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## COMMUNICATION

# Reversible C-C coupling in phenanthroline complexes of divalent samarium and thulium

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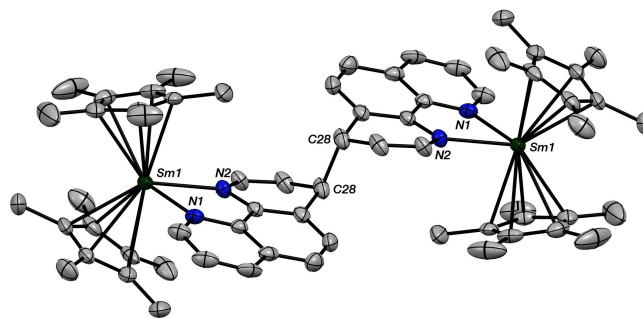
**The reaction of a series of organolanthanide fragments of samarium and thulium with phenanthroline is reported. All adducts couple in the 4-4' position of the phenanthroline ligand to yield the 4-4' dimers when they crystallize. The analysis of the solution structure revealed a thermally reversible C-C coupling in all cases.**

Redox non-innocent ligands are a matter of much recent interest in the development of catalytic species capable of releasing more electrons than the sole classic metal complex would do.<sup>1</sup> The seminal work of Wieghardt and Chirik led to the fast development of such catalysts capable of allowing important chemical reactions at lower economic and environmental costs.<sup>2</sup> The use of delocalized substituted pyridyl fragments is a typical strategy for the design of such redox non-innocent ligands because of their inherent  $\pi$ -acceptor character and the convenient N- coordination that lowers the energy of the LUMO(s) and allows the electron(s) transfer to occur.<sup>3</sup> The extent of delocalization and the shape of the symmetry orbital that accept the electron(s) is of crucial importance because if significant spin density is built up at a specific site of the ligand, chemistry will occur and the stored electron(s) may be lost.<sup>4</sup> Several mechanisms are possible for this to happen, one of them is of great importance and features a C-C reductive coupling, which can be both intra-<sup>5</sup> or intermolecular<sup>6</sup> and irreversible or reversible.<sup>5-6</sup> The conditions for the reversibility or irreversibility of such coupling is not obvious, yet very important since the formation of a reversible C-C bond can be viewed as a way to store electrons in the bond that is formed and does not affect the redox non-innocence of the ligand in further reactivity.<sup>7</sup>

Recently, some of us reported a reversible sigma C-C bond formation in phenanthroline complexes with decamethylterbocene.<sup>8</sup> The reason why the phenanthroline adduct couples while the analogous bipyridine complex does not has been rationalized by the larger amount of spin density that develops in *para* positions to the nitrogen atoms (position 4 and 7) in the phenanthroline ligand compared to the bipyridine ligand. However, the origin of the reversibility of this particular coupling while other reductive C-C couplings that are

reported with organolanthanides are irreversible, remains in question.<sup>6c, 6d</sup> The present work reports the preparation of several phenanthroline adducts with divalent lanthanide fragments having different redox potential and different steric hindrance. Despite their very different electronic nature, these complexes feature a C-C reversible coupling between the phenanthroline moieties in all cases albeit they show different thermodynamics in solution.

The synthesis of  $\text{Cp}^*_2\text{Sm}(\text{phen})$  was performed from  $\text{Cp}^*_2\text{Sm}(\text{OEt}_2)_2$  and sublimed phenanthroline in toluene and results in the formation of a dark precipitate in moderate yield. Dark green crystals, suitable for X-ray diffraction, were grown by slow diffusion of a toluene solution of phenanthroline into a toluene solution of the  $\text{Cp}^*_2\text{Sm}(\text{OEt}_2)_2$  and reveal the formation of the dimer  $[\text{Cp}^*_2\text{Sm}(\text{phen})]_2$  (**1**).



**Figure 1.** ORTEP of **1**. Carbon atoms are shown in grey, samarium in green and nitrogen in blue. Thermal ellipsoids are represented at 50 % level and hydrogen atoms are omitted for clarity.

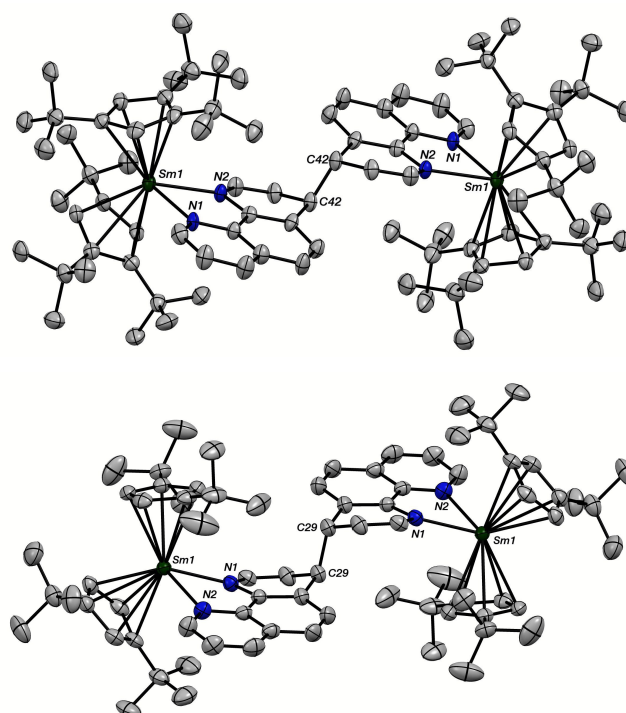
The X-ray crystal structure is similar to that reported for  $[\text{Cp}^*_2\text{Yb}(\text{phen})]_2$ .<sup>8</sup> In agreement with a larger ionic radius for samarium, the Sm-Cp distances of 2.433(3) Å are 0.09 Å longer than those found in  $[\text{Cp}^*_2\text{Yb}(\text{phen})]_2$ , as well as the Sm-N distances of 2.376(4) Å and 2.482(4) Å, respectively (to be compared to the Yb-N distances of 2.285(4) Å and 2.358(5) Å).<sup>8</sup> The dissymmetric nature of these distances and the distances and angles of the phenanthroline

moieties are in agreement with the formation of a dianion of 4,4'-phen<sub>2</sub>.<sup>8</sup> The C-C bond that forms the link between the two phenanthroline moieties (C(28)-C(28)') is of 1.61(1) Å and is similar to that found in the ytterbium complex (1.62(1) Å). Interestingly, the larger ionic radius of Sm compared to Yb only emerges from the M-M distance (of 11.07 Å in **1** and 10.92 Å in Cp\*<sub>2</sub>Yb(phen)) but not from the C(28)-C(28)' distance. This shows that a longer M-M distance, *i.e.*, a decrease of the steric crowding, does not lead to a shorter linkage between the two phenanthroline moieties in the solid state, in this case.

The very insoluble nature of the crystals did not allow a NMR analysis in toluene-d<sub>8</sub> or in thf-d<sub>8</sub>. However, in pyridine-d<sub>5</sub>, a gentle warming of the crystals allowed a partial solubilization to yield a deep green solution. The <sup>1</sup>H NMR spectrum shows 16 peaks, integrating each for about one proton, which are attributed to the phenanthroline protons and 3 peaks for the Cp\* resonances, integrating for 30, 15 and 15 respectively (Figure S1). A careful integration of the phenanthroline resonances allowed the separation of two distinct sets of 8 peaks in a 55:45 ratio, in agreement with the presence of a dimer in solution. The presence of two different isomers is explained by the two different coupling positions (4 and 7) on the phenanthroline ligand. In this spectrum, the presence of an additional singlet at around 2.5 ppm was not yet rationalized and was intriguing to us. Therefore, the solution was heated and the spectral window was extended. At 60 °C, the singlet at 2.5 increases in intensity and three other broad peaks appear at -67.5, -172.10 and -220.8 ppm (figure S2). Although one peak is still missing, these four signals show the presence of a symmetrical species (C<sub>2v</sub>) and can be attributed to the resonances of the monomeric form of Cp\*<sub>2</sub>Sm(phen) (**2**). A variable temperature experiment from 20 °C to 70 °C and a Van't Hoff analysis allowed the extraction of the thermodynamics for the dimerization reaction which are -19.9(1) kcal.mol<sup>-1</sup> for ΔH and -52(3) cal.mol<sup>-1</sup>.K<sup>-1</sup> for ΔS, *i.e.* a ΔG<sub>0</sub> of -4.5(6) kcal.mol<sup>-1</sup> at 298 K. This compares with a ΔG<sub>0</sub> of +2 kcal.mol<sup>-1</sup> found in the very similar Cp\*<sub>2</sub>Yb(3,8-Me<sub>2</sub>phen) complex.<sup>8</sup> The visible effect of these thermodynamics is that Cp\*<sub>2</sub>Yb(3,8-Me<sub>2</sub>phen) possesses a majority of its monomeric form at room temperature while Cp\*<sub>2</sub>Sm(phen) has a majority of its dimeric form at room temperature in solution.

In order to get insights in the possible role of the sterics in this reversible bond formation, we decided to move toward the synthesis of more sterically hindered complexes of samarium containing phenanthroline and synthesized the bulkier complexes Cp<sup>ttt</sup><sub>2</sub>Sm(phen), where Cp<sup>ttt</sup> is for 1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>, and Cp<sup>tt</sup><sub>2</sub>Sm(phen), where Cp<sup>tt</sup> is for 1,3-(Me<sub>2</sub>C)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>. These complexes were synthesized in pentane from base free Cp<sup>ttt</sup><sub>2</sub>Sm<sup>10</sup> and Cp<sup>tt</sup><sub>2</sub>Sm, respectively, and from sublimed phenanthroline. Both complexes are soluble in thf-d<sub>8</sub> and toluene-d<sub>8</sub> and X-ray suitable dark purple crystals were grown from respective concentrated toluene and thf solutions. The two crystal structures are similar and, again, show the presence of dimers of [Cp<sup>ttt</sup><sub>2</sub>Sm(phen)]<sub>2</sub> (**3**) and [Cp<sup>tt</sup><sub>2</sub>Sm(phen)]<sub>2</sub> (**5**) (Figure 2). Selected distances and angles are reported in Table 1. The distances alteration around the samarium metal center from **1** to **3** is noticeable with an increase of the Cp-Sm average distance of 0.1 Å while the Sm-N distances increase remain modest (0.02 Å). The Sm-Sm distance is of 11.27 Å and is increased by 0.2 Å from **1** but despite the evident increased steric bulk, the C-C bond that links the two phenanthroline

moieties, C(42)-C(42)' (see Figure 2), decrease to 1.57(1) Å. On the other hand, **5** has similar metrics than that of **1** around the metal center but the smaller Cp'-M-Cp' angle of 131 ° (compared to 139 ° - 140 °, see Table 1) leads to a large shrinkage of the Sm-Sm distance to 10.61 Å, while the C-C bond formed between the phenanthroline ligands (C(29)-C(29)', see Figure 2) is of 1.581(8) Å, that is about the same than that of **3**. In other words, the modulation of the steric hindrance on the ligand does not affect much the C-C distance of the bond that is created. The clear – and very important, message here is that the various solid state metrics of **1**, **3** and **5** give very little information on their solution behaviour and on the reversible or irreversible character of the C-C bond that is formed.



**Figure 2.** ORTEPs of **3** (above) and **5** (below). Carbon atoms are shown in grey, samarium in green and nitrogen in blue. Thermal ellipsoids are represented at 50 % level and hydrogen atoms are omitted for clarity.

**Table 1.** Selected Distances (Å) and angles (deg) for **1**, **3**, **5** and **7**.

	<b>1</b>	<b>3</b>	<b>5</b>	<b>7</b>
M-C(Cp) average	2.71(3)	2.79(6)	2.75(4)	2.71(6)
M-Cp	2.433(3)	2.534(5)	2.478(7)	2.432(9)
M-N(1)	2.482(4)	2.517(4)	2.356(3)	2.391(4)
M-N(2)	2.376(4)	2.385(4)	2.498(3)	2.288(4)
M-M	11.07	11.27	10.61	11.14
C(X)-C(X) <sup>a</sup>	1.61(1)	1.57(1)	1.581(8)	1.58(1)
Cp'-M-Cp'	139	139	131	140

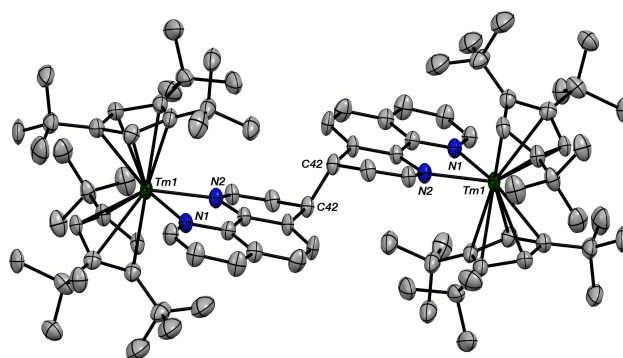
a) X: C28 for **1**, X: C42 for **3** and **7** and X: C29 for **5**.

The solution <sup>1</sup>H NMR analysis of **3** revealed a similar spectrum than that observed for **1** with a pair of enantiomers in a 55:45 ratio showing for each: 6 resonances for the <sup>1</sup>Bu groups on the Cp ligand, 4 resonances for the protons of the Cp ligand and 8 resonances for the phenanthroline ligand, in a 12:2:2 ratio, in agreement with the presence of a dimer (Figure S3). Several other resonances are present

at about 14 ppm and around 1 ppm while two other resonances are observed downfield at -88.6 ppm and -178.9 ppm. As already observed for **1**, increasing the temperature to 60 °C leads to the increase in intensity of these shifted resonances while the two sets of resonances corresponding to the dimeric isomers decrease in intensity (Figure S4 and S5). This behaviour is similar to **1** and is attributed to a dimer - monomer equilibrium,  $[\text{Cp}^{\text{III}}\text{Sm}(\text{phen})]_2$  (**3**) = 2  $\text{Cp}^{\text{III}}\text{Sm}(\text{phen})$  (**4**). The Van't Hoff analysis for this equilibrium allows the extraction of the thermodynamic parameters that are of -21.5(1) kcal.mol<sup>-1</sup> for  $\Delta H$  and -61(1) cal.mol<sup>-1</sup>.K<sup>-1</sup> for  $\Delta S$ , *i.e.* a  $\Delta G_0$  of -3.2(2) kcal.mol<sup>-1</sup> at 298 K. The same type of analysis was performed for the dimerization reaction  $[\text{Cp}^{\text{III}}\text{Sm}(\text{phen})]_2$  (**5**) = 2  $\text{Cp}^{\text{III}}\text{Sm}(\text{phen})$  (**6**) and leads to thermodynamic parameters of -19.3(1) kcal.mol<sup>-1</sup> for  $\Delta H$  and -51(3) cal.mol<sup>-1</sup>.K<sup>-1</sup> for  $\Delta S$ , *i.e.* a  $\Delta G_0$  of -4.3(2) kcal.mol<sup>-1</sup> at 298 K. In both cases the values are similar to those obtain for **1**. Because of rather large errors in the measurements (that are due to the difficulty of integrating very accurately resonances of paramagnetic complexes), we found it difficult to build a connection between steric bulk and thermodynamic data for the samarium series. However, it is interesting to note that although the formation of the bond is favourable in enthalpy, this is almost compensated by the entropy loss that is due to the dimerization, which explains why heating a solution of the dimers **1**, **3** or **5** in solution leads to the easy formation of their monomeric forms **2**, **4** and **6**.

It is now interesting to turn back to the comparison of the thermodynamics of the samarium complexes **1**, **3** and **5** with those of the ytterbium complex  $\text{Cp}^*\text{Yb}(\text{3,8-Me}_2\text{phen})$ . A value of  $\Delta G_0$  of +2 kcal.mol<sup>-1</sup> is found for the latter complex<sup>8</sup> while in **1**, **3** and **5** they are comprised between -4.5 and -3.2 kcal.mol<sup>-1</sup>. Because these values oscillate around zero, the net observation is that  $\text{Cp}^*\text{Yb}(\text{3,8-Me}_2\text{phen})$  is largely monomeric in solution at room temperature while **1**, **3** and **5** are largely dimeric. A  $\Delta G_0$  difference of about 5 to 6 kcal.mol<sup>-1</sup> constitutes a small difference for these two different lanthanides ions whose metallocene fragments have very different redox potentials. In our attempts to measure the redox potential of **1**, **3** and **5**, only an extremely small current was noticed at room temperature (probably because of their major dimeric form at this temperature), which did not allow us to draw any decent conclusion. However, the redox potential of  $\text{Cp}^*\text{Yb}(\text{phen})$  - monomer, was recorded by Morris et al. in thf and a value of -1.64 V vs.  $\text{Fc}^+/\text{Fc}$  was reported for the reversible redox couple centred on the phenanthroline ligand ( $\text{phen}/\text{phen}^-$ ).<sup>11</sup> The same group also reported the direct comparison in the electrochemical behaviour between  $\text{Cp}^*\text{Yb}(\text{tpy})$  and  $\text{Cp}^*\text{Sm}(\text{tpy})$  - both monomers, and the authors noted that the redox potential centred on the ligand differed only by 20 mV (-1.72 V vs -1.74 V, vs.  $\text{Fc}^+/\text{Fc}$ , respectively).<sup>12</sup> The group of Mazzanti came to the same conclusion with their electrochemical study on Schiff bases ligands whether there are coordinated to europium or neodymium.<sup>5c</sup> These two examples illustrate that, in lanthanide complexes, when the ligand is reduced by the metal, no matter what is the redox potential of the metal, it seems that the redox properties of the ligand remain very close and only the Lewis acidity variation can explain the small differences that are observed. If this conjecture is true, a metallocene fragment with a stronger reduction potential should display the same behaviour with phenanthroline than that of **1**, **3** and **5**. We therefore turned to the

$\text{Cp}^{\text{III}}\text{Tm}$  complex already reported by Nief et al. and added phenanthroline to the latter in pentane.<sup>6c, 13</sup> A dark purple solution forms and crystallization in toluene yields purple X-ray suitable crystals of  $[\text{Cp}^{\text{III}}\text{Tm}(\text{phen})]_2$  (**7**) (Figure 3). As expected, the structure features a dimer in which the Cp-Tm and the Tm-N distances are about 0.1 Å shorter than those of **3**. The Tm-Tm distance is comprised between that of **1** and **3** and the C(42)-C(42) distance is of 1.58(1) Å, in the same order than those of **3** and **5**. Again, if the M-Cp' and M-N distances are in agreement with the smaller ionic radius of thulium compared to samarium, it is very difficult to predict the behaviour of **7** in solution with the only information given by the metric parameters. A <sup>1</sup>H NMR of the crystals was performed in thf-d<sub>8</sub> and led to the observation of multiple very broad resonances at room temperature. Although their attribution is not possible because of the broadness of the signals, the presence of multiple signals is in agreement with a dimeric form in solution which contrasts with  $\text{Cp}^*\text{Yb}(\text{phen})$ . Heating this thf-d<sub>8</sub> solution to 60 °C lead to a substantial modification in the spectrum (see Figures S8, S9 and S10) and to a gradual increase of two resonances (in a 2:1 ratio) that were not present before, *viz.* to the gradual apparition of the monomer in solution, indicating a reversible C-C bond formation. Although a Vant' Hoff analysis cannot be performed in this case, the presence of the dimer in a large majority at room temperature while it becomes minor at 60 °C indicate that the thermodynamics are qualitatively similar to those measured for the samarium complexes, **1**, **3** and **5**. Additionally, the qualitative visible spectra of **7** recorded at different temperatures (from 0 °C to 100 °C) show a substantial evolution of the spectrum with the temperature (See Figure S17) and reinforce the picture of a reversible C-C bond formation in **7**.



**Figure 3.** ORTEP of **7**. Carbon atoms are shown in grey, thulium in green and nitrogen in blue. Thermal ellipsoids are represented at 50 % level and hydrogen atoms are omitted for clarity.

In conclusion, the information gathered in this work shows that when an electron is transferred from a divalent samarium, thulium or ytterbium fragment to a phenanthroline ligand, a reversible C-C coupling occurs between two phenanthroline ligands in all the studied cases. The analysis of the solid state metrics and the measurement of the thermodynamic data in solution indicate that the reversibility of the C-C bond is not only due to the sterics of the metallocene fragment (large entropic term) and also not only driven by the enthalpy of the C-C bond. A synergistic effect of both is more appropriate to explain this equilibrium. The important messages here are the following: (i) the observation of the solid-state crystal

structure does not allow predicting the solution behaviour of the complexes. (ii) If an equilibrium exists in solution between the dimer and the monomer, it is likely that an eventual oxidant will react, in solution, with the monomer and then displace the equilibrium, rather than oxidize the dimer. This is very important in the design of redox active ligand because it means that despite a dimerization can occur, the electron may still be available for reactivity provided that the entropic and enthalpic terms cancel themselves. This work also highlights the need of more information on the electronic structure of these complexes in order to rationalize the subtle changes observed along the series. Work is currently in progress in this direction.

## Notes and references

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Electronic Supplementary Information (ESI) available: general details on the syntheses, NMR studies and X-ray studies of **1**, **3**, **5**, and **7** (CCDC #1038893, 1038894, 1038895 and 1038896, respectively). See DOI: 10.1039/c000000x/

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