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Dinitrogen Reduction via Photochemical Activation of Heteroleptic Tris(cyclopentadienyl) Rare-Earth Complexes

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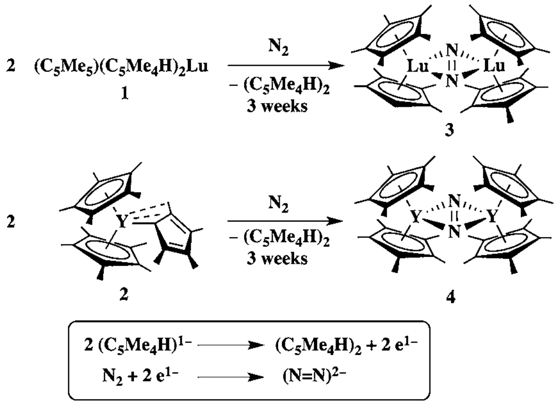
Supporting Information

ABSTRACT: Dinitrogen can be reduced by photochemical activation of the Ln^{3+} mixed-ligand tris(cyclopentadienyl) rare-earth complexes $(\eta^5\text{-}C_5Me_5)_{3-x}(C_5Me_4H)_xLn$ (Ln = Y, Lu, Dy; x = 1, 2). $[(C_5Me_4R)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ products (R = H, Me) are formed in reactions in which N_2 is reduced to $(N{=}N)^{2-}$ and $(C_5Me_4H)^-$ is oxidized to $(C_5Me_4H)_2$. Density functional theory indicates that this unusual example of rare-earth photochemistry can be rationalized by absorptions involving the $(\eta^3\text{-}C_5Me_4H)^-$ ligands.

Scheme 1. Reduction of N_2 by 1 and 2 and the Formal Half-Reactions



Although lanthanide complexes are well-known for their outstanding emission properties, particularly with Eu^{3+} in the red and Tb^{3+} in the green, they are rarely involved in photochemical reactions.[1] Ln^{3+} ions are poor absorbers because the contracted nature of the 4f orbitals limits vibronic relaxation of the Laporte-forbidden nature of 4f → 4f transitions. Hence, lanthanide-based emission requires sensitizers. Laporte-allowed ligand-to-metal charge transfer (LMCT) and ligand-to-ligand charge transfer (LLCT) transitions have been reported for the lanthanides,[1e] but photochemistry is generally not an option for productive lanthanide-based transformations.[1,2] Photochemical reactivity with complexes of the other rare-earth ions, Sc^{3+} and Y^{3+}, is also limited since they are d^0 species.[1] Even among actinide complexes there are relatively few examples of photochemically activated reactions.[3] It was therefore unexpected that the unusual dinitrogen reduction reactions shown in Scheme 1 would be photochemically activated as described in this report.

The initial observation that $(C_5Me_5)(C_5Me_4H)_2Lu$ (**1**) and $(C_5Me_5)_2(C_5Me_4H)Y$ (**2**) react slowly with N_2 to form $[(C_5Me_5)(C_5Me_4H)Lu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**3**) and $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**4**), respectively,[4] was puzzling because Lu^{3+} and Y^{3+} ions are not redox-active ions and $(C_5Me_4H)^-$ is normally stable under N_2. Since $(C_5Me_4H)_2$ is the byproduct of these reactions, the half-reactions shown in Scheme 1 are the formal explanation of the observed reactivity.

Among the ligand-based reductions known in organolanthanide chemistry,[5] the ligand-based $(C_5Me_4H)^-$ half-reaction is most reminiscent of the $(C_5Me_5)^-$ half-reaction of sterically induced reduction (SIR)[6] involving sterically crowded $(C_5Me_5)_3M$ complexes (M = rare earth, U) (e.g., eq 1).[6b] Steric crowding in $(C_5Me_5)_3M$ enforces unusually long metal−ligand distances, making the $(C_5Me_5)^-$ ligand a reactive reductant that forms (C_5Me_5) radicals, which dimerize. Although SIR can reduce substrates with reduction potentials as negative as those of cyclooctatetraene (−1.62 to −1.86 V vs SCE), it has never been observed to be powerful enough to reduce N_2.[6b]

$$(C_5Me_5)_3Ln \rightarrow [(C_5Me_5)_2Ln]^+ + {}^1\!/_2(C_5Me_5)_2 + e^- \qquad (1)$$

Sterically induced reduction does not explain the reactions in Scheme 1, since **2** does not contain unusually long metal−ligand bond distances and the more crowded analogue of **1**, namely, $(\eta^5\text{-}C_5Me_5)_2(\eta^3\text{-}C_5Me_4H)Lu$ (**5**), was not observed to reduce N_2.[4] Moreover, if steric crowding were the cause of the N_2 reduction, the larger and more reducing $(C_5Me_5)^-$ anion would be expected to be the effective reductant, not $(C_5Me_4H)^-$. Since **2** exhibited a new type of η^3-cyclopentadienyl coordination, it was possible that this unusual structure was the source of the reactivity. The structure of **1**, however, was unknown, and no reaction was observed with **5**, which has an $(\eta^3\text{-}C_5Me_4H)^-$ ligand.[4] Hence, the 3 week N_2 reductions in Scheme 1 were difficult to rationalize on the basis of any known reduction pathway in rare-earth chemistry.

We now report that this N_2 reduction reaction is photochemically induced. The photoactivity was discovered while examining a variety of factors that could affect the reactions in Scheme 1. Neither heating nor increased metal complex concentration decreased the reaction times. In fact, these changes led to ligand redistribution products such as $(C_5Me_4H)_3Ln$ that showed no reductive reactivity. Increasing the N_2 pressure also had no noticeable effect. To probe the

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importance of the $(\eta^3\text{-}C_5Me_4H)^-$ ligand in **2**, renewed efforts to obtain the solid-state structure of **1** were made, and it was found to contain the unusual trihapto structural feature: $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4H)(\eta^3\text{-}C_5Me_4H)Lu$ (Figure 1a). This supported the idea that the N_2 reduction reactivity was related to this unusual ligand.

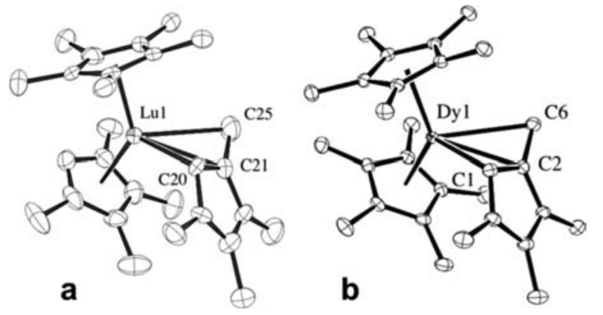


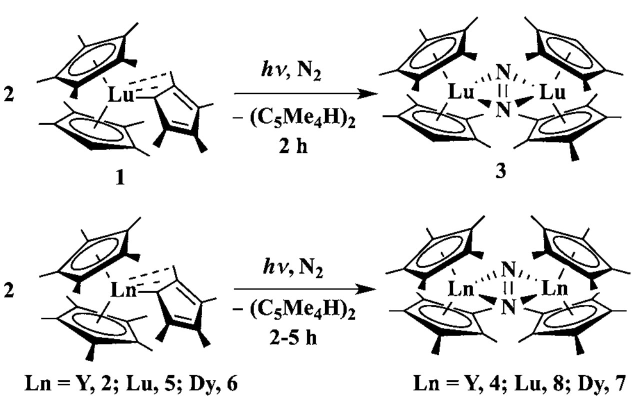
Figure 1. Thermal ellipsoid plots of (a) $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4H)(\eta^3\text{-}C_5Me_4H)Lu$ (**1**) and (b) $(\eta^5\text{-}C_5Me_5)_2(\eta^3\text{-}C_5Me_4H)Dy$ (**6**) drawn at the 50% probability level. H atoms have been omitted for clarity.

Since the N_2 reductions in Scheme 1 involved only closed-shell $4d^0$ Y^{3+} and $4f^{14}$ Lu^{3+} complexes, reactions with an open-shell ion were examined to probe the generality of this photochemistry. The $4f^9$ Dy^{3+} ion was chosen because it is similar in size to Y^{3+} and reduced dinitrogen complexes of dysprosium had previously been modeled by density functional theory (DFT).[7] The reaction of $[(C_5Me_5)_2Dy][(\mu\text{-Ph})_2BPh_2]$ with 1.1 equiv of KC_5Me_4H yielded $(C_5Me_5)_2(C_5Me_4H)Dy$ (**6**), which was found by X-ray crystallography to contain an $(\eta^3\text{-}C_5Me_4H)^-$ ligand and be isomorphous with **2** (Figure 1b). Complex **6** also reduced N_2 over a period of weeks to form the $(N{=}N)^{2-}$ complex $[(C_5Me_5)_2Dy]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**7**).

After the conventional methods of increasing the rare-earth reaction rates were tried, photoactivation was investigated. Surprisingly, irradiation of NMR samples of yellow **1** and **2** with a mercury vapor lamp changed the time scale for producing the red dinitrogen complexes **3** and **4** from 3 weeks to 2 h (Scheme 2). The orange Dy^{3+} complex **6** could also be photochemically activated. Moreover, irradiation of previously unreactive yellow **5** led to the reduced dinitrogen product $[(C_5Me_5)_2Lu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**8**), although this required 5 h.

To explore the origin of this photoreactivity, the UV−vis spectra of the mixed-ligand complexes **1**, **2**, **5**, and **6** were obtained, and each was found to contain two broad absorptions. These results are in contrast to the UV−vis spectra of the closely related homoleptic tris(polyalkylcyclopentadienyl) complexes $(C_5Me_4H)_3Lu$, $(C_5Me_4H)_3Y$, and $(C_5Me_5)_3Y$, each of which contains only one absorption. The spectra of **2** and $(C_5Me_4H)_3Y$ are compared in Figure 2. Dinitrogen was reduced even when a GG.420 glass filter was used to block light with wavelengths below 420 nm, suggesting that the photochemically active band is the lower-energy band not found in the homoleptic complexes.

Scheme 2. Reduction of N_2 under Photolytic Conditions



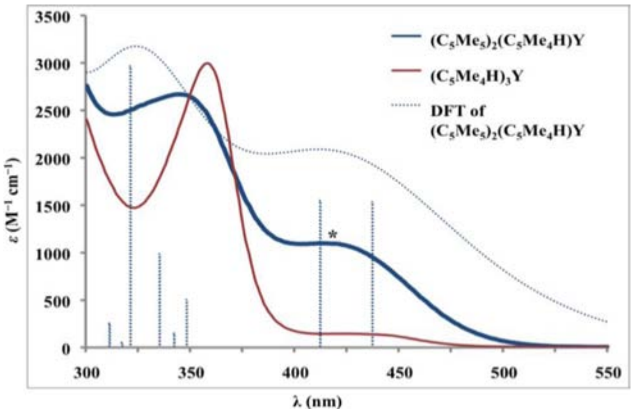


Figure 2. UV−vis spectra of **2** and $(C_5Me_4H)_3Y$ along with the DFT-simulated spectrum of **2**. The vertical lines represent the computed excitations, with heights determined by the theoretical oscillator strengths.

DFT calculations on **1**, **2**, **5**, and **6** converged on lowest-energy C_1-symmetric structures with the unusual trihapto coordination of the $(C_5Me_4H)^-$ ligand observed crystallographically. The highest occupied molecular orbital (HOMO) of these complexes, shown for **2** in Figure 3a, is a ligand-based orbital localized on the $(\eta^3\text{-}C_5Me_4H)^-$ ligand. This is significantly different from the HOMOs of the homoleptic $(C_5Me_4H)_3Y$ and $(C_5Me_5)_3Y$ complexes, in which the electron density is distributed evenly over all three rings (Figure 3b).

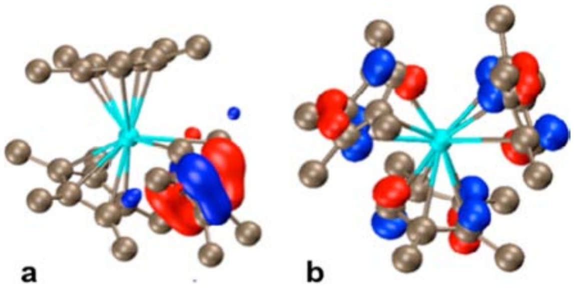


Figure 3. HOMOs of (a) **2**, showing electron density localized on the $(\eta^3\text{-}C_5Me_4H)^-$ ligand, and (b) $(C_5Me_4H)_3Y$, showing electron density delocalized over all three ligands.

Time-dependent DFT calculations were used to simulate the UV−vis absorption spectrum of **2**. As shown in Figure 2, the shape of the simulated spectrum is a reasonable match for the experimental spectrum. The calculations showed two LMCT transitions at wavelengths greater than 400 nm that make up the broad peak denoted with an asterisk in Figure 2. These two LMCT excitations occur at 412 and 437 nm, and each represents the transfer of an electron from an orbital localized on the (η^3-C_5Me_4H)$^-$ ligand to the empty 4d$_{z^2}$ orbital on the metal center, the lowest unoccupied molecular orbital (LUMO) of the complex (Figure 4). Hence, these calculations provide a rationale for the observed reactivity. The single electron transfer associated with this excitation would form a C_5Me_4H radical and a "$(C_5Me_5)_2Y^*$" moiety with the yttrium center in an excited 4d^1 state. The C_5Me_4H radical would be expected to dimerize to the observed $(C_5Me_4H)_2$ product, and "$(C_5Me_5)_2Y^*$" would be expected to be able to reduce dinitrogen on the basis of recent Y^{2+} reactivity studies.[8]

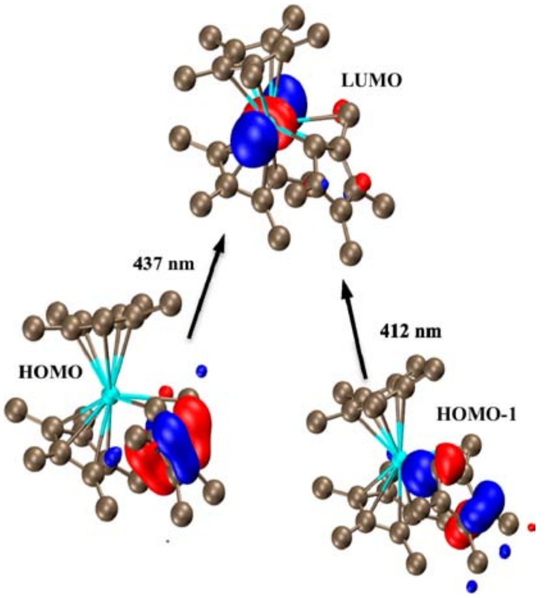


Figure 4. DFT-predicted LMCT bands in the visible-light region for complex **2**.

Analogous LMCT excitations to the 5d LUMO at 412 and 434 nm were predicted for **6**. A table summarizing the excitation energies and oscillator strengths is given in the Supporting Information (SI). Also described in the SI are additional calculations on the open-shell Dy system that indicate a 5d^1 character for the resulting "$(C_5Me_5)_2Dy^*$" moiety.

Excited-state geometry optimizations[9] were performed for the first two singlet states of **2** and **6**. A complete description of the excited-state optimizations is given in the SI. In all cases, the trihapto coordination was broken, and the distance from the metal to the C_5Me_4H ligand increased by more than 0.30 Å. The optimized structures of the ground state and first excited state are superimposed in Figure 5.

Although cyclopentadienyl ligands are generally considered to be photochemically innocent,[10] transition-metal examples of homolytic cleavage through LMCT are known.[11] Equations 2[12]

$$(\eta^5\text{-}C_5H_5)_2TiCl_2 \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)TiCl_2 + C_5H_5^{\bullet} \qquad (2)$$

$$(\eta^5\text{-}C_5H_5)_2Zr(C_6H_4Me\text{-}4)_2 \xrightarrow{h\nu} (4\text{-}MeC_6H_4)_2 + \text{“}(\eta^5\text{-}C_5H_5)_2Zr\text{”} \qquad (3)$$

and 3[13] show examples with d^0 metal complexes.[14] The photolability of (η^3-C_5Me_4H)$^-$ complexes has not been previously studied because this coordination mode was not known before the discovery of **1**, **2**, **5**, and **6**.

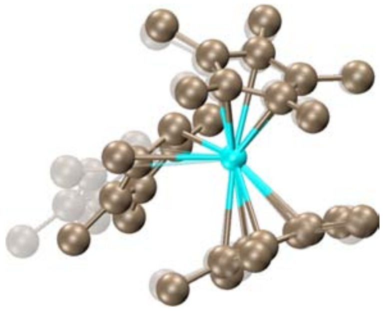


Figure 5. Calculated geometries of the ground state (darkened) and first excited state (faded) of **2**.

In summary, with the appropriate ligand set, photochemical activation of rare-earth complexes can occur, leading to powerful reductive reactivity sufficient to reduce N_2. In this case, complexes with the unusual (η^3-C_5Me_4H)$^-$ ligand have HOMOs with electron density primarily localized on that ligand. These complexes have low-energy LMCT absorptions that can be photoactivated. DFT studies showed that irradiation at these energies could lead to formation of an (η^3-C_5Me_4H) radical and an excited d^1 metal fragment reactive enough to reduce N_2. These results suggest that UV−vis spectra should be routinely obtained for rare-earth complexes since they could reveal potentially unusual electronic features and new opportunities for photochemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and computational details; crystallographic data collection, structure solution, and refinement; and crystallographic data for **5** and **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data for **5** and **6** have also been deposited with the CCDC (919794 and 919795).

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Notes

The authors declare no competing financial interest.

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