

## PAPER

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# Evaluating electrochemical accessibility of $4f^n5d^1$ and $4f^{n+1}$ Ln(II) ions in $(C_5H_4SiMe_3)_3Ln$ and $(C_5Me_4H)_3Ln$ complexes†

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The reduction potentials (reported vs.  $Fc^+/Fc$ ) for a series of  $Cp'_3Ln$  complexes ( $Cp' = C_5H_4SiMe_3$ ,  $Ln =$  lanthanide) were determined via electrochemistry in THF with  $[^nBu_4N][BPh_4]$  as the supporting electrolyte. The  $Ln(III)/Ln(II)$  reduction potentials for  $Ln = Eu, Yb, Sm$ , and  $Tm$  (−1.07 to −2.83 V) follow the expected trend for stability of  $4f^7$ ,  $4f^{14}$ ,  $4f^6$ , and  $4f^{13}$   $Ln(II)$  ions, respectively. The reduction potentials for  $Ln = Pr, Nd, Gd, Tb, Dy, Ho, Er$ , and  $Lu$ , that form  $4f^n5d^1$   $Ln(II)$  ions ( $n = 2–14$ ), fall in a narrow range of −2.95 V to −3.14 V. Only cathodic events were observed for  $La$  and  $Ce$  at −3.36 V and −3.43 V, respectively. The reduction potentials of the  $Ln(II)$  compounds  $[K(2.2.2-cryptand)][Cp'_3Ln]$  ( $Ln = Pr, Sm, Eu$ ) match those of the  $Cp'_3Ln$  complexes. The reduction potentials of nine  $(C_5Me_4H)_3Ln$  complexes were also studied and found to be 0.05–0.24 V more negative than those of the  $Cp'_3Ln$  compounds.

## Introduction

For many years, it was assumed that  $4f^7$   $Eu(II)$ ,  $4f^{14}$   $Yb(II)$ , and  $4f^6$   $Sm(II)$  were the only +2 lanthanide ions accessible in solution.<sup>1–3</sup> The availability of these ions was attributed to the quantum mechanical stabilization and symmetric nature of the half-filled and filled-shells and the  $4f^6$  configuration that approached a half-filled shell. Chemical<sup>4–6</sup> and electrochemical<sup>7,8</sup> studies were consistent with this idea, with  $Eu(II)$  being the most stable, followed by  $Yb(II)$  and then  $Sm(II)$ .  $Ln(III)/Ln(II)$  reduction potentials for the  $4f^n \rightarrow 4f^{n+1}$  couples, estimated on the basis of thermochemical and electrochemical data (see ESI† for a compilation), suggested the  $Ln(II)$  ions of the other lanthanides were so negative that the  $Ln(II)$  ions would react with any solvent.<sup>3,9,10</sup>  $Tm(II)$ ,  $Dy(II)$ , and  $Nd(II)$  were known in the solid state, but were not expected to exist in solution<sup>2,11</sup> until 1997–2001 when Bochkarev and co-workers showed that molecular species of  $4f^{13}$   $Tm(II)$ ,  $4f^{10}$   $Dy(II)$ , and  $4f^4$   $Nd(II)$  could be synthesized.<sup>4,12,13</sup> The  $4f^{13}$   $Tm(II)$  ion was the next most likely  $Ln(II)$  species since it was approaching a filled shell, but the other two ions did not have electron configurations that could be rationalized by this method. Since no other  $Ln(II)$  ions were known even in the solid state, it was believed that  $Eu(II)$ ,  $Yb(II)$ ,  $Sm(II)$ ,  $Tm(II)$ ,  $Dy(II)$ , and  $Nd(II)$  were

the only lanthanides that could be isolable in the +2 oxidation state.

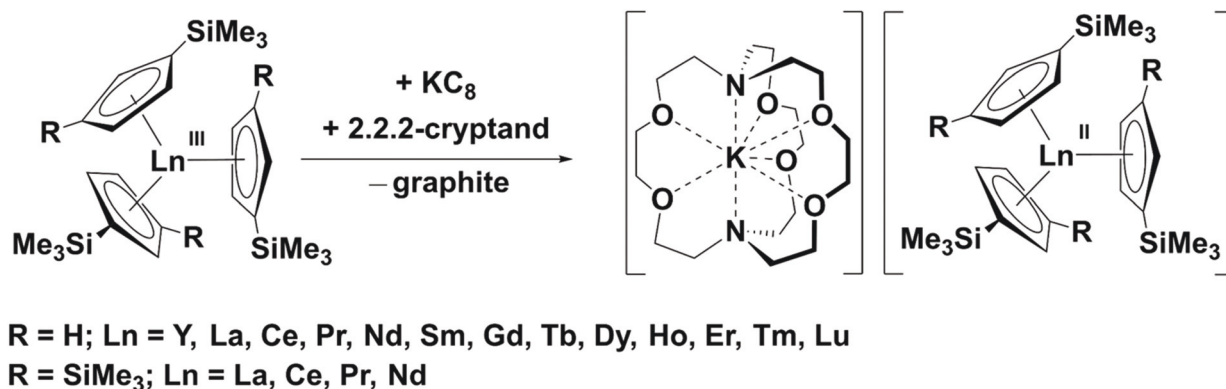
In 2008, Lappert reported  $La(II)$  and  $Ce(II)$  species via reduction of tris(cyclopentadienyl) complexes<sup>14</sup> and by 2013,  $Ln(II)$  were known for all the rest of the lanthanide series (excluding radioactive  $Pm$ ) and yttrium using this reduction method (Scheme 1).<sup>15–21</sup> Lappert reported electrochemical measurements on  $Cp''La$  and a reversible couple was observed with an  $E_{1/2}$  value of −2.80 V vs.  $Fc^+/Fc$ .<sup>22</sup> However, electrochemical analysis of the other  $Ln(III)/Ln(II)$  reduction potentials has focused predominantly on the traditional six  $Ln(II)$  ( $Ln = Nd, Sm, Eu, Dy, Tm$ , and  $Yb$ ) ions with  $4f^{n+1}$  electron configurations<sup>12,13</sup> despite the availability of every lanthanide metal in the +2 oxidation state.

The absence of electrochemical measurements on the non-traditional  $Ln(III)/Ln(II)$  redox couples is due in part to the high reactivity of the new  $4f^n5d^1$   $Ln(II)$  ions and the very negative reduction potentials needed to form them. The most polar solvent that is inert to these  $Ln(II)$  ions<sup>23,24</sup> is THF which leads to a large internal resistance and large peak separations.<sup>25,26</sup> In addition,  $Ln(II)$  species often react with common supporting electrolytes. Recent electrochemical studies of low oxidation state actinide complexes have shown that  $[^nBu_4N][BPh_4]$  is suitable for strongly reducing f element systems.<sup>27–31</sup>

We now find that  $[^nBu_4N][BPh_4]$  is an excellent supporting electrolyte for lanthanide systems. Here, we report the successful electrochemical determination of the  $Ln(III)/Ln(II)$  reduction potential across the entire  $Cp'_3Ln$  ( $Cp' = C_5H_4SiMe_3$ ) series using  $[^nBu_4N][BPh_4]$  in THF. Additionally, the electrochemistry of three  $Ln(II)$  complexes,  $[K(crypt)][Cp'_3Ln]$  (crypt = 2.2.2-cryp-

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**Scheme 1** Reduction of  $(C_5R_5)_3Ln$  to form  $Ln(II)$  complexes.

tand), is reported to verify the data obtained from  $Cp'_3Ln$  studies. Also reported are reduction potentials of nine  $Cp^{tet}_3Ln$  ( $Cp^{tet} = C_5Me_4H$ ) compounds that were analyzed to investigate the impact of the electron-donation strength of the ligand on the reduction potentials of the lanthanide complexes.

## Experimental details

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use.  $Cp'_3Ln$ ,<sup>15–18,32</sup>  $[K(crypt)][Cp'_3Ln]$ ,<sup>17,18</sup> and  $Cp^{tet}_3Ln$ <sup>33–36</sup> were synthesized according to literature procedures.  $[^nBu_4N][BPh_4]$  (Sigma, electrochemical grade >99%) was recrystallized from acetone three times and dried at 80 °C and  $10^{-5}$  Torr overnight before use.  $(C_5Me_5)_2Fe$  (Aldrich) was purified by sublimation before use. Electrochemical measurements were collected with a freshly made THF solution of supporting electrolyte with a glassy carbon working electrode, platinum wire counter electrode, and silver wire pseudo-reference electrode with a Princeton Applied Research PARSTAT 2273 Advanced Electrochemical System and referenced with internal standard  $(C_5Me_5)_2Fe$ . Internal resistance was measured for each solution and resistance was manually compensated by approximately 90% of the measured value. All scans on  $Cp'_3Ln$  and  $Cp^{tet}_3Ln$  were in the cathodic direction while scans on  $[K(crypt)][Cp'_3Ln]$  were in the anodic direction.

### General electrochemistry procedure

Inside the glovebox, a stock 100 mM  $[^nBu_4N][BPh_4]$  electrolyte solution was freshly prepared in THF. Between 1–2 mL of this solution were transferred to a 20 mL scintillation vial and a cyclic voltammogram of this solution was collected to verify the electrolyte solution was free of impurities. Roughly 10–20 mg of the Ln compound were dissolved in the same electrolyte solution to yield approximately a 10 mM solution. Electrodes were placed into the vial and the vial was left open

to the glovebox atmosphere during data collection. The internal resistance was measured and cyclic voltammetry experiments were then recorded.  $(C_5Me_5)_2Fe$  was added to the same solution following all data collection, and a single scan was recorded to measure the internal standard redox event.

## Results

### Electrochemical protocol

Cyclic voltammetry experiments were performed using a glassy carbon disc working electrode, a platinum wire counter electrode, and a silver wire pseudo-reference electrode. Freshly-made 100 mM solutions of  $[^nBu_4N][BPh_4]$  in THF provided the supporting electrolyte. All potentials are reported *versus* the ferrocenium/ferrocene ( $Fc^+/Fc$ ) couple, which is reported as  $-0.40$  V *vs.* SHE.<sup>37</sup> Decamethylferrocene,  $(C_5Me_5)_2Fe$ , which has a reduction potential of  $-0.495$  V *vs.*  $Fc^+/Fc$  under the present experimental conditions,<sup>27</sup> was used as an internal standard for all experiments.

### $(C_5H_4SiMe_3)_3Ln$

The  $Cp'_3Ln$  series was chosen for this study since  $Cp'_3Ln$  can be synthesized for the entire lanthanide series (excluding radioactive promethium), as well as for yttrium.<sup>20</sup> The reduction potentials measured for the  $Cp'_3Ln$  complexes are given in Table 1.

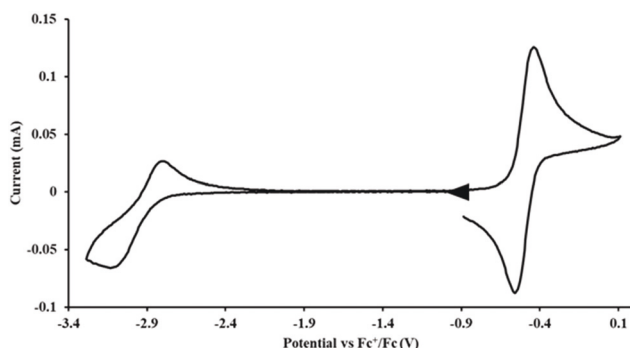
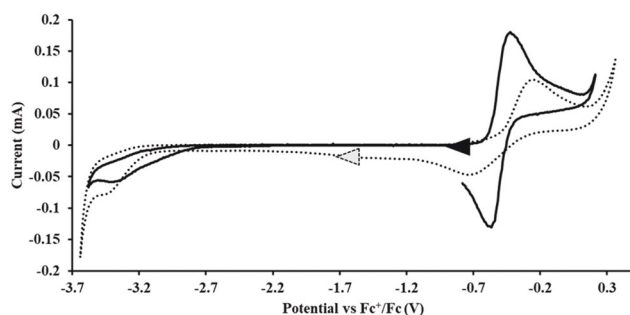
The cyclic voltammograms of all the  $Cp'_3Ln$  complexes, except for  $Cp'_3La$  and  $Cp'_3Ce$ , exhibit a quasi-reversible event assigned to the  $Ln(III)/Ln(II)$  redox couple (see ESI†). A representative example of  $Cp'_3Tb$  is shown in Fig. 1. The  $\Delta E_{pp}$  varies from 0.18 V to 1.08 V, as was previously found for the actinide and lanthanide electrochemistry in THF using  $[^nBu_4N][BPh_4]$  or  $[^nBu_4N][OTf]$ .<sup>27,38</sup>

Variations in scan rate resulted in minimal change to the  $E_{1/2}$  value, see ESI†. The cyclic voltammograms for  $Cp'_3La$  and  $Cp'_3Ce$  displayed only cathodic events (Fig. 2). In both cases, the processes are irreversible up to scan rates of  $\nu = 800$  mV s<sup>-1</sup>. To confirm our assignments,  $Ln(II)$  complexes  $[K(crypt)][Cp'_3Ln]$  ( $Ln = Pr, Sm, Eu$ ) were analyzed (Fig. 3). The measured  $E_{1/2}$  values in Table 2 are in good agreement with the values in Table 1.

**Table 1** Ln(III)/Ln(II) reduction potentials of Cp<sub>3</sub>Ln with 100 mM [t<sup>n</sup>Bu<sub>4</sub>N][BPh<sub>4</sub>] supporting electrolyte in THF at  $\nu = 200 \text{ mV s}^{-1}$ 

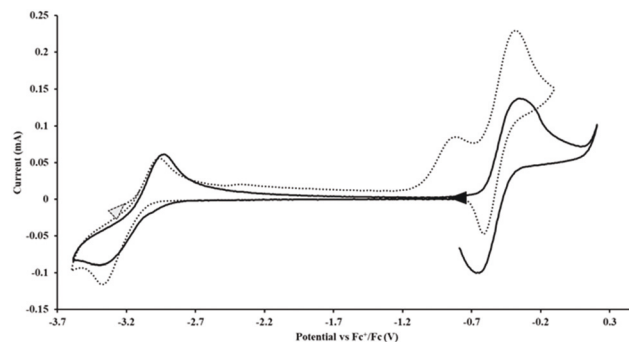
Ln	$E_{PC}$ (V)	$E_{PA}$ (V)	Ln(III)/Ln(II) $E_{1/2}$ (V)
Y	−3.12	−2.94	−3.06
La	−3.36	N/A <sup>a</sup>	N/A
Ce	−3.43	N/A <sup>a</sup>	N/A
Pr	−3.35	−2.93	−3.14
Nd	−3.33	−2.93	−3.14
Sm	−2.76	−2.06	−2.41
Eu	−1.61	−0.53	−1.07
Gd	−3.31	−2.64	−2.98
Tb	−3.10	−2.80	−2.95
Dy	−3.05	−2.86	−2.96
Ho	−3.12	−2.92	−3.02
Er	−3.14	−2.90	−3.02
Tm	−3.04	−2.63	−2.83
Yb	−2.02	−1.27	−1.64
Lu	−3.21	−3.03	−3.12

<sup>a</sup> Denotes the absence of a return oxidation in the cyclic voltammogram.

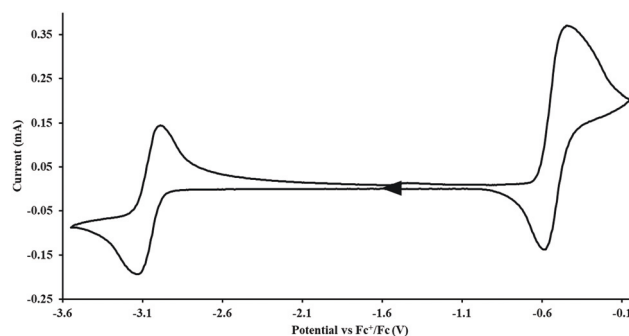
**Fig. 1** Cyclic voltammogram of Cp<sub>3</sub>Tb with the internal standard (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Fe at  $\nu = 200 \text{ mV s}^{-1}$ . The event assigned to the Tb(III)/Tb(II) couple is centered at −2.95 V. The event centered at −0.495 V is due to the internal standard.**Fig. 2** Cyclic voltammogram of Cp<sub>3</sub>La (solid) and Cp<sub>3</sub>Ce (dotted) with the internal standard (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Fe at  $\nu = 200 \text{ mV s}^{-1}$ . The events centered at −0.495 V are due to the internal standard.

### (C<sub>5</sub>Me<sub>4</sub>H)<sub>3</sub>Ln

The Cp<sup>tet</sup><sub>3</sub>Ln compounds were also studied *via* electrochemistry to determine how the ligand electron-donating strength affects the Ln reduction potential (Fig. 4). Ln(II) com-

**Fig. 3** Cyclic voltammogram of Cp<sub>3</sub>Pr (solid) and [K(crypt)][Cp<sub>3</sub>Pr] (dashed) with the internal standard (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Fe at  $\nu = 200 \text{ mV s}^{-1}$ . The events centered at −3.14 V are assigned to the Pr(III)/Pr(II) couple, the anodic event at −0.35 V in the voltammogram of [K(crypt)][Cp<sub>3</sub>Pr] is likely a ligand-based event,<sup>27</sup> and the events centered at −0.495 V are due to the internal standard.**Table 2** Ln(III)/Ln(II) Reduction potentials for Cp<sub>3</sub>Ln and [K(crypt)][Cp<sub>3</sub>Ln] compounds with 100 mM [t<sup>n</sup>Bu<sub>4</sub>N][BPh<sub>4</sub>] supporting electrolyte in THF at  $\nu = 200 \text{ mV s}^{-1}$ 

	$E_{PC}$ (V)	$E_{PA}$ (V)	Ln(III)/Ln(II) $E_{1/2}$ (V)
Cp <sub>3</sub> Pr	−3.35	−2.93	−3.14
[K(crypt)][Cp <sub>3</sub> Pr]	−3.36	−2.93	−3.15
Cp <sub>3</sub> Sm	−2.76	−2.06	−2.41
[K(crypt)][Cp <sub>3</sub> Sm]	−2.76	−2.06	−2.41
Cp <sub>3</sub> Eu	−1.61	−0.53	−1.07
[K(crypt)][Cp <sub>3</sub> Eu]	−1.48	−1.03	−1.26

**Fig. 4** Cyclic voltammogram of Cp<sup>tet</sup><sub>3</sub>Gd with the internal standard (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Fe at  $\nu = 200 \text{ mV s}^{-1}$ . The event centered at −3.04 V is assigned to the Gd(III)/Gd(II) couple and the event centered at −0.495 V is due to the internal standard.

plexes with the Cp<sup>tet</sup> ligand set, *i.e.* [K(crypt)][Cp<sup>tet</sup><sub>3</sub>Ln], have been isolated only for the larger lanthanide metals Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, and Dy (Table 3). The redox couples observed in the cyclic voltammograms for Cp<sup>tet</sup><sub>3</sub>Ln are summarized in Table 3 and Fig. 4 shows a representative example for Cp<sup>tet</sup><sub>3</sub>Gd. Interestingly, with this ligand set, both  $E_{PA}$  and  $E_{PC}$  events are observed for Cp<sup>tet</sup><sub>3</sub>La and Cp<sup>tet</sup><sub>3</sub>Ce, the latter of which has the most negative  $E_{1/2}$  of the series. Overall, the reduction potentials for the Cp<sup>tet</sup><sub>3</sub>Ln series are more negative

**Table 3** Ln(III)/Ln(II) reduction potentials of the Cp<sup>tet</sup><sub>3</sub>Ln compounds with 100 mM [<sup>n</sup>Bu<sub>4</sub>N][BPh<sub>4</sub>] supporting electrolyte in THF at  $\nu = 200$  mV s<sup>-1</sup>

Ln	$E_{PC}$ (V)	$E_{PA}$ (V)	Ln(III)/Ln(II) $E_{1/2}$ (V)
La	-3.48	-3.22	-3.35
Ce	-3.32	-3.22	-3.37
Pr	-3.51	-3.22	-3.27
Nd	-3.27	-3.11	-3.19
Sm	-2.77	-2.43	-2.60
Gd	-3.12	-2.95	-3.04
Tb	-3.19	-3.04	-3.12
Dy	-3.29	-3.10	-3.20
Ho	-3.24	-3.11	-3.18

than the Cp'<sub>3</sub>Ln series which is consistent with the electron-donating strength of the ligand.<sup>27,39–41</sup>

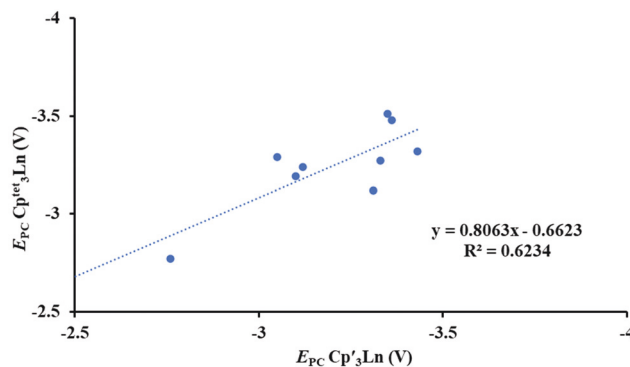
## Discussion

Using [<sup>n</sup>Bu<sub>4</sub>N][BPh<sub>4</sub>] as a supporting electrolyte, it was possible for the first time to collect electrochemical data on all the metals in the lanthanide series (except the radioactive Pm). This is because the Cp'<sub>3</sub> ligand set is the first to support Ln(II) ions across the series in complexes stable enough for electrochemical analysis.

Except for Cp'<sub>3</sub>La and Cp'<sub>3</sub>Ce, quasi-reversible cyclic voltammograms were obtained and the assignment of the redox couple to a Ln(III)/Ln(II) process was confirmed by analyzing the Ln(II) complexes [K(crypt)][Cp'<sub>3</sub>Ln] for Ln = Pr, Sm, and Eu. For Cp'<sub>3</sub>La and Cp'<sub>3</sub>Ce, it is likely that the Ln(II) product participated in a chemical reaction that interfered with the corresponding oxidation in the redox couple.

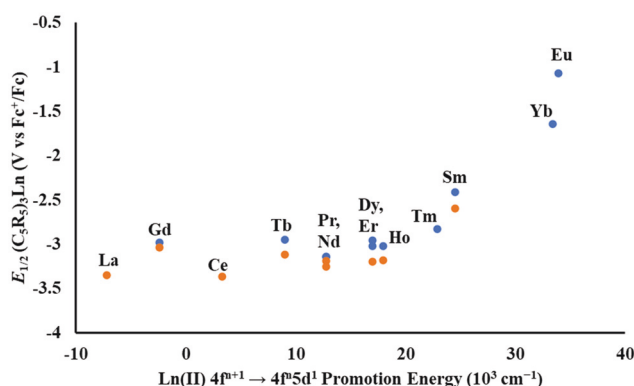
The [<sup>n</sup>Bu<sub>4</sub>N][BPh<sub>4</sub>] supporting electrolyte also led to successful electrochemical analysis of Cp<sup>tet</sup><sub>3</sub>Ln complexes. Since Cp<sup>tet</sup> is a more electron-donating ligand than Cp,<sup>27,39–41</sup> more negative reduction potentials for Cp<sup>tet</sup><sub>3</sub>Ln compared to their Cp'<sub>3</sub>Ln analogs were observed with shifts of 0.05–0.24 V, depending on the metal. In addition, the electrochemistry of Cp<sup>tet</sup><sub>3</sub>La was more reversible than that of Cp'<sub>3</sub>La, even though these are some of the most negative potentials measured. Hence, the electrochemical results appear to be quite sensitive to the specific metal and ligand. A plot of the  $E_{PC}$  for Cp'<sub>3</sub>Ln vs.  $E_{PC}$  for Cp<sup>tet</sup><sub>3</sub>Ln is shown in Fig. 5 (see ESI† for plots of  $E_{1/2}$ ). The low  $R^2 = 0.62$  value shows the variability of the data with metal and ligand and the lack of a consistent correlation.

For the traditional 4f<sup>n+1</sup> Ln(II) ions, the Ln(III)/Ln(II) reduction potentials of the Cp'<sub>3</sub>Ln complexes follow the order of stability expected based on half-filled shells being more stable than filled shells. Hence, the couple for 4f<sup>7</sup> Eu(II) (−1.07 V) was less negative than that of 4f<sup>14</sup> Yb(II) (−1.64 V). The Ln(II) ions with electron configurations approaching half-filled and filled subshells are next, 4f<sup>6</sup> Sm(II) (−2.41 V), and 4f<sup>13</sup> Tm (−2.83 V). These data are valuable since they show consistency with previous studies and match the known reactivity studies in the literature.



**Fig. 5**  $E_{PC}$  for Cp'<sub>3</sub>Ln vs.  $E_{PC}$  for Cp<sup>tet</sup><sub>3</sub>Ln with "best fit" shown as the dotted line ( $R^2 = 0.62$ ).

The reduction potentials of the non-traditional 4f<sup>n</sup>5d<sup>1</sup> Ln(II) ions were all more negative than those of the traditional ions, a trend that is also consistent with chemical studies in the literature. These  $E_{1/2}$  values are plotted against the 4f<sup>n+1</sup> → 4f<sup>n</sup>5d<sup>1</sup> promotion energies for free Ln(II) ions in the gas phase<sup>42</sup> (Fig. 6). The metals (Ln = Eu, Yb, Sm, Tm) with the largest promotion energy have the least negative reduction potentials and are metals that form 4f<sup>n+1</sup> Ln(II) ions. For all the other entries, the plot shows no correlation with the 4f<sup>n</sup> + e<sup>−</sup> → 4f<sup>n</sup>5d<sup>1</sup> reduction potential and the 4f<sup>n+1</sup> → 4f<sup>n</sup>5d<sup>1</sup> promotion energy. This lack of correlation and the narrow range of −2.95 V to −3.14 V reduction potentials for the other metals suggests that the electrochemical potential needed to add an electron to a 4f<sup>n</sup> Ln(III) ion to make the 4f<sup>n</sup>5d<sup>1</sup> Ln(II) ion is similar for all these metals. There is also no obvious correlation between the reduction potentials and the number of 4f electrons in the 4f<sup>n</sup>5d<sup>1</sup> electron configuration (Table 4), but it does appear that the Ln(II) ions that have the most unpaired electrons in their electron configurations are the least difficult to reduce. Hence, 4f<sup>7</sup>5d<sup>1</sup> Gd(II) with a half-filled 4f shell and 4f<sup>8</sup>5d<sup>1</sup> Tb(II) with six formally unpaired 4f electrons have less negative reduction potentials compared to the other ions (Table 4). Since this analysis is at the single electron approxi-



**Fig. 6**  $E_{1/2}$  values of Cp'<sub>3</sub>Ln (blue) and Cp<sup>tet</sup><sub>3</sub>Ln (orange) versus 4f<sup>n+1</sup> → 4f<sup>n</sup>5d<sup>1</sup> promotion energies for free Ln<sup>2+</sup> ions in the gas phase.



**Table 4**  $E_{1/2}$  and  $E_{PC}$  values for  $Cp'_3Ln$  in order of increasing reduction potential

Ln	$E_{1/2}$ (V)	$E_{PC}$ (V)	$n$ in $4f^n5d^1$	Number of unpaired f electrons
Tb	−2.95	−3.10	8	6
Dy	−2.96	−3.05	9	5
Gd	−2.98	−3.31	7	7
Ho	−3.02	−3.12	10	4
Er	−3.02	−3.14	11	4
Lu	−3.12	−3.21	14	0
Nd	−3.14	−3.33	3	3
Pr	−3.14	−3.35	2	2
La		−3.43	0	0
Ce		−3.36	1	1

mation level, this should only be noted as an observation that needs further evaluation in the future. It should also be noted that, at present, Gd, Dy, and Tb form more types of  $Ln(II)$  complexes with various ligands than the other metals.<sup>18,23,33,43,44</sup>

The reduction potentials of  $Cp'_3Dy$  and  $Cp^{tet}_3Dy$  are of special interest since  $Dy(II)$  is a configurational crossover ion<sup>17,20</sup> that has a  $4f^95d^1$  electron configuration in  $[K(crypt)][Cp'_3Dy]$ <sup>17</sup> and a  $4f^{10}$  configuration in  $[K(crypt)][Cp^{tet}_3Dy]$ .<sup>33</sup> The more negative −3.20 V  $E_{1/2}$  for  $Cp^{tet}_3Dy$  compared to −2.96 V for  $Cp'_3Dy$  is consistent with the large electron-donating power of  $Cp^{tet}$ . However, this means that it is easier to populate a 5d orbital in  $Cp'_3Dy$  than to add an electron to the 4f valence orbitals of  $Cp^{tet}_3Dy$ . Again, this shows the strong dependence of the reduction potentials on ligands.

## Conclusion

The reduction potentials for all the metals in the lanthanides series except Pm were determined in  $Cp'_3Ln$  complexes by electrochemical methods using  $[^nBu_4N][BPh_4]$  as a supporting electrolyte in THF. Reactions involving  $4f^n \rightarrow 4f^{n+1}$  reductions have the least negative  $E_{1/2}$  values, −1.07 V to −2.83 V, and follow patterns for the stability of half-filled and filled-shell electron configurations. Reactions involving  $4f^n \rightarrow 4f^n5d^1$  reductions have more negative potentials that fall in the narrower range of −2.95 V to −3.14 V and the correlation with electron configuration is less clear.  $Cp^{tet}_3Ln$  complexes are more difficult to reduce which is consistent with the stronger electron-donating character of  $Cp^{tet}$  vs.  $Cp'$ , but there are variations on the  $Cp^{tet}$  vs.  $Cp'$  data that are dependent on the specific metal.

## Conflicts of interest

The authors declare no competing financial interest.

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## References

- 1 F. Nief, in *Handbook on the Physics and Chemistry of Rare Earths*, ed. K. A. Gschneidner, J.-C. G. Bünzli and V. K. Pecharsky, Elsevier Science, Amsterdam, 2010, pp. 241–300.
- 2 G. Meyer, *Chem. Rev.*, 1988, **88**, 93–107.
- 3 L. R. Morss, *Chem. Rev.*, 1976, **76**, 827–841.
- 4 M. N. Bochkarev, *Coord. Chem. Rev.*, 2004, **248**, 835–851.
- 5 W. J. Evans, *Coord. Chem. Rev.*, 2000, **206–207**, 263–283.
- 6 G. A. Molander, *Chem. Rev.*, 1992, **92**, 29–68.
- 7 N. B. Mikheev, *Inorg. Chim. Acta*, 1984, **94**, 241–248.
- 8 A. M. Bond, G. B. Deacon and R. H. Newnham, *Organometallics*, 1986, **5**, 2312–2316.
- 9 S. G. Bratsch and J. J. Lagowski, *J. Phys. Chem.*, 1985, **89**, 3317–3319.
- 10 L. J. Nugent, R. D. Baybarz, J. L. Burnett and J. L. Ryan, *J. Phys. Chem.*, 1973, **77**, 1528–1539.
- 11 G. Meyer, in *The Rare Earth Elements: Fundamentals and Applications*, ed. D. A. Atwood, Wiley, New York, 2012, pp. 241–300.
- 12 M. N. Bochkarev, I. L. Fedushkin, A. A. Fagin, T. V. Petrovskaya, J. W. Ziller, R. N. R. Broomhall-Dillard and W. J. Evans, *Angew. Chem., Int. Ed.*, 1997, **36**, 133–135.
- 13 M. N. Bochkarev and A. A. Fagin, *Chem. – Eur. J.*, 1999, **5**, 2990–2992.
- 14 P. B. Hitchcock, M. F. Lappert, L. Maron and A. V. Protchenko, *Angew. Chem., Int. Ed.*, 2008, **47**, 1488–1491.
- 15 M. R. MacDonald, J. W. Ziller and W. J. Evans, *J. Am. Chem. Soc.*, 2011, **133**, 15914–15917.
- 16 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.
- 17 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.
- 18 M. R. MacDonald, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2013, **135**, 9857–9868.
- 19 C. T. Palumbo, L. E. Darago, C. J. Windor, J. W. Ziller and W. J. Evans, *Organometallics*, 2018, **37**, 900–905.
- 20 W. J. Evans, *Organometallics*, 2016, **35**, 3088–3100.
- 21 D. H. Woen and W. J. Evans, in *Handbook on the Physics and Chemistry of Rare Earths*, ed. J.-C. Bünzli and V. K. Pecharsky, Elsevier B.V., 1st edn, 2016, pp. 1–57.
- 22 M. C. Cassani, M. F. Lappert and F. Laschi, *Chem. Commun.*, 1997, **2**, 1563–1564.
- 23 D. N. Huh, J. W. Ziller and W. J. Evans, *Dalton Trans.*, 2018, **47**, 17285–17290.
- 24 D. H. Woen, D. N. Huh, J. W. Ziller and W. J. Evans, *Organometallics*, 2018, **37**, 3055–3063.
- 25 I. Noviandri, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A. F. Masters and L. Phillips, *J. Phys. Chem. B*, 1999, **103**, 6713–6722.
- 26 K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart and J. L. Dempsey, *J. Chem. Educ.*, 2018, **95**, 197–206.

- 27 J. C. Wedal, J. M. Barlow, J. W. Ziller, J. Y. Yang and W. J. Evans, *Chem. Sci.*, 2021, **12**, 8501–8511.
- 28 C. J. Inman and F. G. N. Cloke, *Dalton Trans.*, 2019, **48**, 10782–10784.
- 29 D. E. Morris, R. E. Da Re, K. C. Jantunen, I. Castro-Rodriguez and J. L. Kiplinger, *Organometallics*, 2004, **23**, 5142–5153.
- 30 J. A. Hlina, J. R. Pankhurst, N. Kaltsoyannis and P. L. Arnold, *J. Am. Chem. Soc.*, 2016, **138**, 3333–3345.
- 31 J. C. Wedal, S. Bekoe, J. W. Ziller, F. Furche and W. J. Evans, *Dalton Trans.*, 2019, **48**, 16633–16640.
- 32 J. K. Peterson, M. R. MacDonald, J. W. Ziller and W. J. Evans, *Organometallics*, 2013, **32**, 2625–2631.
- 33 T. F. Jenkins, D. H. Woen, L. N. Mohanam, J. W. Ziller, F. Furche and W. J. Evans, *Organometallics*, 2018, **37**, 3863–3873.
- 34 C. J. Windorff, M. T. Dumas, J. W. Ziller, A. J. Gaunt, S. A. Kozimor and W. J. Evans, *Inorg. Chem.*, 2017, **56**, 11981–11989.
- 35 H. Schumann, M. Glanz, H. Hemling and F. E. Hahn, *Z. Anorg. Allg. Chem.*, 1995, **621**, 341–345.
- 36 W. J. Evans, D. B. Rego and J. W. Ziller, *Inorg. Chem.*, 2006, **45**, 10790–10798.
- 37 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.
- 38 D. N. Huh, S. R. Ciccone, S. Bekoe, S. Roy, J. W. Ziller, F. Furche and W. J. Evans, *Angew. Chem., Int. Ed.*, 2020, **59**, 2–8.
- 39 S. A. Moehring and W. J. Evans, *Organometallics*, 2020, **39**, 1187–1194.
- 40 S. A. Moehring and W. J. Evans, *Chem. – Eur. J.*, 2020, **26**, 1530–1534.
- 41 C. E. Zachmanoglou, A. Docrat, B. M. Bridgewater, G. Parkin, C. G. Brandow, J. E. Bercaw, C. N. Jardine, M. Lyall, J. C. Green and J. B. Keister, *J. Am. Chem. Soc.*, 2002, **124**, 9525–9546.
- 42 W. C. Martin, R. Zalubas and L. Hagan, *Atomic Energy Levels-The Rare-Earth Elements*, U.S. Government Printing Office, Washington D.C., 1978.
- 43 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.
- 44 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.