Isolation of Reactive Ln(II) Complexes with C_5H_4Me Ligands (Cp^{Me}) Using Inverse Sandwich Countercations: Synthesis and Structure of [(18-crown-6)K(μ-Cp^{Me})K(18-crown-6)][$Cp^{Me}{}_3Ln^{II}$] (Ln = Tb, Ho)

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Isolation of Reactive Ln(II) Complexes with C_5H_4Me Ligands (Cp^{Me}) Using Inverse Sandwich Countercations: Synthesis and Structure of [(18-crown-6)K(μ-Cp^{Me})K(18-crown-6)][$Cp^{Me}{}_3Ln^{II}$] (Ln = Tb, Ho)

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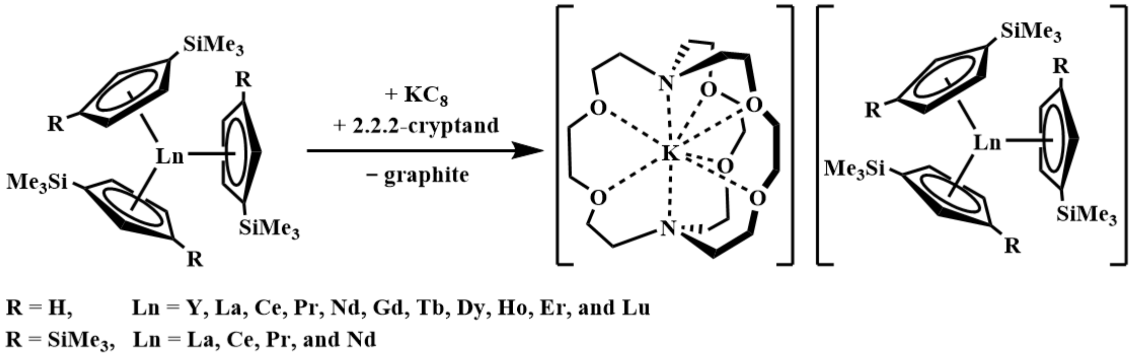
Dedicated to Professor Geoffrey Cloke for enlivening organometallic chemistry by his always innovative contributions and for his groundbreaking discoveries using metal vapor chemistry.

Abstract

Although attempts to make the Y(II) complex, $(Cp^{Me}{}_3Y)^{1-}$ (Cp^{Me} = C_5H_4Me), by reduction of $Cp^{Me}{}_3Y$ with potassium were unsuccessful and the products of potassium reduction of $Cp^{Me}{}_3Ln$ for Ln = La and Pr led to ring-opening reduction of THF, we report that crystallographically-characterizable Ln(II) complexes of Tb and Ho can be isolated by reducing $Cp^{Me}{}_3Ln(THF)$ with KC_8 in THF in the presence of 18-crown-6 (18-c-6). X-ray crystallography revealed that these complexes are isolated with a methylcyclopentadienide inverse sandwich countercation: [(18-c-6)K(μ-Cp^{Me})K(18-c-6)][$Cp^{Me}{}_3Ln$] (Ln = Tb, Ho). Although reduction of $Cp^{Me}{}_3Ln$ with potassium in the presence of the 2.2.2-cryptand (crypt) chelate has not generally provided fully-characterizable, crystalline products, in the case of Dy, crystals of [K(crypt)][$Cp^{Me}{}_3Dy$] could be isolated.

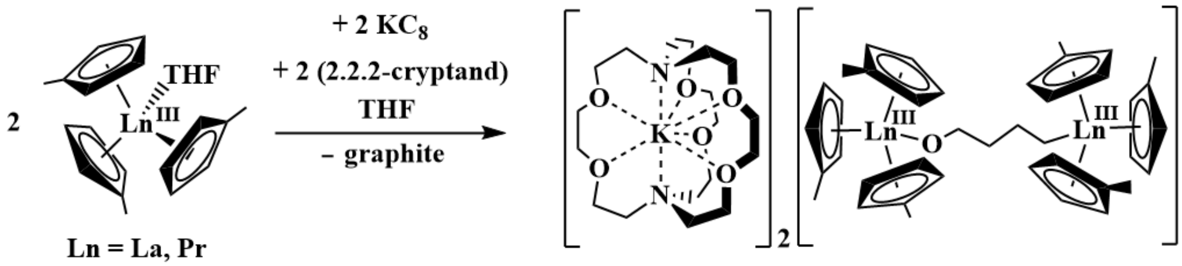
Introduction

The discovery of new oxidation states for the rare-earth metals Y, La, Ce, Pr, Gd, Tb, Ho, Er, and Lu by LnA_3/M reduction reactions initially involved almost exclusively silyl-substituted cyclopentadienyl ligands $C_5H_4SiMe_3$ (Cp′) and $C_5H_3(SiMe_3)_2$ (Cp″), eq 1.[1-8] It was thought that the cyclopentadienyl ligands containing silyl groups were optimum because the silyl groups provided the "right" balance of electronic and steric stabilization.[7] EPR studies of reduction reactions of the yttrium complexes $(C_5H_5)_3Y$, $(C_5H_4Me)_3Y$, $(C_5Me_4H)_3Y$, and $Y(NR_2)_3$ (R = $SiMe_3$) were consistent with this.[9, 10] In each case, an EPR spectrum characteristic of Y(II) was observed, but the complexes proved to have only transient stability and were not crystallographically characterizable.[9, 10]



(1)

Recent studies have shown one reason that the reduction of $Cp^{Me}{}_3Ln$ ($Cp^{Me} = C_5H_4Me$) complexes does not give isolable Ln(II) complexes: for the large metals, La and Pr, reduction of $Cp^{Me}{}_3Ln(THF)$, **1-Ln**, forms solutions that ring-open THF to form $(OCH_2CH_2CH_2CH_2)^{2-}$ dianions, eq 2.[11] Spectroscopic evidence was also obtained for ring opening of THF in the $Cp^{Me}{}_3Y$/K reaction.



(2)

Historically, it has been found that yttrium exhibits similar chemistry to the late lanthanide metals of similar size, *e.g.* holmium and erbium.[2, 4, 12] Hence, it would be expected that the $(Cp^{Me}{}_3)^{3-}$ ligand set would not support Ln(II) complexes for these metals. However, recent studies of the reduction of $Ln(NR_2)_3$ complexes (R = $SiMe_3$) showed that the late lanthanides,[13] as well as scandium,[14] can differ from yttrium[10] in this lower oxidation state chemistry. Accordingly, we have investigated the reduction of $Cp^{Me}{}_3Ln$ with late lanthanides. We report here the surprising result that crystallographically-characterizable complexes of the late lanthanides in the +2 oxidation state can be isolated with the $(Cp^{Me}{}_3)^{3-}$ ligand set and that a cyclopentadienyl inverse sandwich complex, [(18-crown-6)K(μ-Cp^{Me})K(18-crown-6)], is an effective countercation for their isolation.

Results

Reductions of $Cp^{Me}{}_3Ln(THF)$, **1-Ln** (Ln = Tb, Ho, Er), using KC_8 in the presence of 18-crown-6 (18-c-6) yield black solutions at −35 °C that retain their color for at least 3 days at low temperature and provide isolable black solids. Crystals suitable for single-crystal X-ray diffraction were isolated and structurally characterized as [(18-c-6)K(μ-Cp^{Me})K(18-c-6)][$Cp^{Me}{}_3Ln$], **2-Ln** (Ln = Tb and Ho), Figure 1. The unit cell of **2-Er** matched that of **2-Tb** and **2-Ho**, however, due to rapid decomposition of the crystal upon transferring from the sample vial to the diffractometer, suitable data could not be collected for X-ray crystallography.

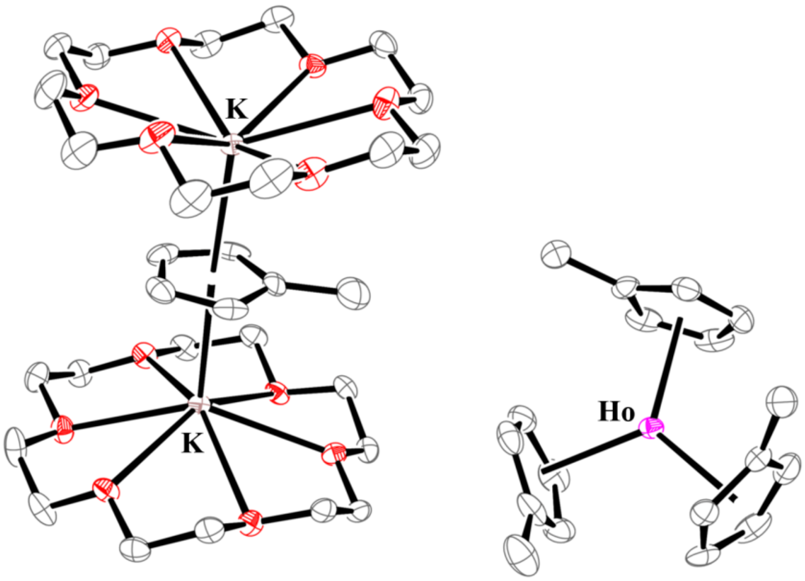
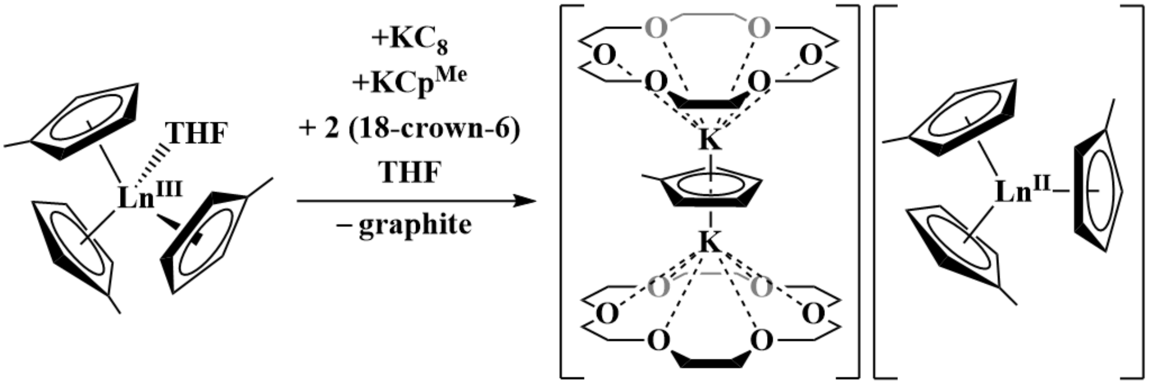


Figure 1. ORTEP representation of [(18-c-6)K(μ-Cp^{Me})K(18-c-6)][Cp$^{Me}{}_3$Ho], **2-Ho**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

The X-ray crystal structure of **2-Ln** showed that it contained an extra equivalent of (Cp^{Me})$^{1-}$ which bridges two [K(18-c-6)]$^{1+}$ units to generate an inverse sandwich complex, [(18-c-6)K(μ-Cp^{Me})K(18-c-6)]$^{1+}$, as the countercation. In subsequent syntheses of **2-Ln**, an extra equivalent of KCp^{Me} was added to improve the yield, eq 3. It appears that this countercation is particularly effective in allowing isolation of these new Ln(II) complexes.



(3)

Several inverse sandwich complexes of this type have been reported with the unsubstituted (C$_5$H$_5$)$^{1-}$ anion, *i.e.* the [(18-c-6)K(μ-C$_5$H$_5$)K(18-c-6)]$^{1+}$ cation,[15-22] but only two examples with substituted-cyclopentadienyl rings are in the literature, one with a (Cp′)$^{1-}$ anion bridge (Cp′ = $C_5H_4SiMe_3$)[3] and one with ($C_5H_4CMe_3$)$^{1-}$ anion bridge.[23] Of these two substituted examples, crystallographically-determined metrical parameters were reported only for the Cp′ complex, [(18-c-6)K(μ-Cp′)K(18-c-6)][Cp′$_3$Tb][3].

Although crystals of two examples of **2-Ln** could be isolated and characterized by X-ray diffraction, further characterization such as elemental analysis was challenging because the complexes decompose within seconds at temperatures above −35 °C. Magnetic measurements of **2-Ln** are also difficult to obtain due to their inevitable contamination of Ln(III) from rapid decomposition. Attempts to obtain UV-visible spectra of **2-Ho** and **2-Er** showed significant decomposition with sharp absorbances characteristic of Ho(III) and Er(III) complexes (ESI, Figure S1). However, the spectra also contained broad features of 490 nm and 493 nm, respectively. These broad absorbances are similar to the most intense absorptions in [K(18-c-6)][Cp′$_3$Ho][2] of 507 nm, [K(18-c-6)][Cp′$_3$Er][2] of 510 nm, [K(crypt)][Cp′$_3$Ho][3] of 499 nm, and [K(crypt)][Cp′$_3$Er][3] of 502 nm. Complex **2-Tb** did survive long enough to provide a UV-visible spectrum absent of sharp Tb(III) features that contained broad absorptions at 458 nm and 660 nm (ESI, Figure S2), similar to those previously reported for [K(18-c-6)][Cp′$_3$Tb] of 446 nm and 650 nm and [K(crypt)][Cp′$_3$Tb] of 464 nm and 635 nm.[3] Each of the latter complexes was characterized as containing a Tb(II) ion with a $4f^85d^1$ electron configuration.[24]

The crystallographic data on complexes of Ln(II) ions normally allows evaluation of the electron configuration since a characteristic of $4f^n5d^1$ Ln(II) complexes vs $4f^{n+1}$ Ln(II) compounds is that the former complexes have metal−ligand bond distances only slightly larger than their Ln(III) analogs, within 0.02-0.05 Å.[3, 25] In contrast, traditional $4f^{n+1}$ Ln(II) complexes have metal−ligand distances 0.1-0.2 Å larger than their Ln(III) counterparts.[25] This comparison cannot be made directly with **2-Ln**, since the X-ray crystal structures of $Cp^{Me}{}_3Ln$ for Tb and Ho are unknown. Structural data have been reported on the $Cp^{Me}{}_3Ln$ complexes of Ln = La,[26] Ce,[27] Pr,[28] and Nd,[29] but they crystallize in oligomeric forms with a higher coordination number for the metal. The structures of $Cp^{Me}{}_3Ln(THF)$ (Ln = Y,[9] Sm,[30] Dy,[31]) are not appropriate for this analysis because the coordination number in these complexes is larger due to the THF.

The structure of unsolvated monomeric $Cp^{Me}{}_3Yb$[32] is known, however, and will be used for comparison. The range of Yb−Cp^{Me} ring centroid distances is 2.29-2.38 Å and the average is 2.35 Å. Since the Shannon radii[33] of Tb(III) and Ho(III) are 0.055 and 0.033 Å larger than that of Yb(III), the predicted Tb(III)−Cp^{Me} and Ho(III)−Cp^{Me} average distances in "$Cp^{Me}{}_3Ln$" are 2.405 and 2.383 Å, respectively. These are similar to Tb(III)−Cp′ and Ho(III)−Cp′ distances, 2.423 and 2.394 Å, in Cp'_3Ln complexes (Cp′ = $C_5H_4SiMe_3$). The observed Ln(III)-Cp^{Me} distances of **2-Tb** and **2-Ho**, 2.456 and 2.432 Å, are about 0.05 Å larger than the estimates for the "$Cp^{Me}{}_3Ln$" analogs. This is slightly larger than the difference found for the Cp′ $4f^n5d^1$ series, but much less than the difference found for $4f^{n+1}$ Ln(II) ions.

The metrical parameters of the $(Cp^{Me}{}_3Ln)^{1-}$ anions in **2-Ln** can be further compared with those of the previously reported $(Cp'_3Ln)^{1-}$ complexes, Table 1. This table shows that the metal−ring centroid distances for **2-Ln** are very close to those of previously reported $(Cp'_3Ln)^{1-}$ anions,[2, 3, 34] which are only slightly larger than those of Cp'_3Ln. All of these metrical data are consistent with the presence of $4f^n5d^1$ electron configurations for **2-Tb** and **2-Ho**.

Table 1. Ln(II)−(ring centroid) distances (Å) in the $[(C_5H_4R)_3Ln]^{1-}$ anions (R = Me, $SiMe_3$)

	Ln−cnt range (Å)	Ln−cnt average (Å)
2-Tb	2.451-2.463	2.456
$[K_2(18\text{-}c\text{-}6)_2(\mu\text{-}Cp')][Cp'_3Tb]$[3]	2.446-2.464	2.454
$[K(18\text{-}c\text{-}6)][Cp'_3Tb]$[3]	2.441-2.453	2.446
$[K(crypt)][Cp'_3Tb]$[3]	2.448-2.461	2.454

[Li(crypt)][Cp′$_3$Tb][34]	2.441-2.472	2.455
2-Ho	2.430-2.435	2.432
[K(18-c-6)][Cp′$_3$Ho][2]	2.417-2.432	2.423
[K(crypt)][Cp′$_3$Ho][2]	2.420-2.433	2.426
[Li(crypt)][Cp′$_3$Ho][34]	2.409-2.440	2.425

The metrical parameters of the [(18-c-6)K(μ-Cp^{Me})K(18-c-6)]$^{1+}$ inverse cyclopentadienyl sandwich cations in **2-Tb** and **2-Ho** are similar, Figure 2. The K−Cp^{Me} centroid distances for **2-Ln** range from 2.848-2.860 Å and the K−(Cp^{Me} ring centroid)−K bond angles in the cations approach linearity, 177.2° and 177.1°, respectively. These metrical parameters are similar to previously reported unsubstituted-cyclopentadienyl [(18-c-6)K(μ-C$_5$H$_5$)K(18-c-6)]$^{1+}$ inverse sandwich complexes.[15-20, 22] The K−C$_5$H$_5$ ring centroid distances in those compounds range from

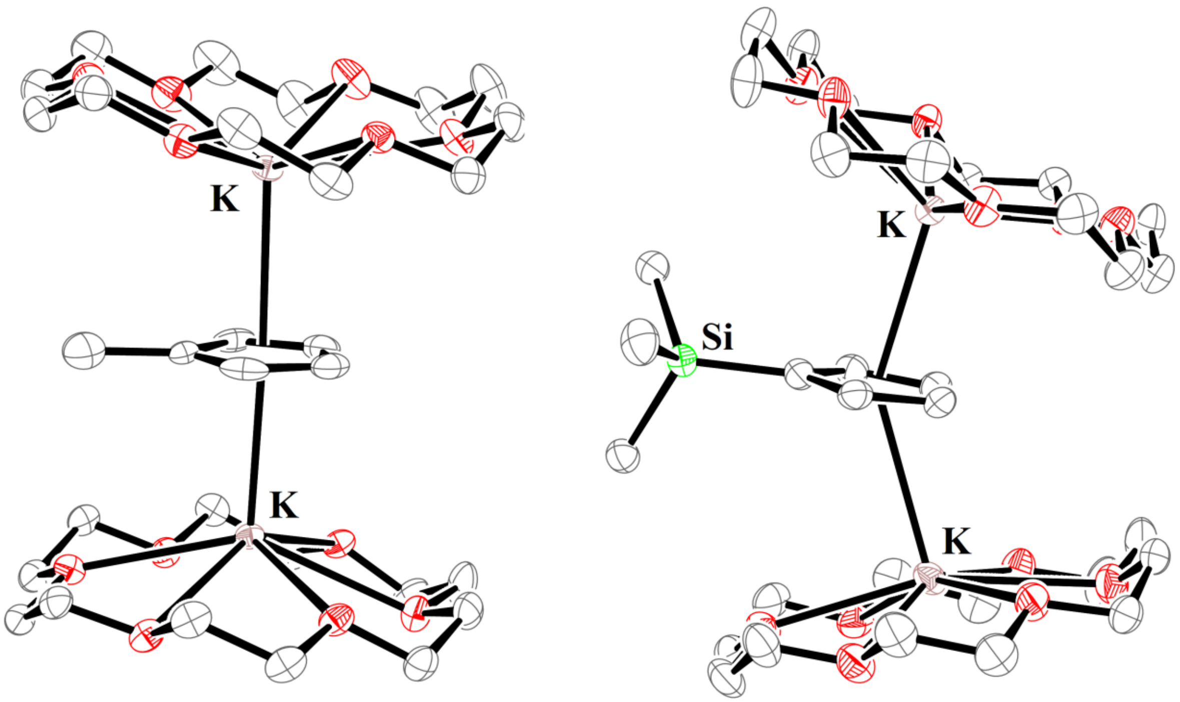
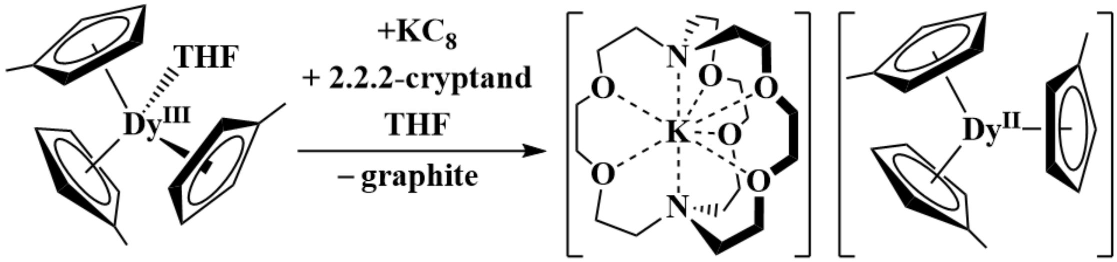


Figure 2. Comparison of the [(18-c-6)K(μ-Cp^{Me})K(18-c-6)]$^{1+}$ cation in **2-Tb** (left) and [(18-c-6)K(μ-Cp′)K(18-c-6)]$^{1+}$ in [(18-c-6)K(μ-Cp′)K(18-c-6)][Cp′$_3$Tb][3] (right).

2.812-2.894 Å and the K−(C_5H_5 ring centroid)−K angles vary from 171.5-179.2°. In contrast, in the Cp′ inverse sandwich cation in [(18-c-6)K(μ-Cp′)K(18-c-6)][Cp′$_3$Tb],[3] the K−(Cp′ ring centroid)−K angle is significantly bent: 147.5°, Figure 2. The steric bulk provided by the silyl substituent on the $(Cp')^{1-}$ ligand evidently causes the K−Cp′−K angle to bend.

Attempts to reduce Cp$^{Me}_3$Ln(THF), **1-Ln**, complexes in the presence of 2.2.2-cryptand (crypt), a chelating agent commonly used with potassium as the reductant, eq 1, gave dark colored solutions. Although crystalline products could be isolated for Ln = Tb, Ho and Er with crypt, these were not suitable for single crystal X-ray diffraction. This was further complicated by the fast decomposition at temperatures above −35 °C. However, reduction of **1-Dy** in THF using KC_8 and crypt at −35 °C yielded a black solution similar to the previously reported reductions of **1-Ln** that persisted for days at this temperature. This allowed the isolation of [K(crypt)][Cp$^{Me}_3$Dy], **3-Dy**, eq 4. Although crystals suitable for single-crystal X-ray crystallography were obtained (ESI, Figure S5), they were not of sufficient quality to provide useful metrical parameters with which to evaluate the presence of either a $4f^{10}$ or $4f^9 5d^1$ configuration.



(4)

Another characteristic of complexes of $4f^n 5d^1$ Ln(II) ions is UV-visible spectra with large extinction coefficients compared to $4f^{n+1}$ Ln(II) complexes. The UV-visible spectrum of **3-Dy**, Figure 3, contained broad absorbances at 424, and 674 nm with ε = 2100 and 1200 $M^{-1}cm^{-1}$, respectively, that were similar to those in the UV-visible spectrum of [K(crypt)][Cp′$_3$Dy],[25] which has broad absorptions at 483 and 644 nm with ε = 3400 and 1000 $M^{-1}cm^{-1}$, respectively. Hence, by this metric, **3-Dy** appears to contain a $4f^95d^1$ ion.

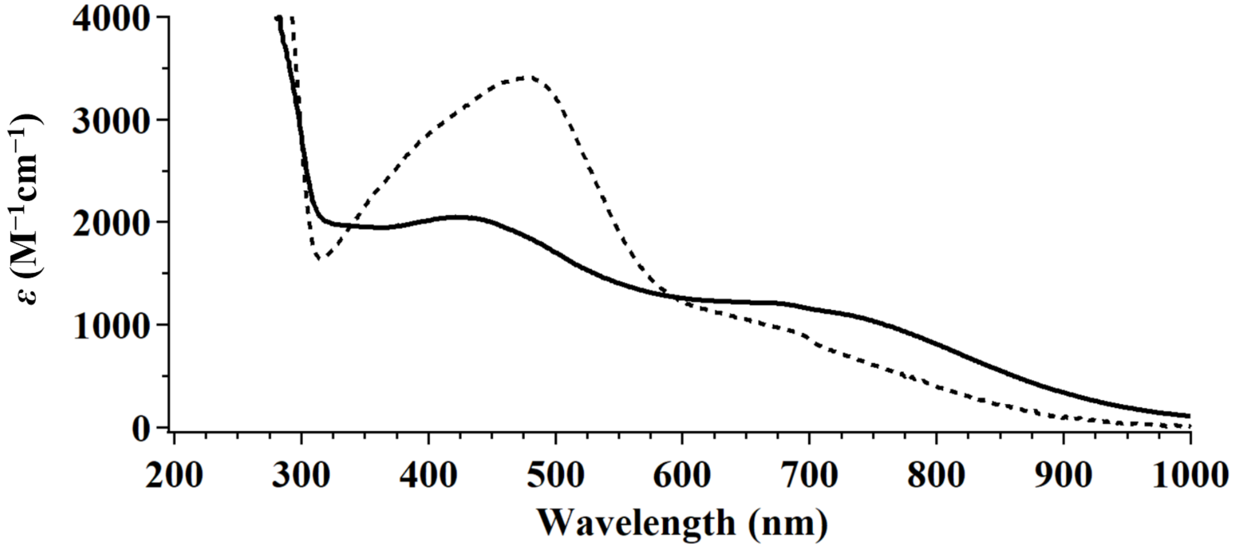


Figure 3. UV-visible spectrum of a ~10 mM solution of [K(crypt)][$Cp^{Me}{}_3Dy$], **3-Dy** (solid) and [K(crypt)][Cp'_3Dy][25] (dashed) in THF.

Discussion

The isolation of **2-Ln** for Ln = Tb and Ho provides another example in which the divalent late lanthanides are not like divalent yttrium. The solutions obtained by reduction of $Cp^{Me}{}_3Ln$ clearly have greater stability than the product of $Cp^{Me}{}_3Y$ reduction. Dissimilar chemistry for yttrium versus the late lanthanides has now been observed in reductions of $Ln(NR_2)_3$ (R = $SiMe_3$),[13] $(C_5Me_4H)_3Ln$,[35] and $Cp^{Me}{}_3Ln$. The origin of this difference is not known, but it is clear that the connection of yttrium with the late lanthanides so common for Y(III) complexes should not be expected to necessarily apply for Y(II) species. It is possible that this is a 4d vs 5d effect which is sometimes seen in transition metal chemistry, *e.g.* in the differences between Pd and Pt.[36, 37]

Since the $(\mathrm{Cp^{Me}}_3\mathrm{Ln})^{1-}$ anions were isolable with an inverse cyclopentadienyl sandwich countercation, these results show yet another variation in the importance of the countercation in isolating Ln(II) complexes. Attempts to crystallize $(\mathrm{Cp^{Me}}_3\mathrm{Ln})^{1-}$ anions with $[\mathrm{K(crypt)}]^{1+}$ did not provide suitable crystals for X-ray crystallography. The inverse cyclopentadienyl sandwich countercation, however, allowed for facile crystallization and crystals were suitable for X-ray crystallography. Crystallographically-characterizable salts obtained from rare-earth metal reduction reactions with 18-c-6 as the chelator have been found with the following types of countercations: $[\mathrm{K(crown)}]^{1+}$,[2-4, 38] $[\mathrm{K(crown)(Et_2O)}]^{1+}$, $[\mathrm{K(crown)(THF)_2}]^{1+}$,[39-42] $\{[\mathrm{K(crown)(Et_2O)}]_2\}^{2+}$,[39] $\{[\mathrm{K(crown)(Et_2O)}][\mathrm{K(crown)}]\}^{2+}$,[43] and $[\mathrm{K_2(crown)_3}]^{2+}$.[39] In each case, it appears that just one of these variations is the optimum countercation for the anion involved, but the reason for the exact pairing is not known. It appears that much remains to be learned about matching cation and anion in these reduction reactions.[44]

Conclusion

It was a surprise that Ln(II) complexes supported by $\mathrm{Cp^{Me}}$ ligands, $[(18\text{-c-}6)\mathrm{K}(\mu\text{-}\mathrm{Cp^{Me}})\mathrm{K}(18\text{-c-}6)][\mathrm{Cp^{Me}}_3\mathrm{Ln}]$, **2-Ln**, could be isolated for the smaller lanthanides, Tb and Ho. This contrasts with the larger metals, La and Pr, that reductively ring-open THF and with the 4d metal, yttrium, that has in the past been used as a mimic of the late small lanthanides but does not form a stable **2-Y** analog. The isolation of these complexes as salts of the inverse sandwich cation, $[(18\text{-c-}6)\mathrm{K}(\mu\text{-}\mathrm{Cp^{Me}})\mathrm{K}(18\text{-c-}6)]^{1+}$, demonstrates another possibility for 18-c-6 to chelate potassium. This also allowed for the facile crystallization with $(\mathrm{Cp^{Me}}_3\mathrm{Ln})^{1-}$ anions to form additional crystallographically-characterized examples of Tb and Ho in the +2 oxidation state.

Experimental Section

All syntheses and manipulations described below were conducted under Ar with rigorous exclusion of air and water using glovebox, Schlenk-line, and high-vacuum-line techniques. $Cp^{Me}{}_3Ln(THF)$ (Ln = Tb, Dy, Ho, Er)[31], KCp^{Me} [45] and KC_8[46] were prepared according to previously published literature. 2.2.2-Cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, Aldrich) was placed under vacuum (10−3 Torr) for 12 h before use. 18-crown-6 purchased from Alfa Aesar was sublimed prior to use. THF and hexanes were sparged with UHP Ar and dried over columns containing Q-5 and molecular sieves. UV-vis spectra were collected on a Cary-60. IR samples were prepared as KBr pellets on a Jasco FT/IR-4700 spectrometer. The thermal instability of the complexes did not allow elemental analytical data to be collected.

[(18-c-6)K(*μ*-Cp^{Me})K(18-c-6)][$Cp^{Me}{}_3Tb$], 2-Tb. In an argon-filled box, a colorless solution of $Cp^{Me}{}_3Tb(THF)$ (50 mg, 0.11 mmol), 18-crown-6 (57 mg, 0.21 mmol), and KCp^{Me} (13 mg, 11 mmol) in THF (2 mL) as well as a vial containing KC_8 (22 mg, 0.16 mmol) were cooled to −35 °C. The THF solution was transferred to the vial of KC_8 and vigorously swirled forming a black mixture. The black mixture was immediately filtered and layered into cold (−35 °C) hexanes and placed in a −35 °C freezer. After 1 d, X-ray quality crystals were isolated (73 mg, 63 %). IR: 3087w, 3059w, 3040m, 2947m, 2892s, 2859s, 2824m, 2792w, 2743w, 2707w, 2687w, 1979w, 1634m, 1618m, 1471m, 1452m, 1432w, 1405w, 1350s, 1283m, 1248m, 1109s, 1059w, 1030w, 1019w. UV−vis (THF) λ_{max} nm: 458, 660.

[(18-c-6)K(*μ*-Cp^{Me})K(18-c-6)][$Cp^{Me}{}_3Ho$], 2-Ho. As described for **2-Tb**, $Cp^{Me}{}_3Ho(THF)$ (50 mg, mmol), 18-crown-6 (55 mg, 0.21 mmol), and KCp^{Me} (12 mg, 0.11 mmol) was reduced in THF using KC_8 (22 mg, 0.16 mmol) producing a black solution. Black single crystals of **2-Ho** were grown from THF/hexanes after 1 d (23 mg, 20 %). IR: 3070m, 3046m, 2948m, 2912s, 2895s, 2858s, 2824m, 2794w, 2743w, 2710w, 2687w, 2173w, 1975w, 1601w, 1490w, 1471m, 1452m, 1407w, 1383w, 1351s, 1283m, 1249m, 1111s, 1046w, 1031w, 1019w. UV−vis (THF) $\lambda_{\max}$ nm: 490.

[(18-c-6)K(*μ*-Cp^{Me})K(18-c-6)][Cp$^{Me}{}_3$Er], 2-Er. As described for **2-Tb**, Cp$^{Me}{}_3$Er(THF) (50 mg, 0.11 mmol), 18-crown-6 (55 mg, 0.21 mmol), and KCp^{Me} (12 mg, 0.11 mmol) was reduced in THF using KC$_8$ (21 mg, 0.16 mmol) producing a black solution. Black crystals of **2-Er** were grown from THF/hexanes after 1 d (18 mg, 16 %). IR: 3083m, 3063m, 3046m, 2946s, 2911s, 2889s, 2857s, 2824s, 2795m, 2744m, 2711w, 2688w, 2173w, 1977w, 1572w, 1492w, 1471s, 1452s, 1433m, 1406w, 1351s, 1283m, 1249s, 1236m, 1110s, 1058m, 1046m, 1031m, 1019w. UV−vis (THF) $\lambda_{\max}$ nm: 493.

[K(crypt)][Cp$^{Me}{}_3$Dy], 3-Dy. In an argon-filled box, a colorless solution of Cp$^{Me}{}_3$Dy(THF) (45 mg, 0.10 mmol), and 2.2.2-cryptand (39 mg, 0.10 mmol) in THF (2 mL) as well as a vial containing KC$_8$ (19 mg, 0.14 mmol) were cooled to −35 °C. The THF solution was transferred to the vial of KC$_8$ and vigorously swirled forming a black mixture. The black mixture was immediately filtered and layered into cold (−35 °C) hexanes and placed in a −35 °C freezer. After 1 d, X-ray quality crystals were isolated (40 mg, 51 %). IR: 3077w, 3059w, 3036w, 2956s, 2882s, 2817s, 2757m, 2727m, 1476m, 1457m, 1443m, 1410w, 1353s, 1296m, 1259m, 1236w, 1173w, 1132s, 1102s, 1178s, 1056m, 1031m. UV−vis (THF) $\lambda_{\max}$ nm (ε, M^{-1}cm^{-1}): 424 (2050), 674 (1200), 728 (1100 shoulder).

X-ray Crystallographic Data. Crystallographic information for complexes **2-Ln** (Ln = Tb, Ho) and **3-Dy** is summarized in the Supporting Information.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgments

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References

1. P. B. Hitchcock, M. F. Lappert, L. Maron and A. V. Protchenko, *Angew. Chem. Int. Ed.*, 2008, **47**, 1488-1491.
2. M. R. MacDonald, J. E. Bates, M. E. Fieser, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2012, **134**, 8420-8423.
3. M. R. MacDonald, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2013, **135**, 9857-9868.
4. M. R. MacDonald, J. W. Ziller and W. J. Evans, *J. Am. Chem. Soc.*, 2011, **133**, 15914-15917.
5. C. T. Palumbo, L. E. Darago, C. J. Windorff, J. W. Ziller and W. J. Evans, *Organometallics*, 2018, **37**, 900-905.
6. Examples with other ligands such as $C_5H_3(CMe_3)_2$ (Cp^{tt}),[7] $C_5H_2(CMe_3)$ (Cp^{ttt}),[8] and the tris(aryloxide) mesitylene ligand, $((^{Ad,Me}ArO)_3mes)^{3-}$, are also known: M. E. Fieser, C. T. Palumbo, H. S. La Pierre, D. P. Halter, V. K. Voora, J. W. Ziller, F. Furche, K. Meyer and W. J. Evans, *Chem. Sci.,* 2017, **8**, 7424-7433
7. M. C. Cassani, D. J. Duncalf and M. F. Lappert, *J. Am. Chem. Soc.*, 1998, **120**, 12958-12959.
8. F. Jaroschik, F. Nief, X.-F. Le Goff and L. Ricard, *Organometallics*, 2007, **26**, 1123-1125. F. Jaroschik, A. Momin, F. Nief, X.-F. Le Goff, G. B. Deacon and P. C. Junk, *Angew. Chem. Int. Ed.*, 2009, **48**, 1117-1121.
9. J. F. Corbey, D. H. Woen, C. T. Palumbo, M. E. Fieser, J. W. Ziller, F. Furche and W. J. Evans, *Organometallics*, 2015, **34**, 3909-3921.
10. M. Fang, D. S. Lee, J. W. Ziller, R. J. Doedens, J. E. Bates, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2011, **133**, 3784-3787.
11. D. H. Woen, D. N. Huh, J. W. Ziller and W. J. Evans, *Organometallics*, 2018, **37**, 3055-3063.
12. J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1976, 480-481.
13. A. J. Ryan, L. E. Darago, S. G. Balasubramani, G. P. Chen, J. W. Ziller, F. Furche, J. R. Long and W. J. Evans, *Chem. Eur. J.*, 2018, **24**, 7702-7709.
14. D. H. Woen, G. P. Chen, J. W. Ziller, T. J. Boyle, F. Furche and W. J. Evans, *Angew. Chem. Int. Ed.*, 2017, **56**, 2050-2053.
15. R. Zitz, H. Arp, J. Hlina, M. Walewska, C. Marschner, T. Szilvási, B. Blom and J. Baumgartner, *Inorg. Chem.*, 2015, **54**, 3306-3315.
16. W. W. Brennessel and J. E. Ellis, *Inorg. Chem.*, 2012, **51**, 9076-9094.

17. C. B. Benda, J.-Q. Wang, B. Wahl and T. F. Fässler, *Eur. J. Inorg. Chem.*, 2011, DOI: doi:10.1002/ejic.201100412, 4262-4269.
18. C. B. Benda, M. Waibel and T. F. Fässler, *Angew. Chem. Int. Ed.*, 2015, **54**, 522-526.
19. J.-Q. Wang and T. F. Fassler, *Z. Naturforsch., B: Chem. Sci.*, 2009, **64**, 985.
20. I. Sanger, T. I. Kuckmann, F. Dornhaus, M. Bolte, M. Wagner and H.-W. Lerner, *Dalton Trans.*, 2012, **41**, 6671-6676.
21. M. Zirngast, U. Florke, J. Baumgartner and C. Marschner, *Chem. Commun.*, 2009, DOI: 10.1039/B910637E, 5538-5540.
22. H. Arp, M. Zirngast, C. Marschner, J. Baumgartner, K. Rasmussen, P. Zark and T. Müller, *Organometallics*, 2012, **31**, 4309-4319.
23. J.-C. Berthet, C. Villiers, J.-F. Le Maréchal, B. Delavaux-Nicot, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Organomet. Chem.*, 1992, **440**, 53-65.
24. K. R. Meihaus, M. E. Fieser, J. F. Corbey, W. J. Evans and J. R. Long, *J. Am. Chem. Soc.*, 2015, **137**, 9855-9860.
25. M. E. Fieser, M. R. MacDonald, B. T. Krull, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2015, **137**, 369-382.
26. Z. Xie, F. E. Hahn and C. Qian, *J. Organomet. Chem.*, 1991, **414**, C12-C14.
27. S. D. Stults, R. A. Andersen and A. Zalkin, *Organometallics*, 1990, **9**, 115-122.
28. X.-G. Zhou, Z.-E. Huang, R.-F. Cai, S.-N. Yu and X.-Y. Huang, *Chin. J. Struct. Chem*, 1997, **16**, 384.
29. J. H. Burns, W. H. Baldwin and F. H. Fink, *Inorg. Chem.*, 1974, **13**, 1916-1920.
30. T. Liu, *Kristallografiya*, 2002, **47**, 470.
31. M. E. Fieser, D. H. Woen, J. F. Corbey, T. J. Mueller, J. W. Ziller and W. J. Evans, *Dalton Trans.*, 2016, **45**, 14634-14644.
32. A. Hammel, W. Schwarz and J. Weidlein, *J. Organomet. Chem.*, 1989, **363**, C29-C35.
33. R. Shannon, *Acta Crystallographica Section A*, 1976, **32**, 751-767.
34. D. N. Huh, L. E. Darago, J. W. Ziller and W. J. Evans, *Inorg. Chem.*, 2018, **57**, 2096-2102.
35. T. F. Jenkins, D. H. Woen, L. N. Mohanam, J. W. Ziller, F. Furche and W. J. Evans, *Organometallics*, 2018, in press.
36. Y. Shimazaki, T. D. P. Stack and T. Storr, *Inorg. Chem.*, 2009, **48**, 8383-8392.
37. N. Leconte, J. Moutet, T. Constantin, F. Molton, C. Philouze and F. Thomas, *Eur. J. Inorg. Chem.*, 2018, **2018**, 1752-1761.
38. F. Jaroschik, A. Momin, F. Nief, X.-F. Le Goff, G. B. Deacon and P. C. Junk, *Angew. Chem. Int. Ed.*, 2009, **48**, 1117-1121.
39. M. Fang, J. H. Farnaby, J. W. Ziller, J. E. Bates, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2012, **134**, 6064-6067.
40. J. D. Rinehart, M. Fang, W. J. Evans and J. R. Long, *J. Am. Chem. Soc.*, 2011, **133**, 14236-14239.
41. M. Fang, J. E. Bates, S. E. Lorenz, D. S. Lee, D. B. Rego, J. W. Ziller, F. Furche and W. J. Evans, *Inorg. Chem.*, 2011, **50**, 1459-1469.
42. J. D. Rinehart, M. Fang, W. J. Evans and J. R. Long, *Nature Chemistry*, 2011, **3**, 538.
43. D. H. Woen, G. P. Chen, J. W. Ziller, T. J. Boyle, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2017, **139**, 14861-14864.
44. P. M. D. Mingos and A. L. Rohl, *Inorg. Chem.*, 1991, **30**, 3769-3771.
45. L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1959, **9**, 86-92.

46. D. E. Bergbreiter and J. M. Killough, *J. Am. Chem. Soc.*, 1978, **100**, 2126-2134.

TOC Graphic: