

A New Class of Organometallic Compounds Produced via Electron Transfer from Lanthanides

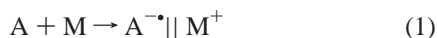
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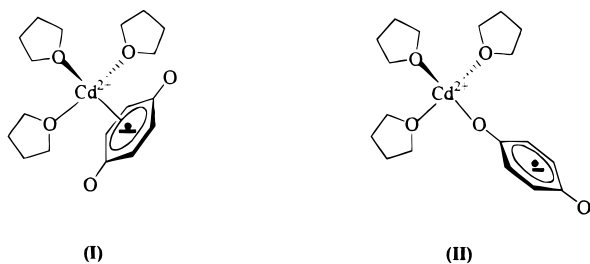
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The simplest organometallic compounds, which are produced by electron transfer from an alkali¹ or alkaline earth² metal to an organic acceptor (e.g., reaction 1) are of significant theoretical as well as practical use.³ The interaction between the metal cation and the resulting anion radical is usually a simple ion association moderated by the coulombic attraction between the two species and the competitive ion solvating nature of the solvent.⁴ However, we report here that exposure of an organic one-electron acceptor to a metallic f-block lanthanide results in the formation of a new class of organometallic complexes in which both acceptor molecules are ligated to the metal dication. Further, the donated electrons are spin-paired, and electron paramagnetic resonance (EPR) analysis (in the case of europium) reveals a lanthanide nucleus that appears as if it is interacting with a single unpaired electron.



The lanthanide results are reminiscent of the organometallic complexes that were formed when Cd ($d^{10}s^2$) metal was used to reduce benzoquinone in tetrahydrofuran.⁵ In that case, EPR proved to reveal a wealth of information concerning the resulting solvated organometallic compounds, and it was found that the anion radical could be simply ion-associated with the Cd^{2+} or coordinated to the metal dication as in Structures I and II.⁵



Since an anion radical generated by electron transfer from a lanthanide has not been reported, we were motivated to carry out an electron transfer from the doubly occupied s orbital of an f-block lanthanide (e.g., f^7s^2) to gain a preliminary understanding of the interactions between the resulting organic anion radical and the metal ion. To maximize the probability of a successful electron transfer, europium, having the lowest ionization potential

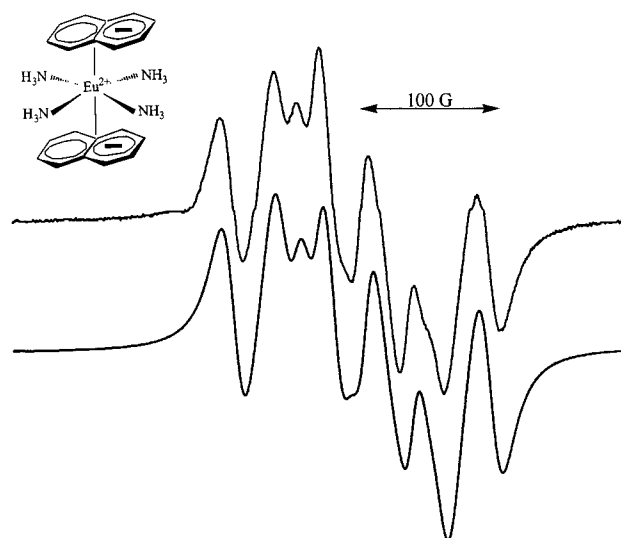


Figure 1. (Upper) X-band EPR spectrum taken immediately after the exposure of a 0.01 M solution of naphthalene in liquid ammonia to europium metal at -80 °C. The spectrum was recorded at -73 °C. (Lower) A computer simulation generated combining a 47.8% contribution from ^{151}Eu ($a_{151Eu} = 35.0$ G) and a 52.2% contribution by ^{153}Eu ($a_{153Eu} = 15.7$ G). The peak-to-peak line width is 17 G, and the spectrum for the heavier isotopic system has a 2.5 G upfield shift. The structure shown above the spectrum is tentative, but it is known that: (1) europium ions prefer an octahedral geometry, (2) they complex well with ammonia, and (3) (in this case) two naphthalene units are involved.

of the lanthanides,⁶ was the metal of choice for our initial studies. The large spin-orbit coupling to excited^{6b} states together with strong lattice couplings leaves most lanthanide complexes EPR silent at temperatures above 20 K.^{7,8} This has prevented most previous observations of lanthanide hyperfine splitting in mobile solution.

Exposure of naphthalene ($C_{10}H_8$, electron affinity = 3.5 kcal/mol)^{1d} dissolved in liquid ammonia to europium metal immediately results in the forest green color of the naphthalene anion radical. EPR analysis of this solution clearly exhibits a fleeting signal (lifetime ~ 10 min at room temperature). This signal comes from an unpaired electron ($g_{isotropic} = 1.99$) interacting with the ^{151}Eu ($I = 5/2$) and ^{153}Eu ($I = 5/2$) nuclei with coupling constants of $a_{153Eu} = 15.7$ G and $a_{151Eu} = 35.0$ G, Figure 1. This spectrum is identical to that expected for a single electron interacting with the metal nucleus.⁹ Surprisingly, no hyperfine interaction with the protons on $C_{10}H_8$ is exhibited.

To prove that the naphthalene had, indeed, accepted the electron from the europium, water was added. The organic products were 1,4-dihydronaphthalene ($C_{10}H_{10}$) and naphthalene, meaning that the $C_{10}H_8$ was reduced to its anion radical and underwent a normal Birch reduction.¹⁰ There was also the possibility that the hyperfine

(1) (a) Chang, R.; Johnson, C. S. *J. Am. Chem. Soc.* **1966**, *88*, 2338. (b) Zandstra, P. J.; Weissman, S. I. *J. Am. Chem. Soc.* **1962**, *84*, 4408. (c) Hirota, N. *J. Phys. Chem.* **1967**, *71*, 127. (d) Szwarc, M. In *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley-Interscience: New York, 1974.

(2) (a) Stevenson, C. D.; Schock, L. E.; Concepcion, R.; Peterson, R. A. *J. Phys. Chem.* **1985**, *89*, 175. (b) Stevenson, C. D.; Nieves, I.; Echegoyen, L. *J. Phys. Chem.* **1984**, *88*, 4332.

(3) For example see House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; Chapter 3.

(4) (a) Stevenson, C. D.; Caldwell, G.; Williams, E. *J. Phys. Chem.* **1979**, *83*, 643. (b) Stevenson, C. D.; Williams, E. *J. Am. Chem. Soc.* **1979**, *101*, 5910. (c) Stevenson, C. D.; Chang, Y. *J. Phys. Chem.* **1980**, *84*, 2255.

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(6) (a) The reduction potentials ($M^{3+} + 3e^- = M$) of europium and ytterbium are -1.99 and -2.22 V, respectively. (b) Cotton, A. F.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley-Interscience: New York, 1980; pp 981–990. (c) The various states arising from the f^n configurations are split by the lattice only to the extent of ~ 100 cm^{-1} ($kT \approx 200$ cm^{-1}) leaving more than one Kramer's double thermally accessible. Cotton, A. F.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley-Interscience: New York, 1980; p 981–990.

(7) (a) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance Elementary Theory and Practical Applications*; Chapman and Hall: New York, 1972, p 339. (b) Short relaxation times are due to coupling of the electronic spin-lattice relaxation with molecular vibration and collisions, which lead to fluctuations in the crystal field potential, see: Marks, T. J. *Prog. Inorg. Chem.* **1978**, *24*, 51.

(8) For a recent example, see: Hou, Z.; Fujita, A.; Zhang, Y.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 754.

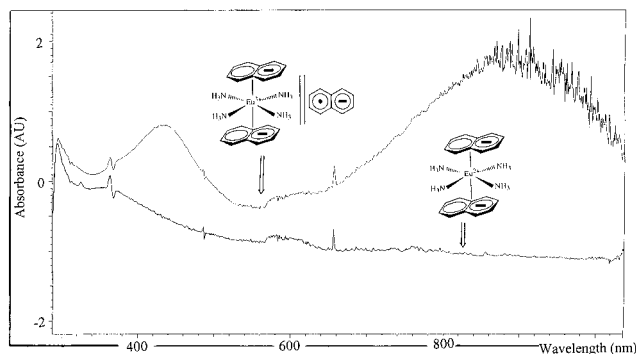


Figure 2. (Lower) UV-vis spectrum taken immediately after the exposure of a solution of naphthalene in liquid ammonia to europium metal at $-80\text{ }^{\circ}\text{C}$. The spectrum was recorded at $-73\text{ }^{\circ}\text{C}$. (Upper) UV-vis spectrum taken after the decay of the EPR active species. This spectrum clearly shows the presence of the naphthalene anion radical (broad band at $\sim 900\text{ nm}$ stretching well into the visible region) and the charge-transfer bands at 295 and 435 nm expected for a Eu^{3+} system. Note their absence in the lower spectrum.

splittings from the naphthalene were significantly smaller than the line width, which would mean that they could not be resolved and would only contribute to the line width of the europium hyperfine components. This proved not to be the case, as replacing the C_{10}H_8 with C_{10}D_8 did not alter the spectrum in any way. Further, an identical EPR spectrum is observed when anthracene, benzoquinone, or benzophenone is used as an electron acceptor. Clearly, the electron acceptor does not contribute to the hyperfine pattern or the EPR line shapes.

Apparently the two s electrons that were donated to the naphthalene remain spin-paired in the organometallic complex. Despite the seven f electrons left to interact with the metal dication, the $(\pm 7/2 \text{ to } \pm 5/2, \pm 5/2 \text{ to } \pm 3/2, \pm 3/2 \text{ to } \pm 1/2)$ EPR transitions are broadened to oblivion.^{7b} This allows a relatively uncomplicated observation of the europium nucleus through the $-1/2 \text{ to } +1/2$ transition. EPR analysis of the frozen solution at 160 K reveals some evidence of the other transitions. A weak, very broad line (peak to peak line width, 930 G) centered at 3360 G and a line at 1570 G (line width, 180 G) can be observed.

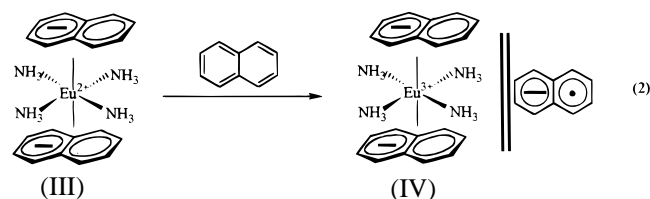
These results are consistent with the initial donation of the two s electrons to two acceptor molecules, with consequent tight coordination of the $\text{C}_{10}\text{H}_8^{\cdot-}$ to the Eu^{2+} nucleus, presumably through the europium s orbital. Since the two electrons, donated by the Eu, are in the same molecular orbital they are spin paired. Hence, only the remaining seven unpaired f electrons can contribute to the EPR signal. Further, only the $-1/2 \text{ to } +1/2$ transition in liquid solution is not broadened out of existence, and the resulting EPR spectrum appears to reflect the interaction of the europium nucleus with a single electron spin.

In the presence of excess organic acceptor, this EPR signal decays within a few minutes, and is replaced with the 25-line pattern normally observed for the solvated naphthalene anion

(9) (a) The solvated electron in dimethylamine associates with alkali metal cations to produce an EPR spectrum indicating the interaction of a single electron with the metal nucleus, see: Dye, J. L.; Dalton, L. R. *J. Phys. Chem.* **1967**, *71*, 184. (b) When an electron is transferred from sodium metal to benzophenone, the resulting sodium anion radical ion pairs aggregate to form an ion quartet consisting of two anion radicals and two sodium cations. EPR analysis of this solution yields a spectrum that appears as it would if one electron were interacting with only two sodium nuclei, see: Hirota, H.; Weissman, S. I. *J. Am. Chem. Soc.* **1964**, *86*, 2538.

(10) For a modern example, see: Zimmerman, H. E.; Wang, P. A. *J. Am. Chem. Soc.* **1993**, *115*, 2205.

radical.¹ The lifetime of the Eu^{2+} oxidation state is limited, and further oxidation occurs to give the more stable $3+$ oxidation state. The third electron is ejected from a 4f orbital to an available naphthalene molecule. The resulting solvated f^6 $\text{Eu}^{3+}(\text{C}_{10}\text{H}_8^-)_2(\text{NH}_3)_4$ complex does not have a simple Kramer's doublet transition available and is EPR silent. Thus, only the naphthalene anion radical, ion associated to the charged complex (Structure IV), is observed (reaction 2). The absence of an excess amount of naphthalene, does not prevent the EPR signal for the $\text{Eu}^{2+}(\text{C}_{10}\text{H}_8^-)_2(\text{NH}_3)_4$ complex (Structure III) from the same quick¹¹ decay and subsequent replacement by that of the solvated electron. This suggests that the driving force for the transition from Eu^{2+} to Eu^{3+} is relatively large.



Removal of the solvent (NH_3) under reduced pressure concentrates the solvated electron and renders it less thermodynamically stable. As a consequence of this, the electron "jumps" back into the Eu^{3+} complex, and the EPR signal can, again, be observed for the Eu^{2+} complex.

Immediately after the initial electron transfer from Eu to naphthalene, the absorption spectrum of $\text{Eu}^{2+}(\text{C}_{10}\text{H}_8^-)_2(\text{NH}_3)_4$ can be recorded. It shows a broad absorption at 365 nm, which trails into the visible region, Figure 2. Just as observed via EPR, one can see the oxidation of the europium II with UV-vis spectroscopy. Whenever an easily oxidized ligand is bound to a trivalent europium, which can be reduced to the divalent state, charge-transfer bands are present in the UV-vis spectrum.¹² In a typical complex, e.g., EuBr_6^{3-} , these bands are at 270 and 410 nm. When the $\text{Eu}^{2+}(\text{C}_{10}\text{H}_8^-)_2(\text{NH}_3)_4$ solution oxidizes to the trivalent state, $\text{Eu}^{3+}(\text{C}_{10}\text{H}_8^-)_2(\text{NH}_3)_4$, such bands are, indeed, exhibited. Spectra of these solutions show charge-transfer bands at 295 and 435 nm, Figure 2. This spectrum also reveals a very broad band starting at 650 nm with a maximum at 990 nm. This very large band is absent in the $\text{Eu}^{2+}(\text{C}_{10}\text{H}_8^-)_2(\text{NH}_3)_4$ solution and is due to the uncomplexed naphthalene anion radical.

The lanthanide with the penultimate lowest ionization potential is ytterbium, an $f^{14}s^2$ system.⁶ Exposure of ammonia solutions of naphthalene to ytterbium results in the same forest green color observed in the europium-naphthalene system. However, the ytterbium solution is EPR silent, as $\text{Yb}^{2+}(\text{C}_{10}\text{H}_8^-)_2(\text{NH}_3)_4$ is, as expected, a 14 f-electron diamagnetic species. The Eu and Yb results suggest that analogous EPR-active and -inactive complexes can be obtained with the other lanthanides and a host of electron acceptors. However, the larger ionization potentials of the other lanthanides may necessitate the use of the Rieke^{13,5} metals to effect electron transfer. This issue is under current investigation.

Acknowledgment. We thank the National Science Foundation (Grant CHE-9617066) for support of this work.

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(11) The EPR spectrum for $\text{Eu}^{2+}(\text{C}_{10}\text{H}_8^-)_2(\text{NH}_3)_4$ persists for only a few minutes at room temperature, but remains for a few hours at 200 K.

(12) Thompson, L. C. In *Handbook of the Physics and Chemistry of Rare Earth*, Vol. 3; Gschneidner, K. A., Eyring, L. R., Eds.; North-Holland Publishing Co.: New York, 1979.

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