preparation of complexes **2**–**7**.

Structure elucidation of **2–4** evidenced a monomeric compound containing three [3,5-*t*Bu_2dp]$^-$ ligands and two solvated THF molecules (Figure 1).[17] The coordination sphere about the metal ion possesses a slightly distorted trigonal bipyramidal geometry, as defined by the centers of the N–N bonds of the 1,2,4-diazaphospholides. The two coplanar oxygen atoms of the THF molecules, located at the two vertices, are arranged in the O–M–O angles of 150.53(10)° for **2**, 150.9(2)° for **3**, and 150.36(12)° for **4**, respectively. The bond lengths of M–N (Y(1)–N(1) 2.357(2), Y(1)–N(2) 2.413(2) Å in **2**; Er(1)–N(1) 2.337(5), Er(1)–N(2) 2.398(5) Å in **3**;

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Dy(1)–N(1) 2.362(2), Dy(1)–N(2) 2.411(2) Å in **4**) suggest an η^2-bonding mode. The three phosphorus atoms ($\sigma^2\lambda^3$) at the periphery of **2**–**4** have donor lone pairs available as would be expected. The $^{31}P\{^1H\}$ NMR spectrum (DMSO-d_6, 243 MHz, 23°C) showed only one resonance at δ = 86.3(s) ppm for **2** and 97.6(s) for **4** (vs. 50.65 ppm of **1**).[6a]

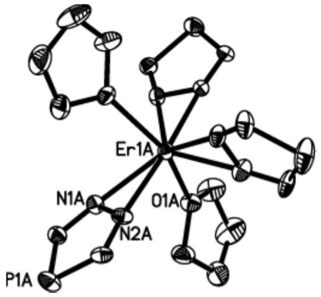


Figure 1. Molecular structures of **3** with thermal ellipsoids at the 30% probability level. The *t*Bu groups are not shown for clarity. **2**–**4** are isostructural. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): **2**: Y1–O1 2.388(19), Y1–N1 2.357(2), Y1–N2 2.413(2); O1–Y1–O1A 150.53(10), N1–Y1–N2 33.7(7). **3**: Er1A–N1A 2.337(5), Er1A–N2A 2.398(5), Er1A–O1A 2.369(4); N1A–Er1A–N2A 33.82(14), O1A–Er1A–O1 150.9(2). **4**: Dy1–N1 2.362(2), Dy1–N2 2.411(2), Dy1–O1 2.405(2); O1–Dy1–O1A 150.36(12), N1–Dy1–N2 33.48 (7).

As heterobimetallic lanthanide complexes are expected to be prepared in the presence of excessive organo-alkali species,[11c] the reaction of **1** and MCl_3 (M = Y, Er, Eu) in a ratio of 4:1 was thus carried out and subsequently afforded two novel charge-separated heterobimetallic complexes $\{[K(THF)_6]^+[(\eta^2(N,N)\text{-}3,5\text{-}t\text{Bu}_2\text{dp})_4M]^-\}$ (M = Y(**5**), Er(**6**)) (Scheme 1).[‡,16] Compounds **5** and **6** were isolated as colorless and pink crystals, respectively, and are only soluble in aprotic polar solvents such as in THF, DMSO, and in hot toluene.

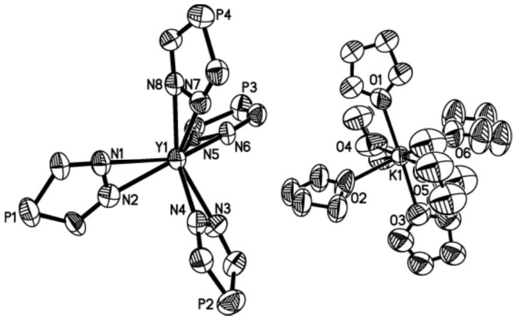


Figure 2. Molecular structure of **5** with thermal ellipsoids at the 30% probability level. The *t*Bu groups are not shown for clarity. Selected bond lengths (Å) and angles(°): Y1–N1 2.377(4), Y1–N2 2.381(5), K1–O6 2.711(8); N1–Y1–N2 33.72(14), O5–K1–O6 93.7(3).

The X-ray structure analysis of **5**(or **6**) revealed an ionic associated species which consists of $[Y(\eta^2(N,N)\text{-}3,5\text{-}t\text{Bu}_2\text{dp})_4]^-$ (or $[Er(\eta^2(N,N)\text{-}3,5\text{-}t\text{Bu}_2\text{dp})_4]^-$) anion and counter cation $[K(THF)_6]^+$ (Figure 2).[17,18] In the anionic moiety of **5**, each yttrium atom is coordinated to eight nitrogen atoms of four terminal η^2-1,2,4-diazaphospholides, and the average Y–N distance (2.3736(5) Å) is comparable with those of eight coordinate complex **2** (2.3860(5) Å). The geometries around the yttrium atom, assuming that the centers of the N–N bonds of the 3,5-tBu$_2$dp ligands are treated as monodentate donors, are highly distorted from tetrahedral (P–Y–P 89.39° and 112.62°). Likely, these derivations minimize the steric repulsions between the bulky *t*Bu groups. In the counter cation $[K(THF)_6]^+$, potassium atom was coordinated to six oxygen atoms of the THF molecules. The geometries around the potassium atom are close to distorted octahedron with the O–K–O angles (106.60°). The average distances of K–O bonds (2.744(5) Å) are comparable with those found in $[\{\text{penta(organo)[60]fullerene}\}\{K(thf)_6\}^+]$ (av. 2.716(5) Å).[19]

The reaction of **1** and $EuCl_3$ in a ratio of 5:1 afforded, however, an unusual low-valent 1,2,4-diazaphospholide europium(II) $[(\eta^2(N,N)\text{-}3,5\text{-}t\text{Bu}_2\text{dp})_4\text{Eu}]K_2\}_\infty$ (**7**) as red crystals (Scheme 1) under similar conditions.[‡,16] Complex **7** is well soluble in most of common organic solvents. The X-ray structure analysis of **7** displayed a remarkable polymeric dipotassium ate species containing four 3,5-tBu$_2$dp ligands (Figure 3).[16] Each Eu(II) is 4-coordinate, being bound to four $[\mu\text{-}\eta^2(N,N)\text{-}3,5\text{-}t\text{Bu}_2\text{dp})]$ ligands whereas each potassium ion is 10-coordinate being bound to two 1,2,4-diazaphospholide rings in a $\eta^4{:}\eta^5$ coordination mode (slipped π–bonding) and σ-bound to the phosphorus atom of neighboring molecule (K1–P4A 3.373(18) Å, K2–P2A 3.397(18) Å). In turn, two phosphorus atoms of each molecule are σ-bound to two neighboring potassium ions thereby afforded the two-dimensional sheet structure of **7**. The linkages between potassium ions and the phosphorus atoms of the neighboring ligands consisted of square arrays formed by potassium ions and neighboring ligands, producing a honeycomb network when viewed along the crystallographic *b* axis. The europium ion is set beside the N–N bond of the ligand, suggesting σ-donation of the in-plane nitrogen atom lone pairs to europium. The average distances of Eu–N [2.623(4) Å] are slight longer than the corresponding value found in the monofunctionalized pyrazolato europium(II) complex $[(\eta^2\text{-}3,5\text{-Ph}_2\text{pz})\text{EuI(thf)}_4]$ (2.5353(17) Å) (pz = pyrazolato).[20] The bond lengths of K–N (2.810(4)–3.026(4) Å), K–C (3.153(4)–3.519(4) Å), and K–P (π-bonding: 3.713(18)–3.883(19) Å; σ-bonding: 3.373(18)–3.397(18) Å) are comparable with those found in the previous reported π–bonding 1,2,4-diazaphospholide-1,2,4-diazaphosphinato potassium (K–N 2.841(2) Å, K–C 3.205(3) Å, and K–P 3.6310(16) Å).[6b]

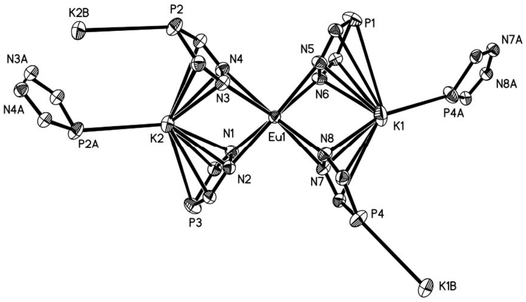
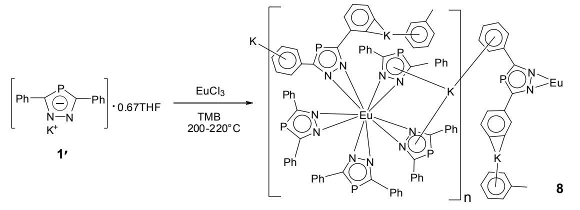


Figure 3. One unit for the molecular structure of **7** with thermal ellipsoids at the 30% probability level. The *t*Bu groups are not shown for clarity. Selected bond lengths (Å) and angles(°): Eu1–N1 2.659(4), Eu1–N2 2.570(4), Eu1–N3 2.678(4), Eu1–N4 2.604(4), K2–N1 2.978(4), K2–N2 2.810(4), K2–N3 3.026(4), K2–N4 2.888(4), K2–P2A 3.397(18), K2–P3 3.713(2), K2···P2 3.883(2), Eu1–N5 2.601(4), Eu1–N6 2.608(4), Eu1–N7 2.624(4), Eu1–N8 2.643(4), K1–N5 2.992(4), K1–N6 2.881(4), K1–N7 2.904(4), K1–N8 2.969(4), K1–P4A 3.372(18); N1–Eu1–N2 30.58(10), K1–Eu1–K2 175.77(3), N5–Eu1–N7 97.38(12).

The $^{31}P\{^1H\}$ NMR ($CDCl_3$, 243 MHz, 23°C) spectrum showed two sharp resonances at δ = 93.5(s) and 97.5(s) ppm for **5**, probably due to the highly labile nature of the complex, consistent with three singlets (δ = 1.25, 1.33, and 1.42 ppm) for *t*Bu groups in ^1H NMR spectrum ($CDCl_3$, 600 MHz, 23°C). The two broad resonances at δ =

3.70, 1.85 ppm are assigned to the six THF-solvated molecules. In the $^{31}P\{^1H\}$ NMR (DMSO-d_6, 243 MHz, 23°C) spectrum, two sharp resonances are observed at δ = 72.7(s) and 49.5(s) ppm for **7**. The two observed resonances are consistent with the structure in the solid state assigned to σ-bonding (^{31}P 72.7 ppm) and π-bonding (^{31}P 49.5 ppm) phosphorus atoms, respectively.

Treatment of $EuCl_3$ and 3,5-di-phenyl-1,2,4-diazaphospholide potassium K[3,5-Ph_2dp] (**1′**)[6a] in a ratio 1:5 under a similar condition produced a novel dipotassium ate complex of 1,2,4-diazaphospholide europium(III) (**8**) as red crystals in good yield (Scheme 2).[‡,16] Compound **8** is fair soluble in toluene but well soluble in DMSO and THF.



Scheme 2. The preparation of complex **8**.

The X-ray structure analysis of **8** revealed a polymeric dipotassium ate complex containing five [3,5-Ph_2dp]$^-$ ligands and two ate potassium ions and one europium(III) atom (Figure 5).[16] The coordination sphere about the europium ion possesses a slightly distorted trigonal bipyramidal geometry, as defined by the centers of the N–N bonds of the 1,2,4-diazaphospholides. The bond lengths of Eu–N suggest an η^2-bonding mode. One of two potassium ions is 16-coordinate being bound to two 1,2,4-diazaphospholides in a η^5 coordination mode (slipped π bonding) and further coordinate to one phenyl ring of neighboring molecule in a η^6 coordination mode while another potassium ion in the molecule is 2-coordinte being bound to one phenyl ring and 6-coordinate to a toluene molecule. The $^{31}P\{^1H\}$ NMR (DMSO-d_6, 243 MHz, 23°C) spectrum presented only one resonance at δ = 94.4(s) ppm for **8**, probably indicating the dynamic process or dissociation of **8** in solution.

Due to the broadening resonances in the NMR spectra with the paramagnetism of **3**, **6**, **7**, and **8**, the X-band EPR spectroscopy analyses were performed. The large spin-orbit coupling to excited[21a] states together with strong lattice coupling leaves most lanthanide complexes EPR silent at temperatures above 20K[21b] but we observe one EPR resonance at 3100 gauss (g = 2.204) in a THF-solution for **7** at 77 K, one resonance at 3300.10 gauss (g = 2.150) for **3** and two resonances at 2815.2 (g = 2.354) and 3216.1 gauss (g = 2.102) for **6** in the solid state at 298 K, respectively.[16] Fortunately, one strong EPR spectrum[16] corresponding to diluted THF solution of **8** displays a hyperfine of well-resolved coupling multiplet with 9 observed lines at 3120–3250 gauss (g = 2.120) at 77 K (Figure 4),[16] which likely will be complicated by interference of the electron spins of the neutral 1,2,4-diazaphospholide radical and Eu(II) and the nuclear spins of ^{151}Eu and ^{153}Eu, apart from ^{14}N and ^{1}H couplings.[22] Namely, a transient system Eu(II)||[3,5-Ph_2dp]$^\bullet$ may produced via a electron transfer from ligand anion [3,5-Ph_2dp]$^-$ to europium (III) in the solution,[6e,f] where a_{151Eu} = 39.1 G (the highest peak-to-peak line width), a_{153Eu} = 11.7 G are obtained from the spectrum (Figure 4).[22] It is also possible that the observed EPR hyperfine arises from the radical ligand [3,5-Ph_2dp]$^\bullet$.[6e,f]

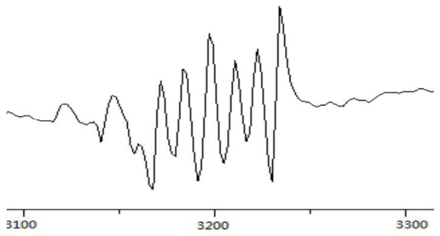


Figure 4. X-Band EPR spectrum of complex **8** in frozen THF at 77K.

Whereas no reaction of MCl_3 and **1**(or **1**′) occurred even under refluxing for several days in toluene, the elevated-temperature metathesis[23] of MCl_3 and **1**(or **1**′) afford **2**–**8** smoothly. Complexes **5** and **6** do not undergo a structure frame rearrangement or even rupture back to **2** and **3** in the presence of the donor THF, reflecting the rigid character of the cation units. Eu(II) ion in **7** is obviously resulting from the reduction of the non-innocent ligand in the reaction, which have been recently demonstrated from Fe^{3+}, Cu^{2+}, and Bi^{3+} 1,2,4-diazaphospholide systems in our lab.[6e,f] The resultant 5π neutral 1,2,4-diazaphodpholide radicals would self-dimerize via N–P coupling or cause the hydrogen abstraction from the tetrahydrofuran molecule to afford the corresponding neutral ligands.[6e,f]

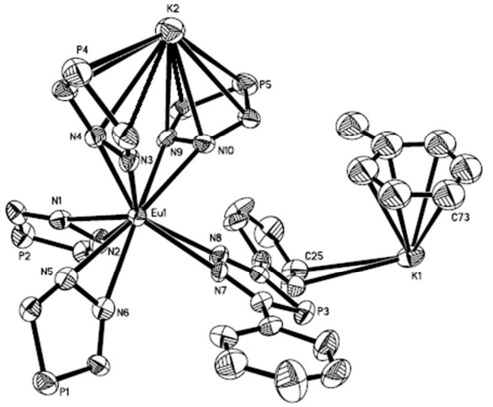


Figure 5. One unit of the molecular structure of **8** with thermal ellipsoids at the 30% probability level. The Ph groups are not shown. Selected bond lengths (Å) and angles(°): Eu1–N1 2.482(6), Eu1–N2 2.509(8), Eu1–N3 2.497(7), Eu1–N4 2.484(7), Eu1–N5 2.645(8), Eu1–N6 2.506(8), Eu1–N7 2.499(6), Eu1–N8 2.431(6), Eu1–N9 2.566(7), Eu1–N10 2.508(7), K2–N3 3.608(8), K2–N4 3.200(8), K2–N9 3.335(8), K2–N10 3.069(8), K2–P4 3.628(8), K2–P5 3.639(9), K1–C73 3.273(15), K1–C25 3.303(12); N1–Eu1–N2 31.2(2), N4–Eu1–N9 77.6(2), P4–K2–P5 142.5(3).

In conclusion, several novel 1,2,4-diazaphospholide heteroleptic and heterobimetallic lanthanide complexes were prepared by the reaction of MCl_3 with **1** (**1'**) at 200–220°C, suggest that extensive 1,2,4-diazaphospholide lanthanide complexes could be accessible by this simple path. The charge-separated heterobimetallic 1,2,4-diazaphospholide complexes **5** and **6** have proven of high rigidity against THF molecules due to the unique electronic nature of the ligand. The potassium-ate complexes **7** and **8** involved an electron transfer from ligand to europium, evidenced by the X-ray structural characterization and EPR spectroscopy analysis.

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Notes and references

‡Syntheses of **2**–**8**: To a mixture of MCl_3 (1.0 mmol) and **1** (3.0 mmol for preparation of **2**–**4**; 4.0 mmol for **5**–**6**; 5.0 mmol for **7**–**8**) was added TMB (2.0 g) in a Carius tube (inner diameter 0.4 cm, about 15 cm long). The tube was sealed in vacuum and then heated at 200–220°C for 3 days. After the resultant mixture was cooled down to room temperature, TMB was removed under reduced pressure (0.01 mmHg) at 70–75°C in a Büchi Glass Oven. The remaining solid was dissolved in THF (40 mL) for **2**–**6** (in 40 mL toluene for **7**; in a mixture (40 mL) of toluene and THF for **8**). The solution was filtered through Celite. The filtrate was concentrated to give **2**–**8** as colorless/colored crystals at 5°C.

X-ray structure determinations for **2**–**8**: Suitable single crystals were sealed under argon in thin-walled glass capillaries. X-ray diffraction data were collected on a Xcalibur CCD diffractometer (graphite-monochromated Mo-$K\alpha$ radiation, φ-ω-scan technique, λ = 0.71073 Å). The intensity data were integrated by means of the SAINT program.[24] SADABS[25] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against F^2 using all reflections with the aid of the SHELXTL package.[17] All non-hydrogen atoms in **2**-**8** were refined anisotropically. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All non-hydrogen atoms were found from the difference Fourier syntheses. All calculations were performed using the Bruker Smart program.

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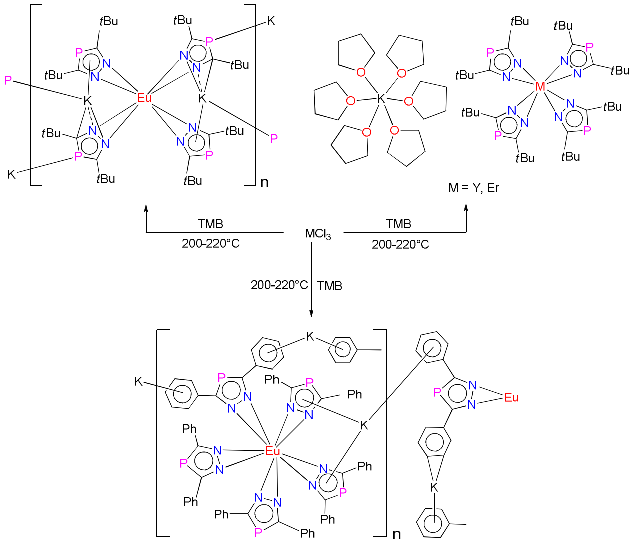
Heteroleptic, charge-separated heterobimetallic, and polymeric alkali metal ate complexes of 1,2,4-diazaphospholide yttrium(III), dysprosium(III), erbium(III), europium(III) and europium(II) were prepared.



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