Heteroleptic Lanthanide Compounds with Chalcogenolate Ligands: Reduction of PhNNPh/PhEEP (E = Se or Te) Mixtures with Ln (Ln = Ho, Er, Tm, Yb). Thermolysis Can Give LnN or LnE

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Lanthanide metals reduce mixtures of azobenzene and PhEEP (E = Se or Te) in pyridine to give the bimetallic compounds [(py)2Ln(EPh)(PhNNPh)]2 (E = Se, Ln = Ho (1), Er (2), Tm (3), Yb (4); E = Te, Ln = Ho (5), Er (6), Tm (7), Yb (8)). The structures of [(py)2Er(μ-η2-η2-PhNNPh)(SePh)]2-2py (2) and [(py)2Ho(μ-η2-η2-PhNNPh)(TePh)]2-2py (5) have been determined by low-temperature single-crystal X-ray diffraction, and the nearly identical unit cell volumes of the remaining compounds indicate they are most likely isomorphous to 2 or 5. In all compounds, the Ln(III) ions are bridged by a pair of μ-η2-η2-PhNNPh ligands that, from the N-N bond length, have clearly been reduced to diamions. Charge is balanced by the single terminal EPh ligand on each Ln, and the coordination sphere is saturated by two pyridine donors to give seven coordinate metal centers. Thermal decomposition of 5 gives HoTe, 8 gives a mixture of YbN and YbTe, and 1 does not give a crystalline solid-state product. Crystal data (Mo Kα, 153(2) K) are as follows: 2, monoclinic clinic P21/n, a = 11.864(3) Å, b = 14.188(2) Å, c = 17.624(2) Å, β = 91.62(2)°, V = 2965(1) Å3, Z = 4; 5, triclinic space group P1, a = 10.349(2) Å, b = 17.662(4) Å, c = 17.730(8) Å, α = 75.82(3)°, β = 74.11(3)°, γ = 89.45(2)°, V = 3016(2) Å3, Z = 2.

Introduction

Recent reports detailing the reactions of Ln(EPh)3 with elemental chalcogen (E, E = S, Se) to give Ln clusters with E2+ ligands,1–7 with the concomitant oxidative elimination of PhEEP and reduction of elemental E (reaction 1), have provided an important entry into this previously inaccessible molecular class. The reaction appears general for the entire lanthanide series, yielding a variety of chalcogenido cluster compounds with unconventional physical properties. Since the chemistry of these chalcogenolates is still best described with ionic terms, the reactivity is explained by noting that in the lanthanide naphthalide system oxidative elimination of PhN2 ligands, 8–11 and a reasonable approach to these materials, via the four-electron reductive cleavage of the N=N bond in RNRR by Ln(EPh)3, with concomitant oxidative elimination of PhEEP, was proposed. Similar reductions have been noted in organolanthanide chemistry where, for example, in the lanthanide naphthalide system oxidative elimination of neutral naphthalene yields a lanthanide cluster with both PhN=Ph2+ and PhN2+ ligands.8

Complexes with NR and EPh ligands would be interesting synthetic targets, because the subsequent thermolysis chemistry can lead either to the formation of LnE or LnN. A molecular source of LnN would be important, as there has recently been a considerable effort devoted to the synthesis of Ln-doped GaN materials.12

This paper reports our initial studies on the reduction of PhNNPh/PhEEP heteroligand mixtures with elemental Ln and the reactions of Ln(EPh)3 with PhN=NPh. Heteroleptic Ln compounds with EPh (E = Se, Te) and (PhN=Ph)2+ ligands are described, and the solid-state phases that result from thermolysis of these compounds are identified.

Given the facility with which EPh ligands are oxidatively eliminated as PhEEP, sometimes quantitatively and always at room temperature, it was of interest to determine whether this reactivity could be extended to other, potentially more elusive molecular classes. The paucity of Ln compounds with NR2- ligands is notable,5–10 and a reasonable approach to these materials, via the four-electron reductive cleavage of the N=N bond in RNRR by Ln(EPh)3, with concomitant oxidative elimination of PhEEP, was proposed. Similar reductions have been noted in organolanthanide chemistry where, for example, in the lanthanide naphthalide system oxidative elimination of neutral naphthalene yields a lanthanide cluster with both PhN=Ph2+ and PhN2+ ligands.8

In this paper we report our initial studies on the reduction of PhNNPh/PhEEP heteroligand mixtures with elemental Ln and the reactions of Ln(EPh)3 with PhN=NPh. Heteroleptic Ln compounds with EPh (E = Se, Te) and (PhN=Ph)2+ ligands are described, and the solid-state phases that result from thermolysis of these compounds are identified.

Notes

(9) Xie, Z.; Wang, S.; Yang, Q.; Mak, T. Organometallics 1999, 18, 5435.
Experimental Section

General Methods. All syntheses were carried out under ultrapure nitrogen (JWNS), using conventional drybox or Schlenk techniques. Solvents (Fisher) were refluxed continuously over molten alkali metals or K/benzophenone and collected immediately prior to use. Anhydrous pyridine (Aldrich) was purchased and refluxed over KOH. PhNNPh and PhSePh were purchased from Aldrich and recrystallized. PhtTePPh was prepared according to the literature procedure. ¹¹¹Ln and Hg were purchased from Strem. Melting points were taken in sealed capillaries and are uncorrected. IR spectra were taken on a Mattus Cygnus 100 FTIR spectrometer and recorded from 4000 to 450 cm⁻¹ as a Nujol mull on KBr plates. Electronic spectra were recorded on a Varian DMS 100S spectrometer with the samples in a 1.0 mm quartz cell attached to a Teflon stopcock. Elemental analysis was performed by Quantitative Technologies, Inc. (Whitehouse, NJ). These compounds are sensitive to the thermal dissociation of lattice solvent at room temperature, and so the experimentally determined elemental analyses are often found to be lower than the computed analyses. Calculated values for compounds both with and without lattice solvent are included, the latter in parentheses. Products appear homogeneous, and for most samples several crystals of each compound were examined by single-crystal X-ray diffraction in an attempt to find a crystal suitable for a complete structural determination. The same unit cell was used consistently for each compound, but no attempt was made to determine whether the same compound would repeatedly crystallize in the same space group. NMR spectra were obtained on Varian Gemini 300 or 400 MHz NMR spectrometers, and chemical shifts are reported in δ (ppm).

Synthesis of [(py)₂Ho(µ-η²-η²-PhNNPh)(SePh)]₂·2py (1). PhSePh (0.31 g, 1.0 mmol) was added to a Schlenk tube containing Ho (0.33 g, 2.0 mmol) and Hg (0.050 g, 0.25 mmol) in pyridine (50 mL). The mixture was stirred overnight, and then PhNNPh (0.36 g, 2.0 mmol) was added to the gray-khaki solution and unreacted metal. After 4 days all the Ho was dissolved, and the black-green solution was filtered, concentrated to 30 mL, and layered with hexane (15 mL) to give dark red crystals. The black-green solution was filtered, concentrated to 18 mL, and layered with hexane (15 mL) to give red crystals. The mixture was stirred overnight, and then PhNNPh (0.36 g, 2.0 mmol) was added to the yellow-green solution and unreacted Er. After 4 days all the Er was dissolved, and the black-green solution was filtered, concentrated to 30 mL, and layered with hexane (15 mL) to give green crystals (0.54 g, 36%). The compound does not show an optical absorption maximum at 216 °C and melts at 246 °C.

Synthesis of [(py)₂Yb(µ-η²-η²-PhNNPh)(SePh)]₂·2py (4). PhSePh (0.31 g, 1.0 mmol) was added to a Schlenk tube containing Yb (0.35 g, 2.0 mmol) and Hg (0.050 g, 0.25 mmol) in pyridine (50 mL). After 2 days, PhNNPh (0.36 g, 2.0 mmol) was added to the black-purple solution and unreacted metal. After 4 days all the Yb was dissolved, and the black-brown solution was filtered, concentrated to 20 mL, and layered with hexane (15 mL) to give dark red crystals (0.89 g, 59%). The compound turns dark brown at 124 °C and melts at 201 °C. Unit cell (MoKα, −120 °C): a = 11.72(3) Å, b = 12.454(6) Å, c = 12.78(5) Å. {001} space group. NMR spectra were obtained on Varian Gemini 300 or 400 MHz NMR spectrometers, and chemical shifts are reported in δ (ppm).
1846 (s), 1819 (s), 1688 (s), 1598 (s), 1581 (m), 1568 (m), 1514 (s), 1464 (w), 1377 (w), 1315 (s), 1295 (s), 1249 (m), 1236 (m), 1165 (m), 1146 (s), 1098 (s), 1069 (m), 1029 (m), 1012 (m), 992 (s), 886 (m), 871 (s), 839 (s), 793 (m), 764 (s), 743 (m), 722 (s), 699 (w), 643 (s), 629 (s) cm\(^{-1}\).

Synthesis of \([\text{ppy}]_2\text{Te}(\mu-\eta^1-\eta^2-\eta^2-\text{PhNPh})(\text{TePh})_2\) (7). Ph-TeTePh (0.41 g, 1.0 mmol) was added to a Schlenk tube containing \(\text{Te}(0.34 \text{ g}, 2.0 \text{ mmol})\) and \(\text{Hg}(0.050 \text{ g}, 0.25 \text{ mmol})\) in pyridine (50 mL). The mixture was stirred overnight, and then PhNPhN (0.36 g, 2.0 mmol) was added to the dark yellow-green solution and unreacted metal. After 4 days all the Te was dissolved, and the black-green solution was filtered, concentrated to 20 mL, and layered with hexane (15 mL) to give yellow crystals (1.1 g, 69%). Anal. Calcd for C\(_{66}\)H\(_{60}\)N\(_{10}\):

- C, 53.8 (47.2); H, 4.11 (3.52); N, 9.50 (7.80). Found: C, 54.2; H, 4.32; N, 9.20. The compound absorbs visible radiation from 300 to 700 nm.

The compound became light orange at 180 (w), 702 (w), 649 (s) cm\(^{-1}\), 1030 (m), 990 (m), 937 (m), 885 (m), 870 (s), 822 (s), 792 (s), 745 (s), 687 (s), 594 (s), 547 (s), 416 (s), 404 (s), 318 (s), 286 (s), 275 (s), 256 (s), 245 (s), 236 (s), 229 (s), 220 (s), 197 (s), 194 (s), 186 (s), 181 (s), 174 (s), 171 (s), 168 (s), 163 (s), 1596 (m), 1579 (w), 1531 (s), 1461 (s), 1439 (w), 1377 (w), 1295 (m), 1249 (s), 1216 (m), 1144 (m), 1105(s), 1069 (m), 1030 (m), 990 (m), 937 (m), 885 (s), 870 (s), 722 (s), 745 (w), 702 (w), 649 (s) cm\(^{-1}\).

Synthesis of \([\text{ppy}]_2\text{Yb}(\mu-\eta^1-\eta^2-\eta^2-\text{PhNPh})(\text{TePh})_2\) (8). Ph-TeTePh (0.41 g, 1.0 mmol) was added to a Schlenk tube containing Yb (0.35 g, 2.0 mmol) and Hg (0.050 g, 0.25 mmol) in pyridine (50 mL). The mixture was stirred for 1 day, and then PhNPhN (0.36 g, 2.0 mmol) was added to the black solution and unreacted metal. After 3 days all the Yb was dissolved, and the black-brown solution was filtered, concentrated to 20 mL, and layered with hexane (15 mL) to give yellow crystals (1.1 g, 69%). Anal. Calcd for C\(_{66}\)H\(_{60}\)N\(_{10}\):

- C, 53.8 (47.2); H, 4.11 (3.52); N, 9.50 (7.80). Found: C, 54.2; H, 4.32; N, 9.20. The compound absorbs visible radiation from 300 to 700 nm in pyridine, but there is no absorption maximum. Unit cell (MoK\(_\alpha\), 120 °C): triclinic space group P1, \(a = 10.310(6) \text{ Å}, \ b = 17.588(8) \text{ Å}, c = 17.704(9) \text{ Å}, \alpha = 76.60(6)^{\circ}, \beta = 73.73(5)^{\circ}, \gamma = 89.95(5)^{\circ}, V = 2990(5) \text{ Å}^3\): IR: 3146 (s), 3077 (m), 2924 (s), 2927 (w), 2924 (s), 2860 (s), 2849 (s), 2722 (s), 2724 (w), 2670 (s), 2359 (s), 2340 (s), 2037 (s), 1969 (s), 1911 (s), 1863 (s), 1634 (s), 1603 (s), 1579 (m), 1529 (s), 1461 (w), 1377 (w), 1295 (s), 1259 (m), 1218 (m), 1186 (s), 1145 (m), 1094 (s), 1069 (m), 1029 (s), 991 (m), 881 (s), 793 (m), 743 (m), 701 (m) cm\(^{-1}\).

Thermolysis. Samples of 1, 5, or 8 were placed in a quartz tube under vacuum for 5 min to remove coordinated pyridine. The tube was then sealed, and the sample temperature was increased at the rate of ca. 10 °C/min up to 150 °C and then 20 °C/min up to 800 °C. The temperature was held at 800 °C for 24 h and then cooled within minutes to room temperature. Powder diffraction X-ray analyses of the nonvolatile products for 1, 5, or 8 indicated the formation of an amorphous solid (1), HoTe (5), and a mixture of microcrystalline YbN and YbTe phases (8). GCMS analysis of the volatile products in the thermolysis of 5 and 8 identified PhNPhN and TePh.

X-ray Structure Determination of 2 and 5. Data for 2 and 5 were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo K\(_\alpha\) radiation (\(\lambda = 0.71073 \text{ Å}\) at 120 °C). The check reflections measured every 1 h showed less than 3% intensity variation. The data were corrected for Lorentz effects and polarization and absorption, the latter by a numerical (SHELXTL)\(^{14}\) method. The structures were solved by direct methods (SHELXS86).\(^{15}\) All non-hydrogen atoms were refined (SHELXL97) based upon \(F^2\). All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97).\(^{16}\) Scattering factors \((f, f', f'')\) are as described in

Table 3. Significant Distances (Å) and Angles (deg) for 5

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“Symmetry transformations used to generate equivalent atoms:
′, −x, −y, −z + 1; ′′, −x, −y + 1, −z.

general structure appears to be essentially invariant (Figures 1 and 2), with two Ln(III) ions bridged by a pair of η2-coordinated

2Ln + PhEEPh + 2PhNNPh →[(py)2Ln(EPh)(PhNNPh)]2 (2)

(PhNNPh) dianions, a terminal EPh bound to each Ln, and two neutral pyridine donors saturating the Ln coordination sphere. Details for the complete low-temperature single-crystal X-ray diffraction analyses of 2 and 5 are given in Table 1, ORTEP diagrams for 2 and 5 are given in Figures 1 and 2, respectively, and significant bond lengths for 2 and 5 are given in Tables 2 and 3, respectively. The remaining compounds 1, 3, 4, 6, and 8 are either isomorphous with 2 and 5 or crystallize in a unit cell of similar volume. Addition of PhSeSePh to a solution of 4 does not appear to give Yb(SePh)3 (reaction 3) as judged by visible spectroscopy. There appears to be a reaction of Ln(SePh)3 with PhNNPh, but visible spectroscopy could not identify the product unambiguously, and the anticipated heteroleptic product was not isolated from the reaction.

[(py)2Ln(SePh)(PhNNPh)]2 + PhSeSePh → Ln(SePh)3 + PhNNPh (3)

The redox-inactive Ln selenolates 1−3 have colors associated with f−f transitions that are characteristic of the individual Ln, while the tellurolates 5−7 are all deeper yellow, suggesting the possibility that these tellurolate compounds have Te to Ln charge transfer (CT) absorptions that tail from the UV to the visible spectrum. Both Yb compounds 4 and 8 are intensely colored, but only 4 has a diagnostic absorption maximum at 422 nm in THF, which can be assigned as a Se to Yb CT excitation.

Thermal decomposition of 5 gives HoTe, with the elimination of PhNNPh and TePh2. No evidence for the formation of benzene, biphenyl, or compounds with −PH2 units was detected in the GCMS data. The analogous selenolate derivative 1 did not give a microcrystalline product at the same temperature, while the redox active tellurolate 8 gave a mixture of YbN and YbTe.

Discussion

Heteroleptic Ln(EPh)(PhNNPh) compounds do not spontaneously eliminate PhEEPh to form Ln compounds with dianionic ligands. This reactivity is in contrast with the total replacement of EPh by E2− in reactions of Ln(EPh)3 with elemental E, as well as the synthesis of Ln imides via reduction of PhNNPh with Ln naphthalides. Differences in reactivity can be rationalized in terms of the relative stabilities of the naphthalide, chalcogenido, and chalcogenolate ligands. Naphthalide compounds will react with PhNNPh because, even though the carbanion is smaller and more electronegative than EPh,
reduction of naphthalene involves a loss of aromaticity that destabilizes the ligand and thus enhances the reactivity of the naphthalide compound relative to Ln(EPh)₃. When the reactivities of PhNNPh and elemental E with Ln(EPh)₃ are compared, in the chalcogen displacement reactions the final E²⁻-containing products are stabilized considerably by the ability of E²⁻ to coordinate 3, 1,3, 4, 2, or 5⁻ Ln(III) ions, while PhNNPh²⁻ is stabilized by coordination to only two trivalent metals. These observations would lead to the conclusion that Ln(naphthalide) should react with PhEPh to form Ln(EPh)₃ or with E to form LnE, clusters and that there would be no reaction of Ln(EPh)₃ with naphthalene.

Heteroleptic compounds can, however, be prepared in high yield by the direct reduction of PhNNPh/PhEPh mixtures, as found in related iodide chemistry of the early lanthanides, but yield is highly sensitive to the amount of REER present. In the selenium chemistry, yield decreases if additional PhSeSePh is present. The reverse reaction has also been investigated with visible spectroscopy, and it is clear that these dimers do not react with PhSeSePh to form Ln(SePh)₃. If Hg is not present, these reactions will still yield heteroleptic compounds, albeit more slowly. The corresponding thiolate derivatives, while presumably forming in the reactions of Ln with PhSSPh/PhNNPh, have not yet been isolated.

Only the selenolate 4 has a diagnostic LMCT absorption in the visible spectrum, at 550 nm in pyridine and 420 nm in THF. This transition energy is shifted considerably, relative to the analogous LMCT absorption at 510 nm found for Yb(SePh)₃,¹⁹ and is the primary evidence showing that these heteroleptic compounds do not react with additional PhSeSePh to displace the azobenzene. An interpretation of the relative CT absorption energies of 4 and Yb(SePh)₃ is unfortunately complicated by the concentration dependence of the Yb(SePh)₃ absorption spectrum that has been interpreted in terms of an equilibrium between mono- and polynuclear species in solution.

Tellurolate 8 confirms the notion that highly electronegative ancillary ligands are crucial to the stability of Yb ions in the presence of tellurium-based anionic ligands. Without electronegative ancillaries, both solid-state chalcogenido compounds YbTe₂₀ and molecular tellurolates Yb(TeR)₃,²¹ spontaneously reduce to Yb(II). In contrast, the use of amido or carbonyl ligands has led to successful syntheses of several compounds with Yb(II)–Te bonds. Both the terminal tellurolate Cp₂Yb⁻(TePh)(NH₂)₂²² and bridging ditelluride [Cp₂Yb]₂(TeTe)²³ are sufficiently stable to permit complete characterization, including single crystal X-ray diffraction, presumably because the Yb(II) ions are both electronically and sterically passivated by the two relatively electronegative Cp⁻ ligands coordinated to each metal ion. A benzamidinate compound with a terminal TePh ligand (deduced by comparison of unit cell data with a fully characterized SePh derivative) has also been characterized unequivocally.²⁴ While not as sterically demanding as Cp⁺, this resonance stabilized amido ligand also relies on highly electronegative second-row donors to inhibit reduction at the metal center.

Interatomic N–N distances consistently reveal the extent to which the PhNNPh ligand is reduced. Neutral azobenzene has a N=N bond length of 1.24(1) Å,²⁵ and there are two Ln compounds coordinated to PhNNPh radical anions, a pyrazolylborate²⁶ compound (N=N = 1.33(1) Å) and a Cp⁺Sm derivative (N=N = 1.36(1) Å).²⁷ Of the Ln compounds with doubly reduced PhNNPh ligands,²⁸–²⁹ the N–N bond range from 1.47(1) to 1.48(1) Å, essentially indistinguishable from the NN bond length averages in 2 (1.467(5) Å) and 5 (1.465(6) Å).

Comparison of Ln–E bond lengths both within the family of Ln–E(Ph) compounds and between Ln(EPh)₃ and Ln(ER), chalcogenolates with more sterically demanding R (i.e., substituted aryl,³⁰ Si(SiMe₃)₃) has been hindered by the tendency of benzenethiochalcogenolate ligands to bridge metal centers and form a variety of both polymeric and molecular solid-state structures with 2–4 metal ions.³²–³⁵ Compounds 2 and 5 present a unique opportunity to examine isomorphic compounds with Ln(III)–Se and Ln(III)–Te bonds. Given these seven coordinate structures, any covalent contributions to bonding should be minimal, and ionic radii should be accurate predictors of Ln–E bond lengths, as found in the series of divalent (py)₃Yb(EPh₂) coordination compounds.³⁵

Shannon lists the ionic radius of Te as 0.23 Å larger than Se, and with Er being 0.01 Å smaller than Ho, the difference in ionic radii is close but not exactly equal to the observed 0.27 Å difference between HoTe (3.06 Å) and ErSe (2.79 Å) bond lengths in 2 and 5, respectively. Bonds to tellurium would be more susceptible to intermolecular distortions, with an extreme example found in the Sm pyrazolylborate literature.³⁷ In that series of Sm–ER compounds, the thiolate and selenolate ligands form direct bonds to the Sm(III) ion, while the Sm–Te bond is actually cleaved to accommodate stronger binding to the multidentate nitrogen donor.

Thermolytic decomposition of lanthanide chalcogenolates³³,³⁸–⁴² has yielded surprises since the initial observation that Ln(TeR)₃ decomposes to give LnTe.₄¹ Generally, divalent compounds

deliver LnE solids (reaction 4), and trivalent compounds decompose to give Ln$_2$E$_3$ (reaction 5). Exceptions to this rule have been noted with redox active Ln (reaction 6) and in the curious case of Ho(SePh)$_3$, which gives a phase separated mixture of solid-state products (reaction 7).\(^{33}\)

\[
\text{Ln(ER)$_2$} \rightarrow \text{LnE} + \text{ER}_2 \quad (4)
\]

\[
2\text{Ln(ER)$_3$} \rightarrow \text{Ln$_2$E$_3$} + 3\text{ER}_2 \quad (5)
\]

\[
\text{Eu(SR)$_4$} \rightarrow \text{EuS} + \text{SR}_2 + \text{RSSR} \quad (6)
\]

\[
2\text{Ho(SeR)$_3$} \rightarrow \text{HoSe/HoSe$_2$} + 3\text{ER}_2 \quad (7)
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While numerous compounds with Ln–E bonds have been considered as single-source precursors to LnE,\(^{19,31-33,39-42}\) it has generally been presumed that electronegative ancillary ligands would present unnecessary complications in the thermolysis process. The present heteroleptic compounds seemed unlikely candidates for single source deposition of LnE solids because there is an alternative solid-state product, LnN, which contains a highly charged, more electronegative anion.

Thermolysis studies of 1, 5, and 8 gave three different results. For 5, once the neutral Ln–pyridine bonds are removed upon application of a vacuum, the C–Te bond is the weakest in the structure, and this leads to the formation of HoTe.\(^{43}\) Extension of this thermolysis to Yb fails to produce pure YbTe, presumably because reductive elimination of PhTeTePh is facilitated by the stability of the divalent oxidation state, and instead, both microcrystalline YbN\(^{44}\) and YbTe\(^{45}\) are observed in the XRPD profile. Further extension to a redox inactive selenolate fails to give a crystalline product at the same temperatures, either because the C–Se bond is stronger, and competing thermolysis pathways become more favorable, or because metal selenides have higher lattice energies than metal tellurides,\(^{46}\) and the temperatures used were insufficient to adequately anneal the final product.

**Conclusion**

Heteroleptic compounds can be prepared by reduction of azobenzene/PhEPh mixtures with elemental lanthanides. The presence of both SePh and TePh ligands effectively inhibits further reduction of the azobenzene dianion. From a comparison of the electronic properties of redox inactive Ln with the isomorphous Yb compounds, the color in the latter can be assigned as an E to Yb charge-transfer excitation. Thermal decomposition of these compounds can yield LnN or LnE solid-state products.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for complexes [(py)$_2$Er(µ-η$_2$-η$_2$-PhNNPh)(SePh)]$_2$2py and [(py)$_2$Ho(µ-η$_2$-η$_2$-PhNNPh)(TePh)]$_2$2py. This material is available free of charge via the Internet at http://pubs.acs.org.

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