

Heteroleptic Lanthanide Compounds with Chalcogenolate Ligands: Reduction of PhNNPh/PhEPh (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 PhEPh (E = Se or Te) in pyridine to give the bimetallic compounds $[(\text{py})_2\text{Ln}(\text{EPh})(\text{PhNNPh})]_2$ (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 $[(\text{py})_2\text{Er}(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhNNPh})(\text{SePh})]_2\cdot 2\text{py}$ (2) and $[(\text{py})_2\text{Ho}(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhNNPh})(\text{TePh})]_2\cdot 2\text{py}$ (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 $\mu\text{-}\eta^2\text{-}\eta^2\text{-PhNNPh}$ ligands that, from the N–N bond length, have clearly been reduced to dianions. 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 K α , 153(2) K) are as follows: 2, monoclinic group $P2_1/n$, $a = 11.864(3)$ Å, $b = 14.188(2)$ Å, $c = 17.624(2)$ Å, $\beta = 91.62(2)^\circ$, $V = 2965(1)$ Å³, $Z = 4$; 5, triclinic space group $P\bar{1}$, $a = 10.349(2)$ Å, $b = 17.662(4)$ Å, $c = 17.730(8)$ Å, $\alpha = 75.82(3)^\circ$, $\beta = 74.11(3)^\circ$, $\gamma = 89.45(2)^\circ$, $V = 3016(2)$ Å³, $Z = 2$.

Introduction

Recent reports detailing the reactions of $\text{Ln}(\text{EPh})_3$ with elemental chalcogen (E, E = S, Se) to give Ln clusters with E^{2-} ligands,^{1–7} with the concomitant oxidative elimination of PhEPh 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 electrostatic systems stability is proportional to $Z_M Z_L / r_{M-L}$, where Z_M is the charge on the metal, Z_L is the charge on the ligand, and r_{M-L} is the metal–ligand bond distance. Thus E^{2-} coordination is favorable relative to EPh, even when Se^{2-} is the product in the oxidative elimination of the smaller, more electronegative SPh to give PhSSPh.



Given the facility with which EPh ligands are oxidatively eliminated as PhEPh, 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 NR^{2-} ligands is notable,^{8–10} and a reasonable approach to these materials, via the four-electron reductive cleavage of the N=N bond¹¹ in RNNR by $\text{Ln}(\text{EPh})_3$, with concomitant oxidative elimination of PhEPh, 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-NPh^{2-} and PhN^{2-} 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

In this paper we report our initial studies on the reduction of PhNNPh/PhEPh heteroligand mixtures with elemental Ln and the reactions of $\text{Ln}(\text{EPh})_3$ with $\text{PhN}=\text{NPh}$. Heteroleptic Ln compounds with EPh (E = Se, Te) and $(\text{PhN-NPh})^{2-}$ ligands are described, and the solid-state phases that result from thermolysis of these compounds are identified.

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Experimental Section

General Methods. All syntheses were carried out under ultrapure nitrogen (JWS), 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 PhSeSePh were purchased from Aldrich and recrystallized. PhTeTePh was prepared according to the literature procedure.¹³ Ln 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 obtained 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 - η^2 - η^2 -PhNNPh)(SePh)]₂·2py (1). PhSeSePh (0.312 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 18 mL, and layered with hexane (15 mL) to give green-yellow crystals (0.66 g, 45% yield). The compound turns dark gray at 201 °C and melts at 246 °C. Anal. Calcd for C₆₆H₆₀N₁₀-Se₂Ho₂: C, 58.2 (50.8); H, 4.45 (3.82); N, 10.3 (8.47). Found: C, 55.9; H, 4.61; N, 10.5; C, 50.4; H, 4.19; N, 8.65. The compound does not show an optical absorption maximum from 300 to 800 nm in either THF or pyridine. Unit cell (Mo K α , -120 °C): $a = 11.723(8)$ Å, $b = 12.454(6)$ Å, $c = 12.780(5)$ Å, $\alpha = 64.95(4)^\circ$, $\beta = 63.30(5)^\circ$, $\gamma = 68.98(5)^\circ$, $V = 1477(2)$ Å³. IR: 3164 (s), 2723 (s), 2669 (s), 2362 (s), 2343 (s), 1923 (s), 1847 (s), 1719 (s), 1686 (s), 1636 (s), 1600 (s), 1578 (s), 1513 (s), 1463 (w), 1377 (w), 1322 (s), 1294 (s), 1239 (m), 1166 (s), 1149 (s), 1098 (s), 1063 (m), 1038 (m), 1022 (m), 1006 (m), 990 (m), 972 (s), 935 (s), 901 (s), 883 (m), 829 (s), 794 (m), 750 (s), 751 (m), 732 (m), 699 (m), 666 (s) cm⁻¹.

Synthesis of [(py)₂Er(μ - η^2 - η^2 -PhNNPh)(SePh)]₂·2py (2). PhSeSePh (0.31 g, 1.0 mmol) was added to a Schlenk tube containing Er (0.33 g, 2.0 mmol) and Hg (0.05 g, 0.25 mmol) in pyridine (50 mL). After 1 day PhNNPh (0.36 g, 2.0 mmol) was added to the pink solution and unreacted metal. After 7 days all the Er was dissolved, and the black-green solution was filtered, concentrated to 20 mL, and layered with hexane (15 mL) to give green crystals (0.54 g, 36%) that become dark yellow at 197 °C and melt at 230 °C. Anal. Calcd for C₆₆H₆₀N₁₀-Er₂Se₂: C, 58.0 (50.7); H, 4.44 (3.80); N, 10.3 (8.44). Found: C, 57.9; H, 4.29; N, 10.4. The compound does not show an electronic absorption maximum from 300 to 800 nm in THF or pyridine. IR: 3076 (s), 2724 (s), 2669 (s), 2359 (m), 2341 (m), 1976 (s), 1912 (s), 1861 (s), 1684 (s), 1635 (s), 1596 (s), 1579 (m), 1461 (w), 1438 (w), 1377 (w), 1293 (s), 1260 (m), 1215 (s), 1164 (s), 1144 (s), 1069 (m), 1029 (m), 990 (s), 882 (m), 796 (m), 744 (m), 731 (s), 701 (w), 667 (s) cm⁻¹.

Synthesis of [(py)₂Tm(μ - η^2 - η^2 -PhNNPh)(SePh)]₂·2py (3). PhSeSePh (0.31 g, 1.0 mmol) was added to a Schlenk tube containing Tm (0.34 g, 2.0 mmol) and Hg (0.05 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 pink solution and unreacted metal. After 7 days all the Tm was dissolved, and the black-yellow solution was filtered, concentrated to 22 mL, and layered with hexane (15 mL) to give green-yellow crystals (0.70 g, 47%). The compound does not melt but became dark orange at 78 °C and brown at 259 °C. Anal. Calcd for C₆₆H₆₀N₁₀Se₂Tm₂: C, 57.9 (50.5); H, 4.43 (3.79); N, 10.2 (8.42). Found: C, 56.1; H, 4.73; N, 10.5. The compound does not show an optical absorption maximum from 300 to 800 nm in THF and py. Unit cell (Mo K α , -120 °C): $a = 11.854(7)$ Å, $b = 14.192(14)$ Å, $c = 17.654(10)$ Å, $\beta = 91.59(6)^\circ$, $V = 2969(4)$ Å³. IR: 3146 (s), 3077 (m), 3022 (s), 2927 (w), 2725 (s), 2669 (s), 2344 (s), 2291 (s), 1979 (s), 1914 (s), 1861 (s), 1686 (s), 1634 (s), 1597 (m), 1579 (w), 1462 (w), 1438 (w), 1377 (m), 1324 (s), 1293 (m), 1237 (m), 1215 (m), 1165 (s), 1145 (m), 1099 (s), 1067 (m), 1029 (m), 1006 (s), 990 (m), 883 (m), 794 (m), 746 (m), 732 (s), 702 (w), 666 (s) cm⁻¹.

Synthesis of [(py)₂Yb(μ - η^2 - η^2 -PhNNPh)(SePh)]₂·2py (4). PhSeSePh (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 216 °C. Anal. Calcd for C₆₆H₆₀N₁₀Se₂Yb₂: C, 57.6 (50.2); H, 4.40 (3.77); N, 10.2 (8.37). Found: C, 52.3; H, 4.61; N, 9.24. The compound shows an optical absorption maximum at 420 nm ($\epsilon = 115$ (mol·cm)) in THF and at 550 nm ($\epsilon = 150$ (mol·cm)) in pyridine. IR: 3145 (s), 3077 (s), 3022 (s), 2725 (s), 2670 (s), 2388 (s), 2347 (s), 2289 (s), 1977 (s), 1912 (s), 1862 (s), 1813 (s), 1678 (s), 1631 (s), 1595 (s), 1579 (m), 1539 (s), 1461 (w), 1438 (w), 1377 (w), 1306 (s), 1260 (m), 1215 (m), 1185 (s), 1144 (m), 1068 (s), 1029 (m), 990 (m), 934 (s), 799 (s), 767 (m), 745 (m), 702 (w), 662 (s) cm⁻¹. Unit cell (Mo K α , -120 °C): triclinic space group $P\bar{1}$ $a = 11.645(14)$ Å, $b = 12.447(12)$ Å, $c = 12.706(12)$ Å, $\alpha = 64.78(8)^\circ$, $\beta = 63.52(9)^\circ$, $\gamma = 68.94(9)^\circ$, $V = 1458(3)$ Å³.

Synthesis of [(py)₂Ho(μ - η^2 - η^2 -PhNNPh)(TePh)]₂·2py (5). Holmium metal (0.33 g, 2.0 mmol) was added to diphenyl ditelluride (0.82 g, 2.0 mmol) and Hg (0.05 g, 0.25 mmol) in pyridine (30 mL). The next day azobenzene (0.37 g, 2.0 mmol) was added to the yellow solution and unreacted metal. After 12 days the Ho was no longer observable, and the brown solution was filtered, concentrated to 25 mL, and layered with 15 mL of hexanes. The flask was allowed to sit in a dark place, and over the next 7 days orange crystals formed (0.70 g, 44%). The crystals began to darken and desolvate ca. 180 °C and then gradually turned nearly black and melted at ca. 200 °C. Anal. Calcd for C₆₆H₆₀N₁₀Ho₂Te₂: C, 54.3 (47.5); H, 4.16 (3.56); N, 9.61 (7.90). Found: C, 53.6; H, 3.82; N, 9.16. IR: 3077 (m), 3054 (w), 3022 (m), 2926 (s), 2857 (s), 1914 (w), 1595 (m), 1580 (s), 1465 (s), 1438 (s), 1378 (m), 1294 (w), 1244 (w), 1216 (m), 1172 (w), 1144 (m), 1068 (m), 1031 (m), 1016 (w), 990 (m), 942 (w), 868 (m), 796 (w), 746 (s), 728 (m), 702 (s), 620 (m), 606 (w) cm⁻¹. ¹H NMR (C₅D₅N) revealed only pyridine resonances at δ 8.60, 7.55, and 7.18 ppm, and the product is insufficiently soluble to record the spectrum in THF. A visible spectrum of the compound in pyridine did not reveal any well-defined absorption maxima, but a characteristic Ho absorption (454 nm, $\epsilon = 0.033$) was observed.

Synthesis of [(py)₂Er(μ - η^2 - η^2 -PhNNPh)(TePh)]₂·2py (6). PhTeTePh (0.41 g, 1.0 mmol) was added to a Schlenk tube containing Er (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 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 bright yellow crystals (0.84 g, 53%). The compound became dark brown at 183 °C and melts at 211 °C. Anal. Calcd for C₆₆H₆₀N₁₀Te₂Er₂: C, 54.2 (47.2); H, 4.14 (3.54); N, 9.58 (7.87). Found: C, 53.4; H, 3.93; N, 9.69. The compound does not show an optical absorption maximum from 300 to 800 nm in either THF or pyridine. Unit cell (MoK α , -120 °C): $a = 17.665(10)$ Å, $b = 18.378(10)$ Å, $c = 11.828(15)$ Å, $\beta = 127.18(9)^\circ$, $V = 3059(6)$ Å³. IR: 3137 (s), 3076 (s), 2726 (s), 2668 (s), 2614 (s), 2454 (s), 2393 (s), 2290 (s), 2038 (s), 1972 (s), 1913 (s),

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1846 (s), 1819 (s), 1688 (s), 1631 (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), 941 (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 [(py)₂Tm(μ - η^2 - η^2 -PhNNPh)(TePh)]₂·2py (7). Ph-TeTePh (0.41 g, 1.0 mmol) was added to a Schlenk tube containing Tm (0.34 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 dark yellow-green solution and unreacted metal. After 4 days all the Tm was dissolved, and the black-green solution was filtered, concentrated to 25 mL, and layered with hexane (10 mL) to give yellow crystals (1.1 g, 69%). Anal. Calcd for C₆₆H₆₀N₁₀Te₂Tm: C, 54.1 (47.1); H, 4.13 (3.54); N, 9.55 (7.85). Found: C, 54.4; H, 3.42; N, 9.19. The compound became light orange at 180 °C and melted at 199 °C. The compound does not show an optical absorption maximum from 300 to 800 nm in THF or pyridine. IR: 3146 (s), 3077 (m), 3023 (s), 2724 (s), 2668 (s), 2450 (s), 2361 (s), 2292 (s), 2207 (s), 1978 (s), 1914 (s), 1862 (s), 1814 (s), 1749 (s), 1719 (s), 1684 (s), 1632 (s), 1596 (m), 1579 (w), 1531 (s), 1461 (w), 1439 (w), 1377 (w), 1295 (m), 1249 (s), 1216 (m), 1144 (m), 1105(s), 1069 (m), 1030 (m), 990 (m), 937 (m), 885 (m), 870 (s), 822 (s), 792 (s), 745 (w), 702 (w), 649 (s) cm^{-1} .

Synthesis of [(py)₂Yb(μ - η^2 - η^2 -PhNNPh)(TePh)]₂·2py (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 PhNNPh (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%). The compound does not melt but became orange at 182 °C and red-black at 282 °C. Anal. Calcd for C₆₆H₆₀N₁₀Te₂Yb₂: 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 α , -120 °C): triclinic space group $P\bar{1}$, $a = 10.310(6)$ Å, $b = 17.588(8)$ Å, $c = 17.704(9)$ Å, $\alpha = 76.60(6)^\circ$, $\beta = 73.73(5)^\circ$, $\gamma = 89.95(5)^\circ$, $V = 2990(5)$ Å³. IR: 3146 (s), 3076 (s), 2923 (w), 2724 (s), 2670 (s), 2359 (s), 2340 (s), 2037 (s), 1969 (s), 1911 (s), 1863 (s), 1678 (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 (s), 1029 (m), 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 end of the tube that was kept outside the oven was submerged in liquid nitrogen for the first few hours. 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 PhNNPh and TePh₂.

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 α radiation ($\lambda = 0.71073$ 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 (SHELX76)¹⁴ method. The structures were solved by direct methods (SHELXS86).¹⁵ All non-hydrogen atoms were refined (SHELXL97) based upon F_o^2 . All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97).¹⁶ Scattering factors (f_o , f' , f'') are as described in

Table 1. Summary of Crystallographic Details for [(py)₂Er(μ - η^2 - η^2 -PhNNPh)(SePh)]₂·2py (**2**) and [(py)₂Ho(μ - η^2 - η^2 -PhNNPh)(TePh)]₂·2py (**5**)

param	2	5
empirical formula	C ₃₃ H ₃₀ ErN ₅ Se	C ₆₆ H ₆₀ Ho ₂ N ₁₀ Te ₂
fw	742.84	1280.73
space group (No.)	$P2_1/n$ (14)	$P\bar{1}$ (2)
a (Å)	11.864(3)	10.349(2)
b (Å)	14.188(2)	17.662(4)
c (Å)	17.624(2)	17.730(8)
α (deg)	90.00	75.82(3)
β (deg)	91.62(2)	74.11(3)
γ (deg)	90.00	89.45(2)
V (Å ³)	2965.4(9)	3016.2(16)
Z	4	2
D (calcd) (g/cm ⁻³)	1.664	1.738
temp (°C)	-120	-120
λ (Å)	0.71073	0.71073
abs coeff (mm ⁻¹)	4.088	3.601
$R(F)^a$ [$I > 2\sigma(I)$]	0.033	0.032
$R_w(F^2)^a$ [$I > 2\sigma(I)$]	0.082	0.06%

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w(F^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. Additional crystallographic details are given in the Supporting Information.

Table 2. Significant Distances (Å) and Angles (deg) for **2**^a

Er(1)-N(1)'	2.248(3)	Er(1)-N(2)	2.262(3)	Er(1)-N(1)	2.457(3)
Er(1)-N(4)	2.477(4)	Er(1)-N(3)	2.497(3)	Er(1)-N(2)'	2.545(3)
Er(1)-Se(1)	2.7935(7)	N(1)-N(2)	1.467(5)		
N(1)'-Er(1)-N(2)	85.89(12)	N(1)'-Er(1)-N(1)	90.00(12)		
N(2)-Er(1)-N(1)	35.93(12)	N(1)'-Er(1)-N(4)	121.18(12)		
N(2)-Er(1)-N(4)	126.99(12)	N(1)-Er(1)-N(4)	94.87(12)		
N(1)'-Er(1)-N(3)	154.50(12)	N(2)-Er(1)-N(3)	90.76(12)		
N(1)-Er(1)-N(3)	101.99(11)	N(4)-Er(1)-N(3)	80.57(12)		
N(1)'-Er(1)-N(2)'	34.95(11)	N(2)-Er(1)-N(2)'	92.51(11)		
N(1)-Er(1)-N(2)'	75.77(11)	N(4)-Er(1)-N(2)'	90.26(11)		
N(3)-Er(1)-N(2)'	170.39(11)	N(1)'-Er(1)-Se(1)	79.27(9)		
N(2)-Er(1)-Se(1)	121.74(9)	N(1)-Er(1)-Se(1)	156.64(8)		
N(4)-Er(1)-Se(1)	108.45(9)	N(3)-Er(1)-Se(1)	81.10(8)		
N(2)'-Er(1)-Se(1)	104.73(8)	C(1)-Se(1)-Er(1)	110.69(13)		

^a Symmetry transformations used to generate equivalent atoms: $'$, $-x + 1$, $-y + 1$, $-z$.

SHELXL97. Compounds **1** and **4** are isostructural. A full structure determination of **1** was attempted, but because of experimental difficulty there was not enough data collected to fully describe the structure. The available data indicate that the same basic dimeric structure was again present. Compounds **2** and **3** are isostructural; compounds **5** and **8** are isostructural. There are no unit cell data for compound **7**. Unit cell data for **6** indicate that it comprises a fourth phase in this series (see above). Crystallographic data and final R indices for **2** and **5** are given in Table 1. Significant bond distances and angles for **2** and **5** are given in Tables 2 and 3, respectively. Complete crystallographic details are given in the Supporting Information. ORTEP diagrams¹⁷ for **2** and **5** are shown in Figures 1 and 2, respectively.

Results

Azobenzene is not completely reduced to imido ligands by Ln when EPh ligands are present. Instead, heteroleptic compounds are isolated by direct reduction of PhEPh/PhNNPh mixtures with elemental Ln, giving dimeric [(py)₂Ln(EPh)-(PhNNPh)]₂ (E = Se, Te) products (reaction 2). While the compounds crystallize in at least four different unit cells, the

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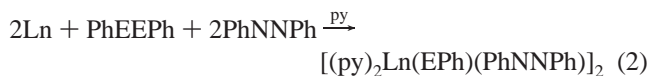
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Table 3. Significant Distances (Å) and Angles (deg) for **5**^a

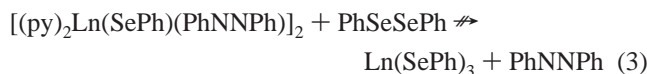
Ho(1)–N(3')	2.234(5)	Ho(1)–N(4)	2.236(4)	Ho(1)–N(1)	2.464(5)
Ho(1)–N(3)	2.511(4)	Ho(1)–N(2)	2.521(4)	Ho(1)–N(4')	2.562(4)
Ho(1)–Te(1)	3.0626(14)				
Ho(2)–N(7)''	2.237(4)	Ho(2)–N(8)	2.237(5)	Ho(2)–N(5)	2.458(5)
Ho(2)–N(8)''	2.474(4)	Ho(2)–N(6)	2.511(5)	Ho(2)–N(7)	2.583(4)
Ho(2)–Te(2)	3.0635(15)	N(8)–N(7)	1.465(6)	N(3)–N(4)	1.465(6)
N(7)–C(39)	1.387(7)				
N(3')–Ho(1)–N(4)	86.74(16)	N(3')–Ho(1)–N(1)	127.84(16)		
N(4)–Ho(1)–N(1)	120.96(16)	N(3')–Ho(1)–N(3)	90.04(15)		
N(4)–Ho(1)–N(3)	35.37(15)	N(1)–Ho(1)–N(3)	91.73(15)		
N(3')–Ho(1)–N(2)	88.28(16)	N(4)–Ho(1)–N(2)	153.61(16)		
N(1)–Ho(1)–N(2)	81.99(16)	N(3)–Ho(1)–N(2)	170.54(14)		
N(3')–Ho(1)–N(4)	34.74(16)	N(4)–Ho(1)–N(4')	91.38(14)		
N(1)–Ho(1)–N(4)	96.63(15)	N(3)–Ho(1)–N(4')	74.47(14)		
N(2)–Ho(1)–N(4)	99.13(14)	N(3)–Ho(1)–Te(1)	124.62(12)		
N(4)–Ho(1)–Te(1)	81.60(12)	N(1)–Ho(1)–Te(1)	103.94(11)		
N(3)–Ho(1)–Te(1)	108.48(10)	N(2)–Ho(1)–Te(1)	80.02(10)		
N(4)–Ho(1)–Te(1)	159.03(11)	N(7)''–Ho(2)–N(5)	119.59(16)		
N(8)–Ho(2)–N(5)	128.76(15)	N(7)''–Ho(2)–N(8)''	35.78(15)		
N(8)–Ho(2)–N(8)	89.79(15)	N(5)–Ho(2)–N(8)''	90.63(15)		
N(7)''–Ho(2)–N(6)	154.74(17)	N(8)–Ho(2)–N(6)	85.67(16)		
N(5)–Ho(2)–N(6)	83.33(16)	N(8)''–Ho(2)–N(6)	167.65(14)		
N(7)''–Ho(2)–N(7)	92.52(14)	N(8)–Ho(2)–N(7)	34.44(15)		
N(5)–Ho(2)–N(7)	97.19(15)	N(8)''–Ho(2)–N(7)	75.02(14)		
N(6)–Ho(2)–N(7)	95.00(14)	N(7)''–Ho(2)–Te(2)	81.92(11)		
N(8)–Ho(2)–Te(2)	124.99(11)	N(5)–Ho(2)–Te(2)	102.89(11)		
N(8)''–Ho(2)–Te(2)	109.34(10)	N(6)–Ho(2)–Te(2)	82.58(11)		
N(7)–Ho(2)–Te(2)	159.31(11)				

^a 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 η^2 -coordinated

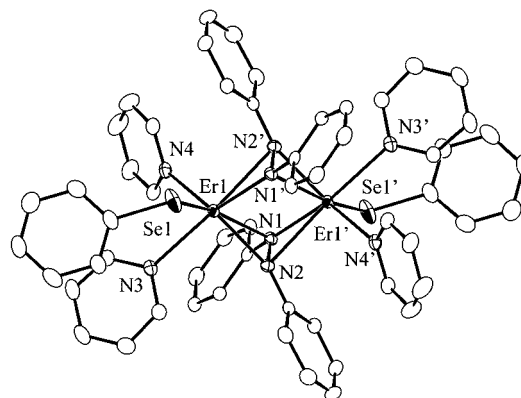
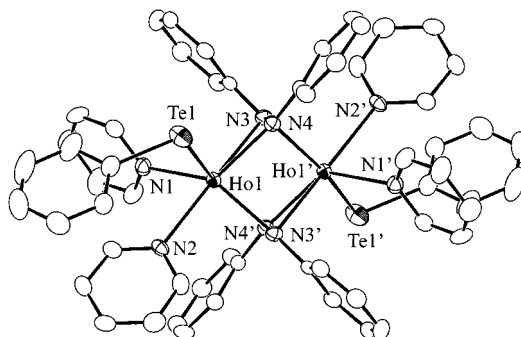


(PhNNPh) dianions, a terminal EPh bound to each Ln, and two neutral pyridine donors saturating the Ln coordination sphere. Details for the complete low-temperature single-crystal X-ray diffraction analyses of **2** and **5** are given in Table 1, ORTEP diagrams for **2** and **5** are given in Figures 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 isostructural 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.



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 -NPh₂ units was

**Figure 1.** Molecular structure of $[(\text{py})_2\text{Er}(\mu_2\text{-PhNNPh})(\text{SePh})]_2$, with the thermal ellipsoids drawn at the 50% probability level.**Figure 2.** Molecular structure of the two inequivalent $[(\text{py})_2\text{Ho}(\mu_2\text{-PhNNPh})(\text{TePh})]_2$ molecules, with the thermal ellipsoids drawn at the 50% probability level.

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 PhEPh 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.⁸ 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 $\text{Ln}(\text{EPh})_3$. When the reactivities of PhNNPh and elemental E with $\text{Ln}(\text{EPh})_3$ are compared, in the chalcogen displacement reactions the final E^{2-} -containing products are stabilized considerably by the ability of E^{2-} to coordinate 3,^{1,3} 4,²⁻⁴ or 5¹ $\text{Ln}(\text{III})$ ions, while PhNNPh^{2-} is stabilized by coordination to only two trivalent metals. These observations would lead to the conclusion that $\text{Ln}(\text{naphthalide})$ should react with PhEPh to form $\text{Ln}(\text{EPh})_3$ or with E to form LnE_x clusters and that there would be no reaction of $\text{Ln}(\text{EPh})_3$ with naphthalene.

Heteroleptic compounds can, however, be prepared in high yield by the direct reduction of $\text{PhNNPh}/\text{PhEPh}$ mixtures, as found in related iodide chemistry of the early lanthanides, but yield is highly sensitive to the amount of REER present.¹⁸ 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 $\text{Ln}(\text{SePh})_3$. 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 $\text{PhSSPh}/\text{PhNNPh}$, 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 $\text{Yb}(\text{SePh})_3$,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 $\text{Yb}(\text{SePh})_3$ is unfortunately complicated by the concentration dependence of the $\text{Yb}(\text{SePh})_3$ absorption spectrum that has been interpreted in terms of an equilibrium between mono- and polymetallic species in solution.

Telluroate **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 YbTe ,²⁰ and molecular tellurolates $\text{Yb}(\text{TeR})_x$ ²¹ spontaneously reduce to $\text{Yb}(\text{II})$. In contrast, the use of amido or carbanion ligands has led to successful syntheses of several compounds with $\text{Yb}(\text{III})$ -Te bonds. Both the terminal telluroate $\text{Cp}^*_2\text{Yb}(\text{TePh})(\text{NH}_3)$ ²² and bridging ditelluride $[\text{Cp}^*_2\text{Yb}]_2(\text{TeTe})$ ²³ are sufficiently stable to permit complete characterization, including single crystal X-ray diffraction, presumably because the $\text{Yb}(\text{III})$ 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,^{9,28-29} the N-N bonds 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 $\text{Ln-E}(\text{Ph})$ compounds and between $\text{Ln}(\text{EPh})_3$ and $\text{Ln}(\text{ER})_x$ chalcogenolates with more sterically demanding R (i.e. substituted aryl,³⁰ $\text{Si}(\text{SiMe}_3)_3$ ³¹) has been hindered by the tendency of benzenechalcogenolate ligands to bridge metal centers and form a variety of both polymeric and molecular solid-state structures with 2-4 metal ions.³²⁻³⁴ Compounds **2** and **5** present a unique opportunity to examine isomorphous compounds with $\text{Ln}(\text{III})$ -Se and $\text{Ln}(\text{III})$ -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 $(\text{py})_x\text{Yb}(\text{EPh})_2$ coordination compounds.³⁵

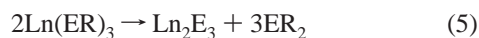
Shannon lists the ionic radius³⁶ of Te as 0.23 Å larger than Se, and with Er being 0.01 Å smaller than Ho, the difference in ionic radii is close but not exactly equal to the observed 0.27 Å difference between HoTe (3.06 Å) and ErSe (2.79 Å) bond lengths in **2** and **5**, respectively. Bonds to tellurium would be most 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 chalcogenolates^{33,38-42} has yielded surprises since the initial observation that $\text{Ln}(\text{TeR})_2$ decomposes to give LnTe .⁴¹ Generally, divalent compounds

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deliver LnE solids (reaction 4), and trivalent compounds decompose to give Ln₂E₃ (reaction 5). Exceptions to this rule have been noted with redox active Ln (reaction 6)⁴² and in the curious case of Ho(SePh)₃, which gives a phase separated mixture of solid-state products (reaction 7).³³



While numerous compounds with Ln–E bonds have been considered as single-source precursors to LnE_x,^{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 YbN⁴⁴ and YbTe⁴⁵ 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)₂Er(μ-η²-η²-PhNNPh)(SePh)]₂·2py and [(py)₂Ho(μ-η²-η²-PhNNPh)(TePh)]₂·2py. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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