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Accessing Lanthanide Metallocene Two-Electron Reduction Chemistry Using 2,2′-Bipyridine

Cary R. Stennett, Joseph Q. Nguyen, Joseph W. Ziller, and William J. Evans*

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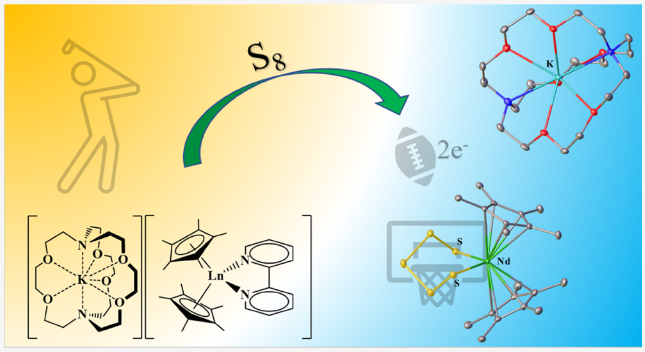

ABSTRACT: The feasibility of using redox-active 2,2′-bipyridine (bipy) as a synthetically convenient electron carrier to enable lanthanide metallocenes to effect two-electron reduction chemistry has been examined. The Ln(III) precursor complexes, $Cp^*_2LnCl(bipy)$, **1-Ln** (Ln = Nd, Gd; Cp* = C_5Me_5), were readily synthesized in 75−81% yield in one pot from $LnCl_3$, KCp*, and bipy and were identified by X-ray crystallography. Treatment of the **1-Ln** compounds with K/KI (4.3 wt %) afforded in 74−77% yield the products, $Cp^*_2Ln(bipy)$, **2-Ln**, which contain $(bipy)^{1-}$ ligands based on their spectroscopic characteristics and X-ray crystal structures. The molecular structure of the previously reported **2-Eu** was also determined, which showed structural features consistent with a neutral bipy ligand. Further reduction of **2-Nd** or **2-Gd**, or the previously reported **2-Sm**, **2-Eu**, and **2-Yb** with K/KI (4.3 wt %) in the presence of 2.2.2-cryptand (crypt) afforded in 58−88% yield the salts, $[K(crypt)][Cp^*_2Ln(bipy)]$, **3-Ln**, which show metrical parameters identified by X-ray crystallography that are consistent with a $(bipy)^{1-}$ ligand for **3-Eu** and **3-Yb** and a $(bipy)^{2-}$ ligand for **3-Nd**, **3-Sm**, and **3-Gd**. The two-electron reduction of azobenzene (PhN=NPh) to $(PhN{-}NPh)^{2-}$ using the **3-Ln** complexes was examined as a proof of concept. The 1:1 reactions of **3-Nd**, **3-Sm**, and **3-Yb** with azobenzene afforded in 36−79% yield the $[K(crypt)][Cp^*_2Ln(N_2Ph_2)]$, **4-Ln** (Ln = Nd, Sm, Yb) complexes, each of which were crystallographically characterized. In another example of two-electron reduction by **3-Ln**, treatment of **3-Nd** or **3-Sm** with elemental sulfur afforded in 70−75% yield $[K(crypt)][Cp^*_2Ln(S_5)]$, **5-Ln** (Ln = Nd, Sm), which were shown by crystallography to be rare examples of *f*-element organometallic complexes that contain the $(S_5)^{2-}$ ligand.

■ INTRODUCTION

Early assessments of rare-earth metal chemistry suggested that these metals were not very useful in reductive chemistry because they lacked the two-electron redox couples so useful in transition metal chemistry.[1−4] In fact, for many years, only three rare-earth metals were known to have one-electron reduction chemistry. Until 1997, the only oxidation states that had been accessed in molecular complexes of the rare-earth metals beyond the most stable +3 oxidation state were Ce(IV) and the "traditional" Ln(II) species Eu(II), Yb(II), and Sm(II). Despite this limitation, the known Ln(II) complexes were found to readily effect two-electron reduction chemistry because they reacted with substrates in a 2:1 ratio to make neutral bimetallic $(substrate)^{2-}$ products, e.g., eq 1 (A = anion).[5,6] Since 1997, molecular complexes containing Pr(IV),[7] Tb(IV),[8] and Ln(II)[9−12] for all of the rare-earth metals except radioactive promethium have been identified. Although this expands the possibilities for two-electron reduction chemistry of the rare-earth metals, accessing these new oxidation states often requires specialized ligands and reaction conditions.

$$2Ln^{II}A_2 + \text{substrate} \rightarrow A_2Ln^{III}(\text{substrate})Ln^{III}A_2 \quad (1)$$

One alternative to expand the redox chemistry of metal complexes beyond the discovery of new oxidation states is to use redox-active ligands. This has been explored extensively with transition metals.[13−15] Studies of redox-active complexes of the rare-earth[16,17] and actinide[18−21] metals have also been reported as well as studies in which ligands as common as $(C_5Me_5)^{1-}$,[22] $(BPh_4)^{1-}$,[23] $(H)^{1-}$,[24] and $(N_2)^{2-}$ [25] can effect reduction chemistry in complexes of these metals. For example, in the sterically induced reduction (SIR) chemistry of $(C_5Me_5)_3Ln$ compounds, the Ln(III) complex effects reduction with a $(C_5Me_5)^{1-}/(C_5Me_5)^{\bullet}$ redox couple.[22,26]

Although an extensive reduction chemistry has been developed for rare-earth metals along these lines, many of the systems require multiple synthetic steps to prepare the rare-earth metal reductant. It was therefore of interest to find an alternative

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redox-active ligand system for the rare-earth metals that could be synthesized easily from $LnCl_3$ precursors in high yield such that this platform could be broadly applied to a wide range of reduction chemistry. Inspired by the rich reduction chemistry recently reported by Walter and co-workers using cyclopentadienyl actinide bipyridyl complexes,[27−29] which was predicated on earlier studies by Andersen and co-workers,[30] we describe in this paper the use of 2,2′-bipyridine (bipy) to accomplish this goal with rare-earth metallocenes.

The bis(pentamethylcyclopentadienyl) lanthanide bipyridine complex, Cp^*_2Yb(bipy), was synthesized as early as 1982 in the Andersen group.[31] Although the cyclopentadienyl samarium bipyridine complex, Cp^*_2Sm(bipy) (Cp^* = C_5Me_5), was synthesized from $Cp^*_2Sm(THF)_2$ and bipy and published in 1989, its reduction chemistry was not explored at that time.[32] Andersen and co-workers published the Eu and Yb analogues in 2002,[33] which led to numerous studies of the multiconfigurational ground states of complexes of a variety of bipyridines with the Cp^*_2Yb unit.[33−39] Despite these extensive studies of neutral Cp^*_2Ln(bipy) complexes, the only two anionic complexes of the form $[Cp^*_2Ln(bipy)]^{1-}$ that have appeared in the literature are the gadolinium and dysprosium complexes $[Cp^*_2Ln(bipy^B)]^{1-}$ ($bipy^B$ = 5,5′-bis-(dimesitylboronyl)-2,2′-bipyridine) involving a specialized bipyridine ligand.[40] On the basis of their magnetic susceptibilities, these complexes were found to contain Ln(III) ions. The dianionic nature of the bipy ligand in these complexes suggested to us that they might be capable of effecting two-electron reduction chemistry, thereby serving as "Ln(I)" equivalents and allowing chemistry that would be otherwise inaccessible to currently known lanthanide complexes.

We report here the facile synthesis of Cp^*_2LnCl(bipy) complexes and their conversion to Cp^*_2Ln(bipy) complexes and $[Cp^*_2Ln(bipy)]^{1-}$ salts. Synthetic, structural, and spectroscopic details are presented, as well as two example reactions that demonstrate the two-electron reduction chemistry that can be achieved using these reagents.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were performed by using modified Schlenk techniques or in a Vacuum Atmospheres glovebox under an atmosphere of argon. Solvents were degassed by sparging with dry argon before drying and collection using an S2 Grubbs-type[41] solvent purification system (JC Meyer). All physical measurements were recorded under strictly anaerobic and anhydrous conditions. Infrared spectra were recorded on compressed solid samples using an Agilent Cary 630 ATR/FTIR spectrometer. Electronic spectra were recorded as dilute solutions in hexane (**2-Ln**) or tetrahydrofuran (THF) (all other complexes) in 3.5 mL quartz cuvettes (1 cm path length) using an Agilent Cary 60 UV/vis spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AVANCE 600 MHz spectrometer at 298 K unless otherwise stated and referenced to residual solvent signals. Magnetic moments were determined by Evans' method and corrected using the appropriate diamagnetic constants.[42−44] Anhydrous lanthanide chlorides were prepared by treatment of their corresponding hydrates with ammonium chloride as previously described.[45] KCp^* was prepared by treatment of HC_5Me_5 with $KN(SiMe_3)_2$ in toluene.[46] Cp^*_2Sm(bipy),[32] Cp^*_2Yb(bipy),[33] $Cp^*_2Eu(THF)_2$,[47] and K/KI (4.3 wt %)[48] were prepared according to literature procedures. 2,2′-Bipyridine was purified by sublimation prior to use. Azobenzene was used as purchased without further purification. Elemental sulfur was purified by recrystallization from toluene.

Synthesis of Cp^*_2NdCl(bipy), 1-Nd. 2,2′-Bipyridine (0.31 g, 2.0 mmol) was added in one portion to a stirred mixture of $NdCl_3$ (0.50 g, 2.0 mmol) in ca. 15 mL of tetrahydrofuran, and the resulting pale blue suspension was stirred for ca. 15 min. Solid KCp^* (0.70 g, 4.0 mmol) was then added in several portions to the mixture over 5 min with stirring. The mixture gradually became orange over ca. 10 min and was stirred overnight. Then, the dark orange mixture was centrifuged, the supernatant was filtered through a pipette packed with ca. 1 cm of filter paper, and the solvent was removed under reduced pressure. The resulting orange powder was washed three times with ca. 2 mL portions of hexanes to give 0.98 g (1.6 mmol, 81%) of **1-Nd** as a bright orange powder. Overnight storage at ambient temperature of a concentrated THF solution of **1-Nd** afforded orange crystals **1-Nd·THF** which were suitable for X-ray diffraction studies. UV−vis: λ_{max}/nm (ε/M^{-1} cm^{-1}): 269 (shoulder, 22 000), 393 (6600). IR (ATR): a sharp absorbance at $\tilde{\nu}$ = 765 cm^{-1} was taken as indicative of the presence of the neutral bipyridine ligand as described below. ^{1}H NMR (600 MHz, benzene-D_6, 298 K): δ = 10.07 (s, 30H, CH_3), 5.67 (s, 1H, CH (bipy)), 5.10 (s, 1H, CH (bipy)), 4.55 (s, 1H, CH (bipy)), 3.48 (s, 1H, CH (bipy)), 1.79−0.88 (m, 8H, THF), −0.59 (s, 1H, CH (bipy)), −6.61 (s, 1H, CH (bipy)), −24.50 (s, 1H, CH (bipy)). ^{13}C NMR (151 MHz, THF, 298 K): δ = 240.97 (s, CCH_3 (Cp^*)), 156.08 (s, C−C′ (bipy)), 138.31 (d, CH, (bipy), J = 167.61 Hz), 136.40 (d, CH (bipy), J = 149.5 Hz), 125.95−119.57 (overlapping multiplets, CH (bipy)), −11.70 (q, CH_3 (Cp^*), J = 123.8 Hz). μ_{eff} = 3.1 μ_B.

Synthesis of Cp^*_2GdCl(bipy), 1-Gd.[49] 2,2′-Bipyridine (0.15 g, 0.95 mmol) was added in one portion to a stirred mixture of $GdCl_3$ (0.25 g, 0.95 mmol) in ca. 15 mL of tetrahydrofuran, and the resulting colorless suspension was stirred for ca. 15 min. Solid KCp^* (0.33 g, 1.9 mmol) was then added in several portions to the stirred mixture over 5 min. The mixture gradually became orange over ca. 10 min and was stirred overnight. Then, the dark orange mixture was centrifuged, the supernatant was filtered through a pipette packed with ca. 1 cm of filter paper, and the solvent was removed under reduced pressure. The resulting orange powder was washed three times with ca. 2 mL portions of hexanes to give 0.44 g (0.71 mmol, 75%) of **1-Gd** as a bright orange powder. Overnight storage of a concentrated THF solution of **1-Gd** at ambient temperature afforded orange crystals of **1-Gd·THF** which were suitable for X-ray diffraction studies. UV−vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) 276 (19 000). IR (ATR): a sharp absorbance at $\tilde{\nu}$ = 766 cm^{-1} was taken as indicative of the presence of the neutral bipyridine ligand as described below. ^{1}H NMR (600 MHz, benzene-D_6, 298 K): no signals were observed in the range of +150 to −150 ppm. μ_{eff} = 7.1 μ_B.

Synthesis of Cp^*_2Nd(bipy), 2-Nd. K/KI (1.12 g, 4.3 wt % K, 1.23 mmol) was added in one portion to a stirred solution of **1-Nd** (0.68 g, 1.12 mmol) in ca. 10 mL of diethyl ether at ambient temperature. The mixture immediately became dark brown/orange. After stirring for 1 h, the mixture was centrifuged and the supernatant was filtered through a pipette packed with ca. 1 cm of filter paper. The solvent was then removed from the supernatant under reduced pressure to give a dark brown powder. The powder was extracted in ca. 2 mL of toluene and the extract was centrifuged. The supernatant was filtered as above and the solvent was removed from the supernatant under reduced pressure to afford dark brown crystals of **2-Nd** (0.47 g, 74%). Crystals that were suitable for X-ray diffraction studies were grown from a concentrated solution of **2-Nd** in toluene that was stored overnight at ca. −35 °C. UV−vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) 262 (shoulder, 23 000), 390 (16 000), 490 (5900), 517 (6300). IR (ATR): a sharp absorbance at $\tilde{\nu}$ = 714 cm^{-1} was taken as indicative of the presence of the radical anionic bipyridine ligand as described below. ^{1}H NMR (600 MHz, benzene-D_6, 298 K): δ = 7.76 (s, 30H, CH_3 $\Delta\nu_{1/2}$ = 16 Hz), 7.22 (s, 2H CH (bipy)), −25.31 (s, 2H, CH (bipy)), −47.55 (s, 2H, (bipy)), −152.97 (s, 2H, CH (bipy)). ^{13}C NMR (151 MHz, benzene-D_6, 298 K): δ = 290.97 (s, CCH_3 (Cp^*)), −23.35 (q, CH_3 (Cp^*), J = 123.8 Hz). No signals for the bipyridyl carbons were found in the range of 400 to −200 ppm. μ_{eff} = 3.6 μ_B.

Synthesis of Cp^*_2Eu(bipy), 2-Eu. 2,2′-Bipyridine (0.12 g, 0.74 mmol) was added in one portion to a stirred, dark orange/red solution of $Cp^*_2Eu(THF)_2$ (0.42 g, 0.74 mmol) in ca. 10 mL of tetrahydrofuran at ambient temperature. The mixture immediately became dark brown. After stirring for 1 h, the solvent was removed under reduced pressure to afford 0.38 g (88%) of dark brown, crystalline needles, the identity of which was confirmed spectroscopically by comparison with the literature spectra.[33] A portion of this material was dissolved in ca. 2 mL of tetrahydrofuran, then the solution was filtered and deposited in a 20 mL vial beneath ca. 3 mL toluene. After standing overnight, a small amount of dark brown, crystalline blocks had grown which were suitable for X-ray diffraction studies. IR (ATR): a sharp absorbance at $\tilde{\nu}$ = 760 cm^{-1} was taken as indicative of the presence of the neutral bipyridine ligand.

Synthesis of Cp$_2$Gd(bipy), **2-Gd**.*[49] In a preparation analogous to that of **2-Nd**, K/KI (1.13 g, 4.3 wt % K, 1.24 mmol) was added in one portion to a stirred solution of **1-Gd** (0.70 g, 1.13 mmol) in ca. 10 mL of diethyl ether at ambient temperature. The mixture immediately became dark brown/orange. After stirring for 1 h, the mixture was centrifuged and the supernatant was filtered through a pipette packed with ca. 1 cm of filter paper. The solvent was then removed from the supernatant under reduced pressure to give a dark brown powder. The powder was extracted in ca. 2 mL of toluene and the extract was centrifuged. The supernatant was filtered as above and the solvent was removed from the supernatant under reduced pressure to afford 0.51 g (0.87 mmol, 77%) of **2-Gd** as dark brown crystals. Crystals that were suitable for X-ray diffraction studies were grown from a concentrated solution of **2-Gd** in toluene that was stored overnight at ca. −35 °C. IR (ATR): a sharp absorbance at $\tilde{\nu}$ = 720 cm^{-1} was taken as indicative of the presence of the radical anionic bipyridine ligand as described below. UV−vis: λ_{max}/nm (ε/M^{-1} cm^{-1}): 260 (shoulder, 19 000), 390 (14 000), 487 (5500), 519 (6800). ^{1}H NMR (600 MHz, benzene-D_6, 298 K): δ = −22.59 (s, $\Delta\nu_{1/2}$ = 3.3 kHz). ^{13}C NMR (100.5 MHz, C_6H_6, 298 K): no signals were detected in the range of 200 to −200 ppm. μ_{eff} = 7.1 μ_B.

Synthesis of K(crypt)[Cp$_2$Nd(bipy)], **3-Nd**.* K/KI (0.17 g, 4.3 wt % K, 0.19 mmol) was added in one portion to a stirred, room temperature solution of 2.2.2-cryptand (0.065 g, 0.17 mmol) in ca. 5 mL of tetrahydrofuran, and the blue mixture was stirred for 5 min. Solid **2-Nd** (0.10 g, 0.17 mmol) was then added in one portion to this mixture. The mixture immediately became dark green. After stirring for 1 h, the mixture was centrifuged and the supernatant was filtered through a pipette packed with ca. 1 cm of filter paper. The solvent was slowly removed under reduced pressure to afford a dark green, microcrystalline solid. The solid was washed twice with ca. 5 mL portions of hexane. Residual volatiles were removed from the microcrystalline solid under reduced pressure to afford 0.14 g (0.14 mmol, 83%) of dark green, microcrystalline **3-Nd**. Crystals that were suitable for X-ray diffraction studies were grown by overnight storage at ambient temperature of a concentrated solution of **3-Nd** in tetrahydrofuran layered beneath hexane. UV−vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) 390 (17 000), 420 (13 000). IR (ATR): a sharp absorbance at $\tilde{\nu}$ = 687 cm^{-1} was taken as indicative of the presence of the dianionic bipyridine ligand as described below. ^{1}H NMR (600 MHz, THF-D_8, 298 K): δ = 9.57 (d, 2H, CH (bipy)), 4.99 (s, 12H, CH_2 (crypt)), 4.85 (s, 12H, CH_2 (crypt)), 4.72 (s, 30H, CH_3 (Cp*)), 3.77 (s, 12H, CH_2 (crypt)), 2.00 (s, 2H, CH (bipy)), −9.51 (s, 2H, CH (bipy)), −47.38 (s, 2H, CH (bipy)). ^{13}C NMR (151 MHz, THF-D_8, 298 K): δ = 226.78 (s, CCH_3 (Cp*)), 149.57 (d, CH (bipy), J = 149.5 Hz), 140.23 (d, CH (bipy), J = 169.1 Hz), 94.56 (d, CH (bipy), J = 155.5 Hz), 80.11 (s, C−C (bipy)), 72.79 (t, CH_2 (crypt), J = 140.4 Hz), 69.83 (t, CH_2 (crypt), J = 140.4 Hz), 56.04 (t, CH_2 (crypt), J = 129.9 Hz), −14.83 (q, CH_3 (Cp*), J = 123.8 Hz). μ_{eff} = 3.2 μ_B.

Synthesis of [K(crypt)][Cp$_2$Sm(bipy)], **3-Sm**.* Cp*$_2$Sm(THF)$_2$ (0.41 g, 0.73 mmol) was added in one portion to a stirred, violet-colored mixture of K/KI (0.73 g (4.3 wt % K), 0.80 mmol), 2,2′-bipyridine (0.11 g, 0.73 mmol), and 2.2.2-cryptand (0.27 g, 0.73 mmol) in ca. 15 mL of tetrahydrofuran. The mixture immediately became dark green. After stirring for 1 h, the mixture was centrifuged and the supernatant was filtered through a pipette packed with ca. 1 cm of filter paper. The solvent was then removed under reduced pressure to give a dark green, almost black, microcrystalline solid. The solid was washed three times with ca. 2 mL portions of hexane and the residual solvent was then removed from the solid under reduced pressure to afford 0.64 g (0.64 mmol, 88%) of **3-Sm** as a dark green solid. Crystals suitable for X-ray diffraction studies were grown by overnight storage at ambient temperature of a concentrated solution of **3-Sm** in tetrahydrofuran layered beneath hexane. UV−vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) 389 (15 000), 420 (shoulder, 11 000). IR (ATR): a sharp absorbance at $\tilde{\nu}$ = 687 cm^{-1} was taken as indicative of the presence of the dianionic bipyridine ligand as described below. ^{1}H NMR (600 MHz, THF-D_8, 298 K): δ = 8.42 (d, 2H, CH (bipy)), 4.60 (m, 2H, CH (bipy)), 3.87 (s, 12H, CH_2 (crypt)), 3.80 (m, 12H, CH_2 (crypt)), 3.48 (m, 2H, CH (bipy)), 2.79 (m, 12H, CH_2 (crypt)), 1.27 (s, 30H, CH_3), −17.30 (s, 2H, CH (bipy)). ^{13}C NMR (151 MHz, THF-D_8): δ = 130.73 (s, C (bipy)), 125.74 (d, CH (bipy), J = 154.4 Hz), 114.59 (d, CH (bipy), J = 150.3 Hz), 113.13 (s, CCH_3 (Cp*)), 71.78 (t, CH_2 (crypt), J = 141.3 Hz), 68.87 (t, CH_2 (crypt), J = 140.5 Hz), 65.12 (d, CH (bipy), J = 168.2 Hz), 55.12 (t, CH_2 (crypt), J = 131.2 Hz), 20.22 (q, CH_3 (Cp*) J = 124.0 Hz). μ_{eff} = 1.5 μ_B.

Synthesis of [K(crypt)][Cp$_2$Eu(bipy)], **3-Eu**.* Cp*$_2$Eu(THF)$_2$ (0.33 g, 0.58 mmol) was added in one portion to a stirred, violet mixture of K/KI (0.58 g, 4.3 wt % K, 0.64 mmol), 2.2.2-cryptand (0.22 g, 0.58 mmol), and 2,2′-bipyridine (0.091 g, 0.58 mmol) in ca. 15 mL tetrahydrofuran. The mixture immediately became dark red/violet. After stirring for 1 h, the mixture was centrifuged and the supernatant was filtered through a pipette packed with ca. 1 cm of filter paper. The solvent was then removed under reduced pressure to give a dark red solid. The solid was washed three times with ca. 2 mL portions of hexane, and residual solvent was removed under reduced pressure to afford 0.50 g (0.50 mmol, 86%) of **3-Eu** as a dark red, microcrystalline solid. Crystals that were suitable for X-ray diffraction studies were grown by overnight storage at ambient temperature of a concentrated solution of **3-Eu** in tetrahydrofuran layered beneath hexane. UV−vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) 268 (shoulder, 27 000), 387 (16 000), 420 (shoulder, 11 000). IR (ATR): a sharp absorbance at $\tilde{\nu}$ = 708 cm^{-1} was taken as indicative of the presence of the radical anionic bipyridine ligand as described below. ^{1}H NMR (600 MHz, THF-D_8, 298 K): no signals were observed in the range of 200 to −200 ppm. μ_{eff} = 6.8 μ_B.

Synthesis of [K(crypt)][Cp$_2$Gd(bipy)], **3-Gd**.* K/KI (1.05 g, 4.3 wt % K, 1.15 mmol) was added in one portion to a stirred, room temperature solution of 2.2.2-cryptand (0.36 g, 0.96 mmol) in ca. 15 mL of tetrahydrofuran, and the blue mixture was stirred for 5 min. Solid **2-Gd** (0.56 g, 0.96 mmol) was then added in one portion to this dark blue mixture. The mixture immediately became dark green. After stirring for 1 h, the mixture was centrifuged and the supernatant was filtered through a pipette packed with ca. 1 cm of filter paper. The solvent was slowly removed under reduced pressure to afford a dark green, microcrystalline solid. The solid was washed twice with ca. 5 mL portions of hexane. Residual volatiles were removed from the microcrystalline solid under reduced pressure to afford 0.56 g (0.56 mmol, 58%) of dark green, microcrystalline **3-Gd**. Crystals that were suitable for X-ray diffraction studies were grown by overnight storage at ambient temperature of a concentrated solution of **3-Gd** in tetrahydrofuran layered beneath hexane. IR (ATR): a sharp absorbance at $\tilde{\nu}$ = 683 cm^{-1} was taken as indicative of the presence of the dianionic bipyridine ligand as described below. μ_{eff} = 7.1 μ_B.

Synthesis of [K(crypt)][Cp$_2$Yb(bipy)], **3-Yb**.* Cp*$_2$Yb(THF) (0.40 g, 0.78 mmol) was added in one portion to a stirred, violet mixture of K/KI (0.78 g, 4.3 wt % K, 0.86 mmol), 2.2.2-cryptand (0.29 g, 0.78 mmol), and 2,2′-bipyridine in ca. 15 mL of tetrahydrofuran. The mixture immediately became dark red/violet. After stirring for 1 h, the mixture was centrifuged and the supernatant was filtered through a pipette packed with ca. 1 cm of filter paper. The solvent was then removed under reduced pressure to give a dark red residue. The residue was washed three times with ca. 2 mL portions of hexane, and residual solvent was removed from the solid under reduced pressure to afford 0.66 g (0.65 mmol, 83%) of **3-Yb** as a dark red, microcrystalline solid. Crystals that were suitable for X-ray diffraction studies were grown from a concentrated solution of **3-Yb** in tetrahydrofuran layered beneath hexane. UV−vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) 250 (shoulder, 15 000), 380 (17 000), 520 (5000), 550 (5000). IR (ATR): a sharp absorbance at $\tilde{\nu}$ = 707 cm^{-1} was taken as indicative of the presence of the radical anionic bipyridine ligand as described below. ^{1}H NMR (600 MHz, THF-D_8): δ = 53.91 (br, 8H, CH (bipy)), 3.39 (s, 12H, CH_2 (crypt)), 3.36 (s, 12H, CH_2 (crypt, overlaps with signal at 3.39 ppm)), 2.95 (s, 30H, CH_3, (Cp*)), 2.40 (s, 12H, CH_2 (crypt)). ^{13}C NMR (151 MHz, THF-D_8): δ = 125.57 (s, CCH_3 (Cp*)), 73.21 (t, CH_2 (crypt), J = 141.8 Hz), 70.19 (t, CH_2 (crypt), J = 140.4 Hz), 56.09 (t, CH_2 (crypt), J = 132.4 Hz),

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-3.47 (q, CH_3 (Cp*) J = 120.9 Hz), no signals were observed for the bipyridyl radical anion in the region of +195 to −195 ppm. μ_{eff} = 2.4 μ_B.

Synthesis of [K(crypt)][Cp$_2$Nd(η^2-N_2Ph_2)],* ***4-Nd***. Azobenzene (0.037 g, 0.20 mmol) was added in one portion at ambient temperature to a stirred, dark green solution of **3-Nd** (0.20 g, 0.20 mmol) in ca. 4 mL of tetrahydrofuran. The solution immediately became dark brown/orange. After stirring overnight, the solvent was completely removed under reduced pressure to afford a sticky, brown residue. The residue was washed three times with ca. 3 mL portions of hexane. Residual volatile material was removed under reduced pressure to afford 0.16 g (0.16 mmol, 79%) of **4-Nd** as a light brown powder. Crystals that were suitable for X-ray diffraction studies were grown from a concentrated solution of **4-Nd** in tetrahydrofuran layered beneath hexane. UV−vis: λ_{max}/nm (ε/M^{-1} cm^{-1}) 284 (15 000), 429 (17 000), 520 (3300). ^{1}H NMR (600 MHz, THF-D_8): δ = 26.75 (s, 2H, CH (azobenzene)), 14.22 (s, 2H, CH (azobenzene)), 5.73 (s, 2H, CH (azobenzene)), 4.31 (s, 12H, CH_2 (crypt)), 4.24 (s, 12H, CH_2 (crypt)), 4.16 (s, 2H, CH, (azobenzene)), 3.22 (s, 12H, CH_2 (crypt)), 2.93 (s, 30H, CH_3 (Cp*)), −9.15 (s, 2H, CH (azobenzene)). ^{13}C NMR (151 MHz, THF-D_8): δ = 132.56 (d, CH (azobenzene), J = 148.0 Hz), 122.22 (d, CH (azobenzene), J = 151.0 Hz), 120.84 (d, CH (azobenzene), J = 155.5 Hz), 114.82 (d, CH (azobenzene) J = 161.6 Hz), 72.04 (t, (CH_2 (crypt)), J = 141.0 Hz), 69.13 (t, CH_2 (crypt), J = 139.5 Hz), 55.38 (t, CH_2 (crypt), J = 131.4 Hz), −18.92 (q, CH_3 (Cp*), J = 123.8 Hz). Note: the singlet signals corresponding to the CN carbons of azobenzene and the CCH_3 carbons of Cp* were not found in the range of 200 to −200 ppm. μ_{eff} = 3.0 μ_B.

Alternate Synthesis of ***4-Nd***. Azobenzene (0.064 g, 0.35 mmol) and 2.2.2-cryptand (0.13 g, 0.36 mmol), were dissolved in ca. 10 mL of tetrahydrofuran at ambient temperature. K/KI (0.36 g (4.3 wt %), 0.40 mmol) was added in one portion to this stirred solution, and the mixture was stirred for 10 min. Solid Cp*$_2$Nd(bipy) (**2-Nd**, 0.20 g, 0.35 mmol) was then added to this mixture in one portion and the mixture was then stirred for 2 h. The mixture was centrifuged and the supernatant was filtered through a pipette packed with ca. 1 cm of filter paper. Removal of the solvent from the supernatant under reduced pressure afforded a brown residue. The residue was washed twice with 3 mL portions of hexane. The residue was then dissolved in ca. 2 mL of tetrahydrofuran and the solution was then filtered as above and deposited beneath ca. 2 mL of hexane and allowed to stand overnight to afford 0.18 g (0.18 mmol, 51%) of dark orange crystals of **4-Nd**.

Synthesis of [K(crypt)][Cp$_2$Sm(η^2-N_2Ph_2)],* ***4-Sm***. Azobenzene (0.028 g, 0.15 mmol) was added in one portion at ambient temperature to a stirred, dark green solution of **3-Sm** (0.15 g, 0.15 mmol) in ca. 4 mL of tetrahydrofuran. The solution immediately became dark brown/orange. The mixture was stirred overnight. The solvent was removed under reduced pressure, and the brown residue was washed three times with 2 mL portions of hexanes. Residual volatiles were then removed under reduced pressure to afford 0.12 g (0.12 mmol, 79%) of **4-Sm** as a brown powder. Dark orange/brown crystals suitable for X-ray diffraction studies were grown from overnight storage of a concentrated solution **4-Sm** in THF layered beneath hexane. ^{1}H NMR (600 MHz, THF-D_8): δ = 12.41 (s, 2H, CH (azobenzene)), 7.84 (s, 2H, CH (azobenzene)), 6.50 (t, 2H, CH (azobenzene)), 4.94 (s, 2H, CH, (azobenzene)), 3.76 (s, 12H, CH_2 (crypt)), 3.72 (s, 12H, CH_2 (crypt)), 2.73 (s, 12H, CH_2 (crypt)), 0.93 (s, 30H, CH_3 (Cp*)), −0.24 (s, 2H, CH (azobenzene)). ^{13}C NMR (151 MHz, THF-D_8): δ = 161.20 (s, C−N (azobenzene)), 131.74 (d, CH (azobenzene), J = 149.5 Hz), 129.00 (d, CH (azobenzene), J = 149.2 Hz), 113.68 (s, C−CH_3 (Cp*)), 111.53 (d, (CH (azobenzene)), J = 148.4 Hz), 109.51 (d, CH (azobenzene), J = 163.1 Hz), 103.95 (d, CH (azobenzene), J = 156.8 Hz), 72.88 (t, CH_2 (crypt), J = 141.8 Hz), 69.78 (t, CH_2 (crypt), J = 142.3 Hz), 55.76 (t, CH_2 (crypt), J = 132.3 Hz), 17.96 (q, CH_3 (Cp*), J = 124.3 Hz). μ_{eff} = 1.6 μ_B.

Alternate Synthesis of ***4-Sm***. Azobenzene (0.065 g, 0.36 mmol) and 2.2.2-cryptand (0.13 g, 0.36 mmol) were dissolved in ca. 5 mL of tetrahydrofuran at ambient temperature. K/KI (0.36 g (4.3 wt %), 0.40 mmol) was added in one portion to this stirred solution. Cp*$_2$Sm(THF)$_2$ (0.20 g, 0.35 mmol) was then added to this dark brown mixture, and stirring was continued for 1 h. Then, the mixture was centrifuged and the dark brown/orange supernatant was filtered through a pipette packed with ca. 1 cm of filter paper. The solvent was then completely removed under reduced pressure to afford a dark brown, microcrystalline residue. This residue was then washed with ca. 3 mL of hexane and residual volatiles were removed from the solid material under reduced pressure to afford 0.25 g (0.25 mmol, 68%) of dark brown, microcrystalline solid. The ^{1}H and ^{13}C NMR spectra of this material were identical to those of **4-Sm** as prepared from **3-Sm** and azobenzene (see the Supporting Information (SI) for spectra).

Synthesis of [K(crypt)][Cp$_2$Yb(η^2-N_2Ph_2)],* ***4-Yb***. Azobenzene (0.036 g, 0.20 mmol) was added in one portion at ambient temperature to a stirred, dark red solution of **3-Yb** (0.20 g, 0.20 mmol) in ca. 4 mL of tetrahydrofuran. The solution immediately became dark brown/orange and was stirred for 1 h. The solvent was removed under reduced pressure, and the brown residue was washed three times with 1 mL portions of hexanes. The residue was then extracted in ca. 4 mL of tetrahydrofuran and filtered through a pipette packed with ca. 1 cm of filter paper. The solution was then layered beneath ca. 2 mL of hexane. This mixture was stored overnight at ambient temperature to afford 0.074 g (0.071 mmol, 36%) of large, dark orange/brown crystals of **4-Yb** from which a crystal suitable for X-ray diffraction studies was selected. ^{1}H NMR (600 MHz, THF-D_8): δ = 90.93 (s, 2H, CH (azobenzene)), 26.64 (s, 2H, CH (azobenzene)), 8.22 (s, 30H, CH_3 (Cp*)), 0.81 (s, 12H, CH_2, (crypt)), 0.74 (s, 12H, CH_2 (crypt)), 0.52 (d, 2H, CH (azobenzene)), −0.09 (s, 12H, CH_2 (crypt)), −10.48 (s, 2H, CH (azobenzene)), −70.61 (s, 2H, CH (azobenzene)). ^{13}C NMR (151 MHz, THF-D_8): δ = 123.23 (d, CH (azobenzene), J = 154.0 Hz), 122.59 (d, CH (azobenzene), J = 128.4 Hz), 94.69 (s, C−N (azobenzene)), 90.95 (d, CH (azobenzene), J = 155.5 Hz), 90.53 (d, CH (azobenzene), J = 137.4 Hz), 68.42 (t, CH_2 (crypt), J = 141.9 Hz), 65.64 (t, CH_2 (crypt), J = 140.5 Hz), 51.98 (t, CH_2 (crypt), J = 130.03 Hz), −8.25 (q, CH_3 (Cp*), J = 125.3 Hz), −80.16 (s, CCH_3 (Cp*)). μ_{eff} = 3.9 μ_B.

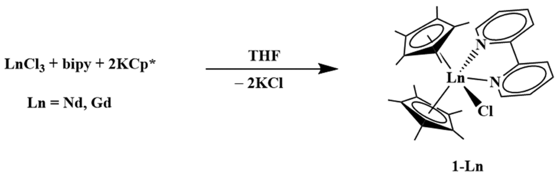
[K(crypt)][Cp$_2$Nd(S_5)],* ***5-Nd***. Elemental sulfur (0.032 g, 1.0 mmol) was added in one portion to a stirred, dark green solution of **3-Nd** (0.20 g, 0.20 mmol) in ca. 10 mL of tetrahydrofuran. The mixture immediately became light green and was stirred overnight. The solvent was removed under reduced pressure to give a sticky, brown residue. The residue was washed three times with ca. 2 mL portions of hexane. Residual volatiles were removed under reduced pressure to afford 0.15 g (0.15 mmol, 76%) of **5-Nd** as an olive-green powder. Light green crystals which were suitable for X-ray diffraction studies were grown from a concentrated solution of this powder in tetrahydrofuran which was layered beneath hexane and stored overnight at ambient temperature. ^{1}H NMR (600 MHz, THF-D_8): δ = 8.58 (s, 30H, CH_3 (Cp*)), 3.32 (s, 12H, CH_2 (crypt)), 3.27 (s, 12H, CH_2 (crypt)), 2.31 (s, 12H, CH_2 (crypt)). ^{13}C NMR (151 MHz, THF-D_8): δ = 71.90 (t, CH_2 (crypt), J = 140.4 Hz), 69.00 (t, CH_2 (crypt), J = 140.4 Hz), 55.08 (t, CH_2 (crypt), J = 131.4 Hz), −11.32 (q, CH_3 (Cp*), J = 116.3 Hz).

[K(crypt)][Cp$_2$Sm(S_5)],* ***5-Sm***. Elemental sulfur (0.032 g, 1.0 mmol) was added in one portion to a stirred, dark green solution of **3-Sm** (0.20 g, 0.20 mmol) in ca. 10 mL of tetrahydrofuran. The mixture immediately became brown and was stirred overnight. The solvent was removed under reduced pressure to give a sticky, brown residue. The residue was washed three times with ca. 2 mL portions of hexane. Residual volatiles were removed under reduced pressure to afford 0.14 g (0.14 mmol, 70%) of [K(crypt)][Cp*$_2$Sm(S_5)], **5-Sm**, as a light yellow/brown powder. Dark yellow crystals which were suitable for X-ray diffraction studies were grown from a concentrated solution of this powder in THF which was layered beneath hexane and stored overnight at ambient temperature. ^{1}H NMR (600 MHz, THF-D_8): δ = 3.57 (s, 12H, CH_2 (crypt), overlaps solvent resonance), 3.52 (m, 12H, CH_2 (crypt)), 2.54 (m, 12H, CH_2 (crypt)), 1.31 (s, 30H, CH_3 (Cp*)). ^{13}C NMR (151 MHz, THF-D_8): δ = 109.87 (s, CCH_3 (Cp*)), 71.30 (t, CH_2 (crypt), J = 140.4 Hz), 68.45 (t, CH_2 (crypt), J = 140.4 Hz, overlaps solvent resonance), 54.73 (t, CH_2 (crypt), J = 134.4 Hz), 17.73 (q, CH_3 (Cp*), J = 123.8 Hz). μ_{eff} = 1.5 μ_B.

X-ray Crystallography. Crystals of **1**−**5** were removed from the crystallization vial in an argon-filled glovebox and then covered in Paratone oil. Suitable crystals were selected, mounted on a nylon loop, and then immediately placed in the cold nitrogen stream of the diffractometer. Data were collected at 93 K (**1-Nd**, **2-Gd**, **2-Nd**, **2-Eu**, **3-Nd**, **3-Yb**, **4-Nd**, **4-Sm**, **5-Nd**, **5-Sm**) or 133 K (**1-Gd**, **3-Sm**, **3-Eu**, **3-Gd**, **4-Yb**) using Mo Kα radiation (λ = 0.71073 Å; **1-Nd**, **1-Gd**, **2-Gd**, **3-Nd**, **3-Sm**, **3-Eu**, **3-Gd**, **3-Yb**, **4-Yb**, **5-Nd**, **5-Sm**) or Cu Kα radiation (λ = 1.54178 Å; **2-Nd**, **2-Eu**, **4-Nd**, **4-Sm**) on a Bruker Apex II diffractometer. Absorption corrections were applied using SADABS.[50] The structures were solved by intrinsic phasing using SHELXT[51] and refined by least-squares methods using SHELXL[52] within the Olex2 GUI.[53] All nonhydrogen atoms were refined anisotropically.

■ RESULTS AND DISCUSSION

Cp*$_2$LnCl(bipy), 1-Ln. The **1-Nd** and **1-Gd** complexes were prepared in a one-pot reaction of $LnCl_3$ with 2 equiv of KCp* and 1 equiv of bipy in THF, eq 2. The best yields of these syntheses, 75−81%, were obtained when the $LnCl_3$ and bipy were combined in THF and stirred for 10−15 min before the addition of solid KCp* to the mixture. After stirring overnight, the mixtures were centrifuged to separate colorless precipitates which are presumably KCl. The supernatants were filtered and the solvent was removed from the supernatant under reduced pressure to afford orange residues. These solid materials were washed with hexane to afford orange, microcrystalline **1-Nd** and **1-Gd**.



(2)

The structure of **1-Nd** is shown in Figure 1 and selected bond distances and angles for **1-Ln** are given in Table 1. The table includes the C_{bipy}−C'_{bipy} distance, which has been shown previously to be a useful indicator of the oxidation state of the bipyridine ligand (neutral, radical anionic, or dianionic).[32,33,54,55] Thus, the C_{bipy}−C'_{bipy} distances of ca. 1.49 Å ($bipy^0$), 1.43 Å ($bipy^{1-}$), and 1.38 Å ($bipy^{2-}$) have been used here as one indicator of the oxidation state of the bipy ligand and thereby the lanthanide ion. For both **1-Nd** and **1-Gd**, this bond distance is consistent with neutral bipyridine and the complexes contain the metals in their most stable +3 oxidation states. The structures of these complexes are essentially analogous to the iodide complexes Cp*$_2$MI(bipy) (M = Ce, U) previously described by Ephritikhine and co-workers[54] and are thus not discussed further.

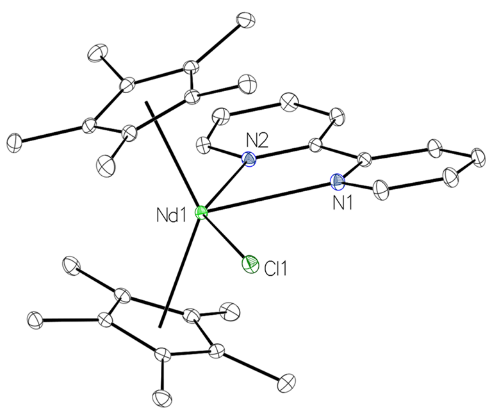
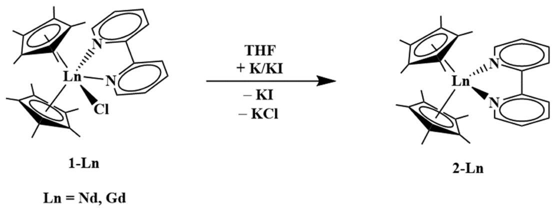


Figure 1. Molecular structure of Cp*$_2$Nd(bipy)(Cl), **1-Nd**. Thermal ellipsoids are shown at 30% probability. For clarity, hydrogen atoms and an unbound solvent of crystallization (THF) are not shown. The structure of **1-Gd** is isomorphous.

Cp*$_2$Ln(bipy), 2-Ln. The orange microcrystalline solids isolated from the syntheses of **1-Nd** and **1-Gd** were stirred in diethyl ether and treated with 1.1 equiv of 4.3 wt % K/KI.[48] KC_8 can also be used as the reductant in this reaction, but in our hands, K/KI consistently provided cleaner products in higher yields. The solvent was then removed under reduced pressure and the residue was extracted in toluene. Filtration and removal of solvent from the filtrate afforded dark brown/orange crystals of Cp*$_2$Ln(bipy), **2-Ln**, in 74−77% yield, which were identified by X-ray crystallography, eq 3, Figure 2.



(3)

Since structurally characterized examples of the neutral Cp*$_2$Ln(bipy) complexes are known only for samarium[32] and ytterbium,[33] we collected structural data of the complex **2-Eu** to compare with the other compounds. A representative molecular structure of this group, **2-Gd**, is shown in Figure 2, and selected bond distances and angles are provided in Table 2.

2-Nd and **2-Gd** have very similar geometries about the metal although they are not isomorphous. The complexes possess identical C_{bipy}−C'_{bipy} bond distances of 1.427(4) Å, indicating that the bipyridyl ligand has been reduced by one electron in both complexes. Consistent with this finding, the Ln−N distances in **2-Nd** (2.463(2) and 2.456(2) Å) and **2-Gd** (2.408(1) and 2.389(1) Å) are significantly shorter than those of **1-Nd** (2.6182(12) and 2.7305(12) Å) and **1-Gd** (2.6450(16) and 2.5426(16) Å). These structural data indicate that **2-Nd** and **2-Gd** have the same Cp*$_2$Ln^{III}(bipy) composition as the previously reported **2-Sm** and **2-Yb**, which were found to consist of Ln(III) metal ions and $(bipy)^{1-}$ ligands.[32,33]

Although **2-Eu** is isomorphous with **2-Gd**, its molecular structure is somewhat different from that of **2-Nd** and **2-Gd**. The C_{bipy}−C'_{bipy} distance in **2-Eu** is 1.492(4) Å, consistent with a neutral state of the bipy ligand. In agreement with this, the Eu−N distances (2.594(2) and 2.658(2) Å) are substantially longer than the analogous distances in **2-Nd** (2.463(2) and 2.456(2) Å) and **2-Gd** (2.408(1) and 2.389(1) Å), which is consistent with a dative interaction between the neutral bipy ligand and Eu. These structural characteristics therefore indicate that **2-Eu** has a formula of Cp*$_2$Eu^{II}($bipy^0$). This finding agrees with the experimental magnetic moment of **2-Eu** (7.4 μ_B, 300 K) determined by Andersen and co-workers, which is also indicative of the presence of Eu(II) in the complex **2-Eu**.[33]

[K(crypt)][Cp*$_2$Ln(bipy)], 3-Ln. Treatment of THF solutions of **2-Ln**, where Ln = Nd, Gd, Sm, Eu, and Yb, with 1 equiv of 2.2.2-cryptand (crypt) and a slight excess (1.1 equiv) of 4.3 wt % K/KI resulted in the formation of intensely colored solutions of **3-Ln**, eq 4. These were green for **3-Nd**, **3-Gd**, and **3-Sm** and red/violet for **3-Eu**, **3-Yb**. The residues isolated from these solutions were repeatedly washed with hexane to afford **3-Ln** in 58−83% yield. As with the preparation of **2-Ln**, KC_8 can also be used as the reductant to prepare **3-Ln**, but in our hands, higher yields were obtained when K/KI was used. While this method was effective for Ln = Nd, Sm, Eu, Gd, and Yb, we found that for Ln = Sm, Eu, and Yb, **3-Ln** could be prepared more simply and in

Table 1. Selected Bond Distances (Å) and Angles (deg) in 1-Ln Complexes

	Ln−C (avg.)	Ln−Cp_{cent}	Ln−N	Ln−Cl	C_{bipy}−C'_{bipy}	Cp_{cent}−Ln−Cp_{cent}
Cp^*_2NdCl(bipy) (**1-Nd**)	2.7955(5)	2.5171(7), 2.5248(7)	2.6182(12), 2.7305(12)	2.7403(4)	1.485(2)	135.62(2)
Cp^*_2GdCl(bipy) (**1-Gd**)	2.7426(6)	2.4715(11), 2.4635(12)	2.6450(16), 2.5426(16)	2.6889(6)	1.479(3)	136.95(5)

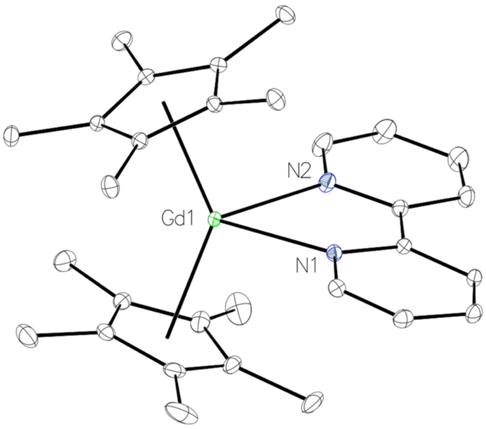


Figure 2. Molecular structure of Cp^*_2Gd(bipy), **2-Gd**. Thermal ellipsoids are shown at 30% probability. For clarity, hydrogen atoms are not shown.

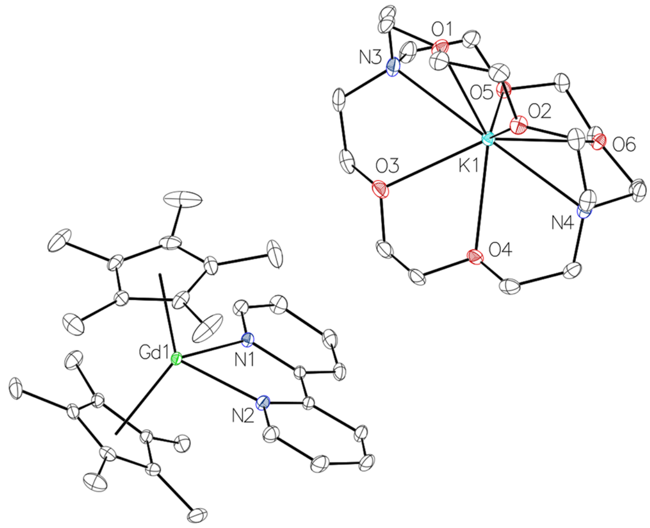
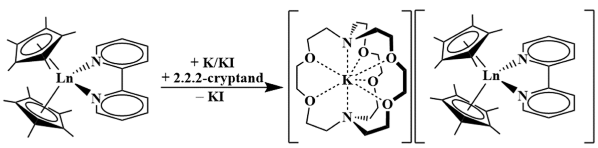


Figure 3. Molecular structure of [K(crypt)][Gd(C_5Me_5)$_2$(bipy)] (**3-Gd**). Thermal ellipsoids are shown at 30% probability. For clarity, hydrogen atoms are not shown. The structures of **3-Nd**, **3-Sm**, **3-Eu**, and **3-Yb** are isomorphous.

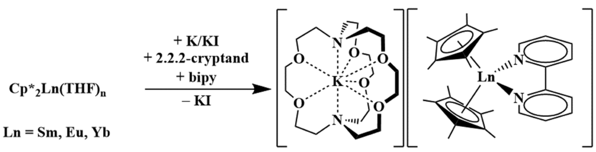
higher overall yield by treating a mixture of K/KI, bipy, and 2.2.2-cryptand with $Cp^*_2Ln(THF)_n$, eq 5. Large crystals of **3-Ln** which were suitable for X-ray diffraction studies were grown from concentrated THF solutions of **3-Ln** layered beneath hexane. A representative structure, **3-Gd**, is shown in Figure 3, and selected bond distances and angles of **3-Ln** are provided in Table 3.



(4)

2-Ln **3-Ln**

Ln = Nd, Sm, Eu, Gd, Yb



(5)

Ln = Sm, Eu, Yb

3-Ln

Complexes **3-Nd**, **3-Sm**, and **3-Gd** have C_{bipy}−C'_{bipy} distances of 1.385(3), 1.383(3), and 1.383(3) Å, respectively, which indicates that the bipy ligand has been reduced by two electrons to the $(bipy)^{2-}$ state. The Ln−N distances in these complexes (**3-Nd**: 2.3876(16) and 2.3940(16) Å, **3-Sm**: 2.3568(19) and 2.3600(16) Å, **3-Gd**: 2.3387(16) and 2.3345(16) Å) are significantly shorter than those of the analogous **2-Ln** complexes. The structural features therefore indicate that these complexes are of the form $[Cp^*_2Ln^{III}(bipy)]^{1-}$.

Complexes **3-Eu** and **3-Yb** possess C_{bipy}−C'_{bipy} distances of 1.423(3) and 1.4258(19) Å, respectively, which are consistent with the presence of a bipyridyl ligand that is monoanionic in these complexes, thus they can be described by the formula $[Cp^*_2Ln(bipy)]^{1-}$. However, it should be noted that Andersen and co-workers have shown in numerous studies that a multiconfigurational ground state description is appropriate for complexes of Cp^*_2Yb with a variety of bipyridines so this must be considered a limiting form of this complex.[33−39] The Eu−N distances in **3-Eu** (2.5730(19) and 2.5758(19) Å) are slightly shorter than those found in **2-Eu** (2.594(2) and 2.658(2) Å) which also contains a Eu(II) ion. In contrast, the Yb−N distances in **3-Yb** (2.4380(12) and 2.4330(12) Å) are ca. 0.1 Å longer than those previously reported for **2-Yb** (2.32 Å) which contains Yb(III) ions. This longer distance is expected for Yb(III) vs Yb(II) and indicates that ytterbium is reduced in preference to the bipy ligand when **2-Yb** is treated with potassium. These data trend well with the reduction potentials for the +3/+2 redox couple of these metals,[56] which show that Eu(III) and Yb(III) are the most easily reduced among these metal ions due to their favorable half-filled or closed-shell

Table 2. Selected Bond Distances (Å) and Angles (deg) in 2-Ln Complexes

	Ln−C (avg.)	Ln−Cp_{cent}	Ln−N	C_{bipy}−C'_{bipy}	Cp_{cent}−Ln−Cp_{cent}
Cp^*_2Nd(bipy) (**2-Nd**)	2.7518(9)	2.4757(13), 2.4718(12)	2.463(2), 2.456(2)	1.427(4)	138.03(4)
Cp^*_2Sm(bipy) (**2-Sm**)[32]	2.727(1)	2.447(1)	2.427(3), 2.436(3)	1.429(4)	137.87(6)
Cp^*_2Eu(bipy) (**2-Eu**)	2.815(1)	2.5404(12), 2.5480(13)	2.594(2), 2.658(2)	1.492(4)	141.15(4)
Cp^*_2Gd(bipy) (**2-Gd**)	2.733(1)	2.4121(8), 2.4073(7)	2.4122(9), 2.4074(9)	1.427(2)	138.89(3)
Cp^*_2Yb(bipy) (**2-Yb**)[33]	2.62	2.34 (avg.)	2.32 (avg.)	1.434	139.89(18)
					138.83(16)

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Table 3. Selected Bond Distances (Å) and Angles (deg) in 3-Ln Complexes

	Ln−C (avg.)	$Ln-Cp_{cent}$	Ln−N	$C_{bipy}-C'_{bipy}$	$Cp_{cent}-Ln-Cp_{cent}$
$[Cp^*_2Nd(bipy)]^{1-}$ (**3-Nd**)	2.7901(6)	2.5077(8), 2.5260(9)	2.3876(16), 2.3940(16)	1.385(3)	134.96(3)
$[Cp^*_2Sm(bipy)]^{1-}$ (**3-Sm**)	2.7573(6)	2.4878(9), 2.4756(9)	2.3568(19), 2.3600(16)	1.383(3)	135.12(3)
$[Cp^*_2Eu(bipy)]^{1-}$ (**3-Eu**)	2.8391(6)	2.5692(10), 2.5764(10)	2.5730(19), 2.5758(19)	1.423(3)	138.07(3)
$[Cp^*_2Gd(bipy)]^{1-}$ (**3-Gd**)	2.7328(6)	2.4478(9), 2.4608(9)	2.3387(16), 2.3345(16)	1.383(3)	135.17(3)
$[Cp^*_2Yb(bipy)]^{1-}$ (**3-Yb**)	2.7374(5)	2.4524(7), 2.4557(7)	2.4380(12), 2.4330(12)	1.4258(19)	138.05(2)

electron configurations, respectively, upon reduction to the +2 oxidation state. Additionally, given that the europium ion in **2-Eu** is in the +2 oxidation state, it is expected that the bipyridyl ligand would be reduced in preference to the metal when **2-Eu** is reduced to **3-Eu**.

Infrared Spectroscopy of 1-Ln, 2-Ln, and 3-Ln. Thorough vibrational spectroscopic studies of bipy complexes of the first-row transition metals were carried out by Nakamoto and co-workers in the early 1970s.[57] This work indicated that neutral bipyridine could be distinguished from the $(bipy)^{1-}$ radical anion which has a diagnostic absorbance between 900 and 1000 cm^{-1}. More recent work by Goicoechea and co-workers on alkali metal salts of radical anionic and dianionic bipy[58] showed that the spectrum of $(bipy)^{2-}$ had strong absorbances at 1560 and 1590 cm^{-1} and several absorbances between 800 and 900 cm^{-1} that are not present in the spectra of the neutral bipy or its radical anion.

The vibrational spectra of the bipy complexes in this study match these literature assignments based on the conclusions about the bipy oxidation state from the X-ray diffraction data. However, in this rare-earth metal metallocene series, some additional IR absorptions appear to be characteristic of the state of the bipy ligand. For example, the spectra of complexes **1-Nd**, **1-Gd**, and **2-Eu**, each of which contain a neutral bipyridine ligand based on the X-ray data, show intense absorbances at 766, 765, and 760 cm^{-1}, respectively. This absorbance is absent in the spectra of complexes **2-Nd**, **2-Gd**, **3-Eu**, and **3-Yb**, which contain the radical anionic $(bipy)^{1-}$ ligand. In these complexes, strong absorbances were observed at 714 (**2-Nd**), 720 (**2-Gd**), and 708 cm^{-1} (**3-Eu** and **3-Yb**). Neither of these characteristic absorbances were apparent in the spectra of complexes **3-Nd**, **3-Sm**, and **3-Gd**, which contain the dianionic $(bipy)^{2-}$ ligand and have strong absorbances at 687 (**3-Nd**, **3-Sm**) and 683 cm^{-1} (**3-Gd**). While assignment of these absorbances is not possible without further analysis due to the complexity of the spectra in this region, these absorbances have proven useful in identifying and determining the nature of the bipyridyl ligand (and thereby the metal ion) in these complexes.

Reactivity of $[Cp^*_2Ln(bipy)]^{1-}$ (3-Ln). Our goal at the outset of this study was to develop monometallic lanthanide complexes that can reduce small molecules by two electrons. Neutral uranium and thorium complexes of the form $(C_5R_5)_2An(bipy)$ (An = Th, U; R = H, alkyl, silyl) have been shown to facilitate transformations of this kind to form products wherein the metal is in the +4 oxidation state.[28,29] Since the +4 oxidation state is not as readily accessible for most of the lanthanides, the analogous lanthanide complexes $Cp^*_2Ln^{III}(bipy)$, **2-Ln**, do not undergo such reactivity. The anionic complexes $[Cp^*_2Ln(bipy)]^{1-}$, **3-Ln**, however, have the necessary electrons to effect two-electron reductions to form Ln(III) products.

Reactions of 3-Ln with Azobenzene. Treatment of a THF solution of **3-Sm** with one equiv of azobenzene resulted in an immediate color change of the solution from dark green to dark orange/brown. After stirring at room temperature for 1 h, recrystallization by layering a THF solution of the brown residue beneath hexane afforded dark orange crystals of [K(crypt)]-$[Cp^*_2Sm(\eta_2\text{-}N_2Ph_2)]$, **4-Sm**, eq 6, the molecular structure of which is shown in Figure 4. The structural data are consistent with the presence of Sm(III) and a $(N_2Ph_2)^{2-}$ dianion. The N1−N2 distance of 1.456(4) is identical within experimental error to the single-bond N−N distance in hydrazine (N_2H_4, N−N = 1.449(2) Å) as determined by gas electron diffraction.[59] The N−N distance in **4-Sm** is longer than the 1.32(1) and 1.39(1) Å N−N distances in $Cp^*_2Sm(N_2Ph_2)(THF)$, which contains a $(N_2Ph_2)^{1-}$ monoanion.[60] The 2.4740(15) and 2.4667(16) Å $Sm-Cp_{cent}$ distances are similar to the $Sm-Cp_{cent}$ distances of 2.4878(9) and 2.4756(9) Å in **3-Sm** and other Sm(III) metallocenes[61] and are much shorter than those of Sm(II) complexes, e.g., the 2.600(4) Å average distance in $Cp^*_2Sm(THF)_2$.[62] The 2.315(3) and 2.282(3) Å Sm−N distances are shorter than the 2.3568(19) and 2.3600(16) Å distances in **3-Sm**, and substantially shorter than the average Sm−N distance of 2.417(5) Å in $Cp^*_2Sm(N_2Ph_2)(THF)$.[60]

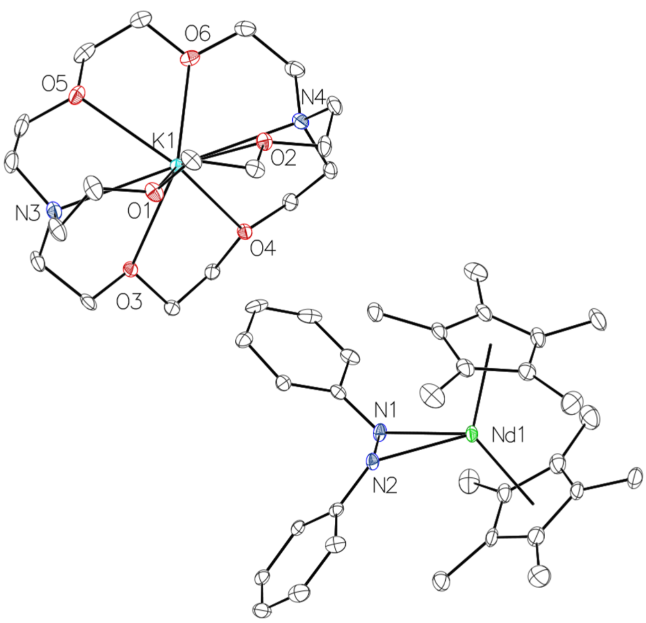

Figure 4. Molecular structure of $[Cp^*_2Nd(\eta^2\text{-}N_2Ph_2)][K(crypt)]$ (**4-Nd**) with thermal ellipsoids drawn at 30% probability. For clarity, hydrogen atoms and a solvent molecule of crystallization (THF) are not shown. The structures of **4-Sm** and **4-Yb** are isomorphous.

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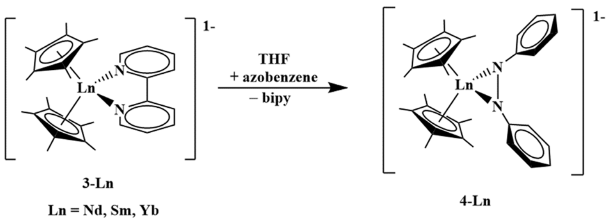
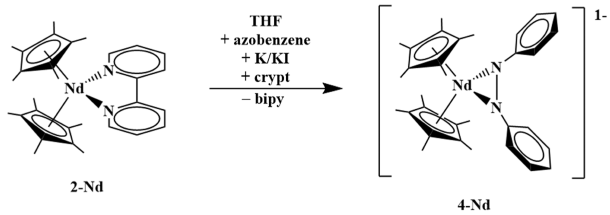
Table 4. Selected Bond Distances (Å) and Angles (deg) in 4-Ln Complexes

	Ln−C (avg.)	Ln−Cp_{cent}	Ln−N	N1−N2	Cp_{cent}−Ln−Cp_{cent}
$[Cp^*_2Nd(\eta^2\text{-}N_2Ph_2)]^{1-}$ (**4-Nd**)	2.779(1)	2.5103(17), 2.5021(18)	2.299(3), 2.342(3)	1.450(4)	136.27(6)
$[Cp^*_2Sm(\eta^2\text{-}N_2Ph_2)]^{1-}$ (**4-Sm**)	2.748(1)	2.4667(16), 2.4740(15)	2.315(3), 2.282(3)	1.456(4)	136.42(5)
$[Cp^*_2Yb(\eta^2\text{-}N_2Ph_2)]^{1-}$ (**4-Yb**)	2.6412(6)	2.3480(8), 2.3535(8)	2.1883(14), 2.2263(14)	1.4633(19)	136.12(3)



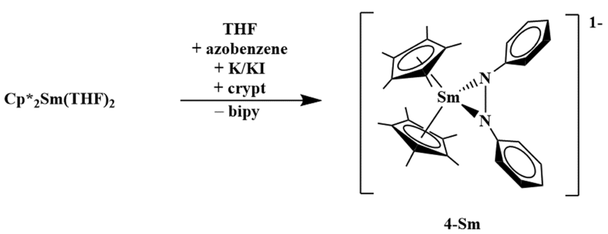
(6)



(8)

Significantly, this two-electron azobenzene reduction reactivity also extended to **3-Nd** and **3-Yb** in reactions that afforded the complexes **4-Nd** and **4-Yb**, the structures of which are isomorphous with **4-Sm**. Selected structural metrics of the **4-Ln** complexes are provided in Table 4. These data show that, irrespective of the oxidation state of the lanthanide in **3-Ln**, azobenzene has been reduced by two electrons to afford a $(N_2Ph_2)^{2-}$ ligand in **4-Ln**. This result contrasts with previous work from this laboratory wherein the one-electron reductant $Cp^*_2Sm(THF)_2$ was shown to react in a 1:1 stoichiometry with azobenzene to form $Cp^*_2Sm(N_2Ph_2)(THF)$ which contains the $(N_2Ph_2)^{1-}$ monoanion. Alternatively, $Cp^*_2Sm(THF)_2$ reacts with azobenzene in a 2:1 ratio to form $(Cp^*_2Sm^{III})(N_2Ph_2)(Sm^{III}Cp^*_2)$, in a reaction of the type in eq 1. Surprisingly, efforts to prepare **4-Gd** resulted only in the isolation of [K(crypt)][N_2Ph_2] (see the SI for a structural description).

It was apparent that **4-Ln** might be prepared by a different route for the metals for which a $Cp^*_2Ln(THF)_n$ complex is readily accessible i.e., samarium, europium, and ytterbium. To test this hypothesis, $Cp^*_2Sm(THF)_2$ was added to a THF solution of [K(crypt)][N_2Ph_2] (prepared from azobenzene, 2.2.2-cryptand, and K/KI), which cleanly afforded **4-Sm** in 68% yield as confirmed by ^1H and ^{13}C NMR spectroscopy, eq 7. In this case, the $(N_2Ph_2)^{2-}$ product is formed by the one-electron reduction of the $(N_2Ph_2)^{1-}$ starting material by the Sm(II) ion. Given this stepwise reduction of azobenzene, it was conceivable that **2-Ln** could display one-electron reduction reactivity similar to that of $Cp^*_2Sm(THF)_2$ as shown in eq 7. Indeed, addition of **2-Nd** to solution of [K(crypt)][N_2Ph_2], eq 8, afforded **4-Nd** in 51% yield, showing the flexibility of the Cp^*_2Ln(bipy) scaffold to be used as a one- or two-electron reductant depending on whether the neutral substrate or anionic mono-reduced substrate salt is used, respectively.



(7)

*Reactions of **3-Ln** with Sulfur.* Treatment of a solution of either **3-Nd** or **3-Sm** in tetrahydrofuran with five equivalents of elemental sulfur afforded [K(crypt)][$Cp^*_2Ln(S_5)$], **5-Ln**, eq 9. This reactivity contrasts with the reaction between $Cp^*_2Sm(THF)_2$ and elemental sulfur, which reacts variably depending on the stoichiometry to give the bridging sulfur complexes $[Cp^*_2Sm(THF)]_2(\mu\text{-}S)$ or $(Cp^*_2Sm)_2(S_3)(THF)$ in reactions of the type shown in eq 1.[63] The molecular structure of **5-Nd**, which is isomorphous with that of **5-Sm**, is shown in Figure 5, and selected structural metrics are provided in Table 5.

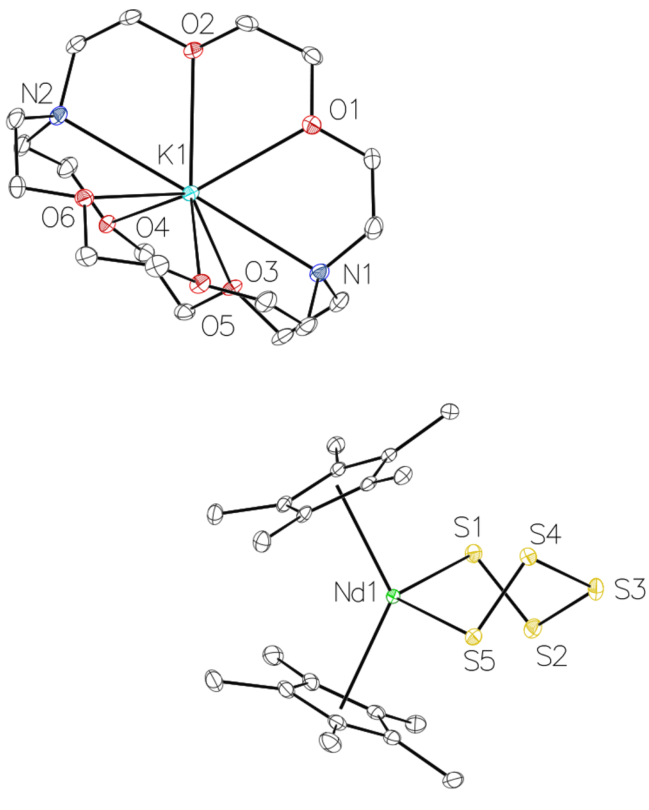


Figure 5. Molecular structure of [K(crypt)][$Cp^*_2Nd(S_5)$] (**5-Nd**) with thermal ellipsoids drawn at 30% probability. For clarity, hydrogen atoms are not shown. The structure of **5-Sm** is isomorphous.

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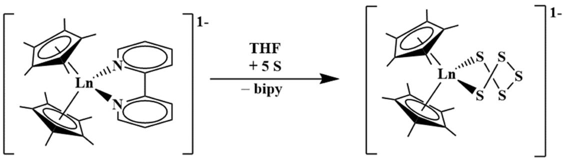
Table 5. Selected Bond Distances (Å) and Angles (deg) in 5-Ln Complexes

	Ln–C (avg.)	Ln–Cp_{cent}	Ln–S	Cp_{cent}–Ln–Cp_{cent}	S–Ln–S
$[Cp^*_2Nd(S_5)]^{1-}$ (**5-Nd**)	2.795(1)	2.5274(10), 2.5153(10)	2.8253(6), 2.8294(6)	129.56(4)	111.84(2)
$[Cp^*_2Sm(S_5)]^{1-}$ (**5-Sm**)	2.7696(6)	2.4875(9), 2.4977(9)	2.7995(6), 2.7970(5)	129.85(3)	111.539(15)



(9)

3-Ln
Ln = Nd, Sm

5-Ln

While organometallic complexes binding an $(S_5)^{2-}$ ligand are somewhat common among the transition metals, complexes **5-Nd** and **5-Sm** are exceptionally rare examples of *f*-block metals that coordinate sulfur in this manner. Indeed, the complexes $Cp^*Th(S_5)$,[64] $(Tp^{iPr2})(\kappa^1\text{-}3,5\text{-}^iPr_2Hpz)Ln(S_5)$ (Ln = Ce, Sm; Tp^{iPr2} = hydro-tris(3,5-diisopropylpyrazolyl)borate; $3,5\text{-}^iPr_2Hpz$ = 3,5-diisopropylpyrazole),[65,66] $\{[DyI_2(THF)_5]^+[DyI_2(S_5)(THF)_2]^-\}$,[67] and $[K(18\text{-crown-}6)][(^{dipp}isq)_2Nd(S_5)]$ (^{dipp}isq = 4,6-di-*tert*-butyl-2-[(2,6-diisopropylphenyl)imino]semiquinone)[16] comprise the complete list of *f*-block complexes binding an $(S_5)^{2-}$ ligand that have been structurally characterized.

It is noteworthy that the complexes **3-Ln** coordinate the $(S_5)^{2-}$ ligand in the twist-boat conformation. This is apparently unique to complexes of the *f*-block elements and closed-shell complexes of *d*-block elements (cf. Y(III) complexes of Zhang and Zhao[68] and Ti(IV) complexes of Stephan and coworkers[69]), although closed-shell *d*-block metal complexes of the $(S_5)^{2-}$ which adopt the chair conformation are also known, e.g., the complex $Cp_2Ti(S_5)$ of Muller, Petersen, and Dahl.[70] In light of this, it is perhaps more unusual that the twist-boat conformation is the only known conformation of the $(S_5)^{2-}$ ligand among *f*-element complexes. A computational study of $Cp^*_2Th(S_5)$, which was both the first organoactinide polysulfide and the first *f*-block metal complex reported to coordinate sulfur in this way, suggested that this conformation is likely to be a consequence of a weak donor–acceptor bonding interaction between the *β*-sulfur atoms of the $(S_5)^{2-}$ ligand and the Lewis acidic Th(IV) ion.[64]

In this context, it is worth comparing the structural characteristics of **5-Nd** and **5-Sm** with the known complexes of Nd and Sm that coordinate an $(S_5)^{2-}$ ligand. **5-Nd** has Nd–S_α distances of 2.8253(6) and 2.8294(6) Å and Nd–S_β distances of 3.1498(8) and 3.1577(8) Å. **5-Sm** has shorter Sm–S_α distances of 2.7995(6) and 2.7970(5) Å as expected based on the smaller ionic radius of Sm.[71] However, the Sm–S_β distances of 3.1667(7) and 3.1772(6) Å are longer than those in **5-Nd**. The 2.8182(12) and 2.8394(12) Å Nd–S_α distances in $[K(18\text{-crown-}6)][(^{dipp}isq)_2Nd(S_5)]$,[16] are similar to those in **5-Nd**, but the 3.0273(10) and 3.0259(11) Å Nd–S_β distances are much shorter. Similarly, the 2.7552(8) and 2.7922(6) Å Sm–S_α distances in $(Tp_2^{iPr})(\kappa^1\text{-}3,5\text{-}^iPr_2Hpz)Sm(S_5)$[65] are close to those in **5-Sm**, but the 3.0898(7) and 2.952(1) Å Sm–S_β distances are much shorter. These metrics show that while the Ln–S_α distances are similar in these pairs of complexes despite the higher coordination number of **5-Ln** in both cases, the Ln–S_β distances are longer by ca. 0.1 Å in **5-Nd** and **5-Sm**. Thus, while structural characterization of more complexes is necessary to draw a meaningful conclusion, the substantially longer Ln–S_β distances in **5-Ln** show that the twist-boat conformation of the $(S_5)^{2-}$ ligand can form for *f*-element complexes even when the Ln–S_β distances are exceptionally long. Hence, the origin of this conformation may be more complicated than simple donor–acceptor interactions between the metal ion and the *β*-sulfur atoms.

CONCLUSIONS

Complexes of the form $Cp^*_2LnCl(bipy)$, **1-Ln**, were shown to be readily accessible in one step through the reaction of $LnCl_3$ with 1 equiv of bipyridine and 2 equiv of KCp* in THF. The **1-Ln** complexes can be reduced to $Cp^*_2Ln(bipy)$, **2-Ln**, by treatment with a slight excess of 4.3 wt % K/KI. Further reduction of **2-Ln** using 4.3 wt % K/KI in the presence of 2.2.2-cryptand affords $[K(crypt)][Cp^*_2Ln(bipy)]$, **3-Ln**. The **3-Ln** complexes (Ln = Nd, Sm, or Yb) function as two-electron reductants with azobenzene, N_2Ph_2, cleanly generating $[K(crypt)][Cp^*_2Ln(N_2Ph_2)]$, **4-Ln**, which features a doubly reduced azobenzene ligand, $(N_2Ph_2)^{2-}$. Additionally, **3-Nd** and **3-Sm** were shown to effect two-electron reductions of elemental sulfur to give $[K(crypt)][Cp^*_2Ln(S_5)]$, **5-Ln**, which are rare examples of *f*-block organometallic complexes which coordinate the $(S_5)^{2-}$ ligand. Although we have shown that **4-Ln** may be prepared by one-electron reduction through the reaction of $Cp^*_2Sm(THF)_2$ with in situ formed $[K(crypt)][N_2Ph_2]$, this method is accessible only for lanthanides for which $Cp^*_2Ln^{II}(THF)_n$ may be prepared. Therefore, the preparation of $[K(crypt)][Cp^*_2Nd(N_2Ph_2)]$, **4-Nd**, and $[K(crypt)][Cp^*_2Nd(S_5)]$, **5-Nd**, from $[K(crypt)][Cp^*_2Nd(bipy)]$, **3-Nd**, shows that **3-Ln** complexes have the potential to be used for two-electron reductions regardless of whether the +2 oxidation state is available for a given lanthanide in this metallocene ligand environment. In addition, the **3-Ln** two-electron reductions in this study provide a route to monometallic $(substrate)^{2-}$ products, $[A_2Ln^{III}(substrate)]^{1-}$ (A = anion = Cp* in this study) in contrast to the bimetallic neutral $A_2Ln^{III}(substrate)Ln^{III}A_2$ complexes formed from $Ln^{II}A_2$, eq 1. These $[Cp^*_2Ln^{III}(substrate)]^{1-}$ salts have different solubility than the neutral bimetallic compounds which may make them easier to definitively identify by X-ray crystallography for certain substrates. They also provide options to generate heterobimetallic versions of $A_2Ln(substrate)Ln'A_2$ by adding cationic reagents such as $[Cp^*_2Ln']^{1+}$. An additional advantage of the **3-Ln** complexes is their thermal stability at room temperature. Overall, this bipy approach to reduction provides metallocene-reducing agents that can be readily synthesized in high yield so that extensive studies are not reagent-limited.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.3c00074.

Spectra (NMR, infrared, UV–vis) and crystallographic data (PDF)

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Accession Codes

CCDC 2176470 (**3-Sm**), 2179109 (**3-Yb**), 2181975 (**1-Nd**), 2183539 (**2-Eu**), 2183624 (**3-Eu**), 2189162 (**3-Gd**), 2189459 (**2-Nd**), 2189778 (**3-Nd**), 2212318 (**4-Sm**), 2213066 (**4-Nd**), 2213599, 2213836 (**4-Yb**), 2227098 (**5-Sm**)−2227099 (**5-Nd**), and 2237236 (**2-Gd**)−2237237 (**1-Gd**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

William J. Evans − *Department of Chemistry, University of California, Irvine, Irvine, California 92697, United States;* orcid.org/0000-0002-0651-418X; Email: wevans@uci.edu

Authors

Cary R. Stennett − *Department of Chemistry, University of California, Irvine, Irvine, California 92697, United States;* orcid.org/0000-0002-2727-5747

Joseph Q. Nguyen − *Department of Chemistry, University of California, Irvine, Irvine, California 92697, United States;* orcid.org/0000-0001-8058-7099

Joseph W. Ziller − *Department of Chemistry, University of California, Irvine, Irvine, California 92697, United States;* orcid.org/0000-0001-7404-950X

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.3c00074

Notes

The authors declare no competing financial interest.

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