ORGANOMETALLICS

Dinitrogen Reduction, Sulfur Reduction, and Isoprene Polymerization via Photochemical Activation of Trivalent Bis(cyclopentadienyl) Rare-Earth-Metal Allyl Complexes

Megan E. Fieser, Casey W. Johnson, Jefferson E. Bates, Joseph W. Ziller, Filipp Furche,* and William J. Evans*

Department of Chemistry, University of California, Irvine, California 92697-2025, United States

Supporting Information

ABSTRACT: Dinitrogen can be reduced by photochemical activation of the trivalent rare-earth-metal bis-(pentamethylcyclopentadienyl) allyl complexes $(C_5Me_5)_2Ln(\eta^3-C_3H_4R)$ (Ln = Y, Lu; R = H, Me) to form the $(N=N)^{2-}$ complexes $[(C_5Me_5)_2Ln]_2(\mu-\eta^2:\eta^2-N_2)$. This demonstrates that productive organolanthanide photochemistry is not limited to complexes of the unusual $(\eta^3-C_5Me_4H)^-$ ligand in the heteroleptic complexes $(C_5Me_5)_2(C_5Me_4H)Ln$ and $(C_5Me_5)-(C_5Me_4H)_2Ln$. Photolytic activation of $(C_5Me_5)_2Ln(\eta^3-C_3H_5)$ (Ln = Y, Lu) in the presence of isoprene provides a rare



photopolymerization route to polyisoprene. Sulfur can also be reduced by photolysis of $(C_5Me_5)_2Ln(\eta^3-C_3H_5)$ (Ln = Y, Lu) to generate the $(S)^{2-}$ complexes, $[(C_5Me_5)_2Ln]_2(\mu$ -S), which have variable Ln–S–Ln angles depending on crystallization conditions.

INTRODUCTION

Recently, the traditional view that rare-earth-metal complexes have minimal photochemistry was overturned by the observation that dinitrogen can be reduced to $(N=N)^{2-}$ by photolysis of the Ln^{3+} mixed-ligand tris(cyclopentadienyl) rare-earth-metal complexes $(C_5Me_5)_2(C_5Me_4H)Ln$ (1-Ln; Ln = Y, Lu, Dy) and $(C_5Me_5)(C_5Me_4H)_2Lu$.¹ The products of the two-electron reductions of N₂, namely $[(C_5Me_5)_2Ln]_2(\mu-\eta^2:\eta^2-N_2)$ (2-Ln) and $[(C_5Me_5)(C_5Me_4H)Ln]_2(\mu-\eta^2:\eta^2-N_2)$, respectively, are formed in reactions in which $(C_5Me_4H)^-$ is oxidized to $(C_5Me_4H)_2$ (Scheme 1).¹

Scheme 1. Reduction of Dinitrogen with $(C_5Me_5)(C_5Me_4H)_2Lu$ (Reaction a) and $(C_5Me_5)_2(C_5Me_4H)Ln$ (1-Ln; Ln = Y, Lu, Dy) (Reaction b) under Photolytic Conditions and Formal Half-Reactions



The fact that photochemical activation with lanthanides could lead to the potent reduction of dinitrogen was surprising, since Ln³⁺ ions are not effective at absorbing light.²⁻⁶ This is because the Laporte-forbidden nature of $4f \rightarrow 4f$ transitions is not relaxed by vibronic coupling, due to the contracted nature of the 4f orbitals. Although lanthanide complexes can display outstanding emission properties, particularly with Eu³⁺ and Tb³⁺ in the red and green parts, respectively, of the visible spectrum, this emission requires sensitizers to absorb the energy. Laporte-allowed ligand to metal charge transfer (LMCT) and ligand to ligand charge transfer (LLCT) transitions are known for the lanthanides,⁴ but photoactivation does not generally lead to productive lanthanide-based transformations.²⁻⁹ Although the 5f valence orbitals have a better radial extension than the 4f orbitals, there are still relatively few examples of photochemically activated reactions with actinide complexes. $^{10-13}$ The other rare-earth ions, $\rm Sc^{3+}$ and Y³⁺, also have limited metal-based photochemistry since they are d⁰ species. However, recently Chirik et al. have shown the dinitrogen can be reduced by photolysis of (C₅Me₄H)₂Zr- $(aryl)_2$ complexes.¹⁴

Density functional theory (DFT) analysis of the unexpected rare-earth-metal photochemistry in Scheme 1 indicated that absorptions involving the unusual $(\eta^3$ -C₅Me₄H)⁻ ligand were responsible.¹ Specifically, two absorptions at 412 and 437 nm that are present in the heteroleptic $(C_5Me_5)_2(C_5Me_4H)Ln$ and



Received: July 16, 2015

 $(C_5Me_5)(C_5Me_4H)_2Ln$ complexes, but not in the homoleptic analogues, $(C_5Me_5)_3Ln$ or $(C_5Me_4H)_3Ln$, appear to be involved. Due to the rare nature of this photochemical activation, it was desirable to test the generality of this photoactivity beyond the two classes of mixed-ligand tris-(cyclopentadienyl) complexes and three metals in Scheme 1. Extending the reactions of Y, Dy, and Lu to the larger metals in the lanthanide series is problematic, because the synthesis of pure $(C_5Me_5)_2(C_3Me_4H)Ln$ and $(C_5Me_5)(C_5Me_4H)_2Ln$ complexes for the larger lanthanides (La, Ce, Pr, Nd, Sm) is complicated by ligand rearrangement.¹⁵ Hence, it was of particular interest to determine if this photoactivity depended on the unusual $(\eta^3-C_5Me_4H)^-$ ligand found in each of these complexes.

Given the η^3 nature of the photoactive $(\eta^3\text{-}C_5\text{Me}_4\text{H})^-$ ligand, the structurally related allyl complexes $(C_5\text{Me}_5)_2\text{Ln}(\eta^3\text{-}C_3\text{H}_5)^{16-18}$ (3) were candidates for possible photoactivation. Reactions analogous to Scheme 1 with allyl complexes would provide a more facile synthetic route to the reduced dinitrogen complexes $[(C_5\text{Me}_5)_2\text{Ln}]_2(\mu \cdot \eta^2 : \eta^2 \cdot N_2)$ (2), since the allyl complexes are precursors to the heteroleptic $(C_5\text{Me}_5)_{3-x}(C_5\text{Me}_4\text{H})_x\text{Ln}$ complexes^{19,20} as well as the loosely ligated tetraphenylborate cationic metallocene complexes $[(C_5\text{Me}_5)_2\text{Ln}][(\mu \cdot \text{Ph})_2\text{BPh}_2]$,^{18,21-23} which are also used as precursors to the $(N=N)^{2-}$ complexes.²⁴

We report here that the allyl complexes are photoactive and this reactivity can be used not only to reduce dinitrogen but also to polymerize isoprene. Photopolymerization of isoprene is rare and generally involves radical initiators.^{25–28} To show the generality of the photoactivity of these common metallocene rare-earth-metal allyl complexes, we also report that S₈ can be reduced by Ln³⁺ allyl complexes. To our knowledge, reduction of S₈ by a trivalent rare-earth-metal complex has only been reported before with {[(Me₃Si)₂N]₂(THF)Y}₂(μ - η ²: η ²-N₂)²⁹ and by alkyl thiolate disproportionation in cyclopentadienyl³⁰ and guanidinate³¹ rare-earth-metal alkyl systems. Density functional theory is used to explain the photochemical activity of this allyl metallocene system.

EXPERIMENTAL DETAILS

The syntheses and manipulations described below were conducted under argon or nitrogen with rigorous exclusion of air and water using glovebox, vacuum line, and Schlenk techniques. Solvents were dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotope Laboratories) were dried over sodium potassium alloy, degassed, and vacuum-transferred prior to use. KC5Me5,³ $(C_5Me_5)_2Ln(\eta^3-C_3H_5)$ (2-Ln; Ln = Y,¹⁷ Lu,¹⁷ Dy¹⁸), and $(C_5Me_5)_2YCl_2K(THF)^{17}$ were prepared according to the literature. (2-Methylallyl)magnesium chloride (0.5 M, in THF), 1,4-dioxane, propene, and isobutylene were purchased from Sigma-Aldrich and were used as received. Sulfur (Fisher) was purified by sublimation before use. Isoprene (Acros) was dried over molecular sieves and degassed by three freeze-pump-thaw cycles. ¹H NMR spectra were obtained on a Bruker DRX500 MHz spectrometer with a BBO probe at 25 °C unless otherwise specified. ¹³C NMR spectra were obtained on a Bruker DRX500 MHz spectrometer operating at 126 MHz with a TCI cryoprobe at 25 °C. IR samples were prepared as KBr pellets and the spectra were obtained on a Varian 1000 FT-IR system. Absorption spectra were collected using a Cary 50 Scan UV-vis spectrometer at 25 °C in toluene or hexane. Mass spectra were recorded on a Thermo Scientific Trace GC Ultra. Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS analyzer.

 $(C_5Me_5)_2Y(\eta^3-CH_2CMeCH_2)$ (4-Y). In a nitrogen-filled glovebox, a solution of (2-methylallyl)magnesium chloride 0.5 M in THF (7.20 mL, 3.60 mmol) was added dropwise to a stirred suspension of

(C₅Me₅)₂YCl₂K(THF) (1.937 g, 3.577 mmol) in toluene (125 mL). After the mixture was stirred overnight, the solvent was removed under vacuum and a pale yellow tacky solid resulted. Dropwise addition of 1,4-dioxane (5 mL) to a stirred slurry of this solid in 125 mL of hexanes gave an immediate color change to bright yellow. After the mixture was stirred for 12 h, the yellow slurry was centrifuged and filtered. The solvent was removed under reduced pressure to yield **4-Y** as a yellow microcrystalline solid (1.05 g, 70%). Yellow crystals suitable for X-ray crystallography were grown from a saturated hexanes solution at -35 °C. ¹H NMR (C₆D₆): δ 2.19 (d, 4H, CH₂C(CH₃)-CH₂), 1.96 (s, 33H, (C₅Me₅)₂, CH₂C(CH₃)CH₂). ¹³C NMR (C₆D₆): δ 169.8, 117.1, 64.6, 29.4, 11.6. IR: 3054 m, 2966 s, 2908 s, 2859 s, 2725 s, 2391 vw, 2287 vw, 1509 m, 1437 w, 1379 w, 1316 m, 1247 m, 1161 w, 1025 s, 951 w, 849 m, 767 s, 677 m cm⁻¹. Anal. Calcd for C₂₄H₃₇Y: C, 69.55; H, 9.00. Found: C, 69.49; H, 9.24.

Photolytic Reaction Conditions. All photolysis experiments were conducted in a hood with aluminum foil covered windows with a Hanovia medium-pressure 450 W mercury vapor lamp (PC451050/610741). The 5.5 in. long lamp was clamped to hang inside a 13 in. \times 1.5 in. diameter cavity of a double-walled quartz water cooling jacket. Tap water at 24 °C flowed through the jacket at a rate of 6.4 L/min, and the temperature in the hood was kept between 25 and 27 °C. Samples were placed adjacent to the outer wall of the cooling jacket in the middle of the hood.

Photolysis of $(C_5Me_5)_2Lu(\eta^3-C_3H_5)$ (3-Lu) To Form $[(C_5Me_5)_2Lu]_2(\mu-\eta^2:\eta^2-N_2)$ (2-Lu). In a nitrogen-filled glovebox, 3-Lu (12 mg, 0.025 mmol) was dissolved in C_6D_6 (1 mL) and transferred to a J. Young NMR tube equipped with a greaseless stopcock. After irradiation for 24 h, the yellow solution became deep red. ¹H NMR analysis revealed full conversion to 2-Lu.²⁴

Photolysis of $(C_5Me_5)_2Y(\eta^3-C_3H_5)$ (3-Y) To Form $[(C_5Me_5)_2Y]_2(\mu-\eta^2:\eta^2-N_2)$ (2-Y). As described for 3-Lu, a yellow solution of 3-Y (10 mg, 0.02 mmol) became red-orange after irradiation for 24 h and generated a 1.5:1 mixture of 3-Y and 2-Y.²⁴

Photolysis of $(C_5Me_5)_2 Y(\eta^3-C_3H_4R)$ (4-Y) To Form $[(C_5Me_5)_2Y]_2(\mu-\eta^2:\eta^2-N_2)$ (2-Y). As described above for 3-Lu, photolysis of a yellow solution of 4-Y (10 mg, 0.02 mmol) for 14 h gave a 1:2 mixture of 4-Y and 2-Y by ¹H NMR spectroscopy.²⁴

Large-Scale Yttrium Photolyses. Large-scale reactions were run in 250 mL round-bottom vessels containing either **3-Y** (500 mg, 1.25 mmol) or **4-Y** (518 mg, 1.25 mmol) dissolved in toluene (50 mL). After the stirred yellow solutions had been irradiated for 24 h, they became red-orange. The solutions were centrifuged and filtered before the solvent was removed under vacuum. The resulting red-orange powders were shown by ¹H NMR spectroscopy to contain the starting material and the **2-Y** product in ratios of 1.2:1 for **3-Y** and 1:1.1 for **4-Y**.

Gas Chromatography/Mass Spectrometry (GC/MS) Studies. Photolyses were run in methylcyclohexane to analyze the gas present in the headspace above the solution. GC/MS analysis of the gas formed after irradiation of 3-Y (50 mg, 0.1 mmol) and 4-Y (61 mg, 0.12 mmol) in methylcyclohexane (7 mL) under N₂ revealed significant molecular ion peaks at m/z 41.16 and 56.03, respectively. These matched the data on pure gas samples of propene and isobutylene. Analogous reactions run with ~50 mg of 3-Y or 4-Y in 4 mL of toluene- d_8 revealed peaks at m/z 42.14 and 57.18.

Isoprene Reactivity. In an argon-filled glovebox, ~50 mg of 3-Ln (Ln = Y, Lu) and a magnetic stir bar were added to a sealable 50 mL side arm Schlenk flask equipped with a greaseless stopcock. The flask was added to the high-vacuum line, and argon was removed under vacuum. Isoprene (approximately 10 mL) was vacuum-transferred into the flask. After irradiation for 12 h, gel had formed on the side of the flask near the light source. The amount of gel continued to increase over the course of 8 days of irradiation. Excess isoprene was removed under vacuum to leave a thick gel that was analyzed by gel permeation chromatography at the Goodyear Tire Co. to have low molecular weight with M_n and M_w <6000. ¹H NMR and ¹³C NMR spectra in CDCl₃ of the polymer that had been washed with MeOH and treated with HCl contained resonances for *cis*-1,4-, *trans*-1,4-, and 3,4-polyisoprene with the largest peaks for 3,4-polyisoprene.

Table 1. X-ray Data Collection Parameters for $(C_5Me_5)_2Y(\eta^3-CH_2CMeCH_2)$ (4-Y), $[(C_5Me_5)_2Y]_2(\mu-S)$ (5-Y(tol)), and Two Forms of $[(C_5Me_5)_2Lu]_2(\mu-S)$ (5-Lu(tol) and 5-Lu(hex))

	4-Y	5-Y(tol)	5-Lu(tol)	5-Lu(hex)
formula	C ₂₄ H ₃₇ Y	C40H60SY2	$C_{40}H_{60}Lu_2S$	$C_{40}H_{60}Lu_2S$
fw	414.44	750.76	922.88	922.88
temp (K)	88(2)	143(2)	88(2)	88(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	tetragonal	tetragonal	triclinic
space group	$P\overline{1}$	$P\overline{4}2_1c$	$P\overline{4}2_1c$	$P\overline{1}$
a (Å)	11.0137(17)	14.7891(7)	14.6701(7)	10.5471(5)
b (Å)	14.194(2)	14.7891(7)	14.6701(7)	11.3849(6)
c (Å)	15.681(2)	18.9371(9)	18.9233(9)	16.6188(9)
V (Å ³)	2195.6(6)	4141.9(4)	4072.5(4)	1894.36(17)
α (deg)	67.4577(18)	90	90	77.2811(7)
β (deg)	75.8753(19)	90	90	76.8625(7)
γ (deg)	84.5088(19)	90	90	85.1302(7)
Z	4	4	4	2
$ ho_{ m calcd}~({ m Mg/m^3})$	1.254	0.204	1.505	1.618
$\mu (\mathrm{mm}^{-1})$	2.660	2.861	4.894	5.261
R1 $(I > 2\sigma(I))$	0.0312	0.0286	0.0141	0.0269
wR2 (all data)	0.0808	0.0633	0.0334	0.0650

 $[(C_5Me_5)_2Y]_2(\mu-S)$ (5-Y). In an argon-filled glovebox, 3-Y (204 mg, 0.51 mmol) was dissolved in toluene (10 mL). S₈ (8 mg, 0.03 mmol) was added to the yellow solution, and the mixture was transferred to a sealable 50 mL side arm Schlenk flask equipped with a greaseless stopcock. During irradiation for 4 h, the stirred bright yellow solution became pale yellow. In an argon-filled glovebox, the solvent was removed under vacuum and the solids were washed with pentane to leave $[(C_5Me_5)_2Y]_2(\mu$ -S) (5-Y) as a pale yellow solid (84 mg, 52%). Colorless single crystals of 5-Y suitable for X-ray diffraction were grown from toluene at -35 °C. ¹H NMR (C₆D₆): δ 2.07 (s, 60H, C_5Me_5). ¹³C NMR (C_6D_6): δ 119.16 (s, C_5Me_5), 11.68 (s, C_5Me_5). IR: 2961 s, 2906 s, 2858 s, 2725w, 1638 w, 1490 w, 1437 m, 1378 m, 1259 w, 1186 w, 1162 w, 1086 m, 801 w cm⁻¹. Anal. Calcd for $C_{40}H_{60}SY_2$: C, 63.99; H, 8.06. Found: C, 64.51; H, 8.50. Eight attempts at elemental analysis on this compound, including use of crystals examined by X-ray diffraction, did not give better analytical data than this (see the Supporting Information).

[(C₅Me₅)₂Lu]₂(μ-S) (5-Lu). As described for 5-Y above, 3-Lu (124 mg, 0.255 mmol) was combined with S₈ in toluene (10 mL). During irradiation for 5 h, the stirred bright yellow solution became pale yellow. In an argon-filled glovebox, the solvent was removed under vacuum to leave a pale yellow solid, $[(C_5Me_5)_2Lu]_2(\mu-S)$ (5-Lu; 65 mg, 55%). Colorless single crystals of 5-Lu suitable for X-ray diffraction were grown from toluene (5-Lu(tol)) and from hexane (5-Lu(hex)) at -35 °C. ¹H NMR (C_6D_6): δ 2.22 (s, 60H, C_5Me_5). ¹³C NMR (C_6D_6): δ 120.96 (s, C_5Me_5), 11.35 (C_5Me_5). IR: 2953 s, 2910 s, 2854 s, 2726 w, 1648 w, 1439 m, 1376 m, 1259 w, 1113 w, 1061 m, 1020 w, 992 w. As found for 5-Y, obtaining satisfactory elemental analyses was difficult. The best data of five attempts (Supporting Information) are given here. Anal. Calcd for C₄₀H₆₀SLu₂: C, 52.06; H, 6.55. Found: C, 53.75; H, 6.32.

X-ray Crystallographic Data. Crystallographic information for complexes 4-Y, 5-Y(tol), 5-Lu(tol), and 5-Lu(hex) is given in Table 1, and details are given in the Supporting Information.

Computational Details. DFT calculations were carried out on $(C_5Me_5)_2Y(\eta^3-C_3H_5)$ (3-Lu) $(C_5Me_5)_2Lu(\eta^3-C_3H_5)$ (3-Y), and $(C_5Me_5)_2Y(\eta^3-CH_2CMeCH_2)$ (4-Y) using the hybrid meta-generalized gradient approximation functional TPSSh.³³ Small-core ECPs³⁴ and def-TZVP basis sets³⁵ were used for Y and Lu. All calculations were performed using the Turbomole quantum chemistry software.³⁶ Time-dependent DFT (TDDFT) calculations^{37,38} were also performed to simulate the UV–vis spectrum for 3-Lu, 3-Y, and 4-Y. A full description of the computational methods is reported in the Supporting Information.

RESULTS

To determine if complexes beyond $(C_5Me_5)_2(\eta^3-C_5Me_4H)Ln$ (1-Ln) and $(C_5Me_5)(C_5Me_4H)_2Ln$ could be photoactivated to reduce N₂ to $[(C_5Me_5)_2Ln]_2(\mu-\eta^2:\eta^2-N_2)$ (2-Ln), photoreduction of $(C_5Me_5)_2Ln(\eta^3-C_3H_5)$ (3-Ln; Ln = Y, Lu) was explored. To aid in identifying organic byproducts of the allyl photolysis, the methylallyl analogue of 3-Ln, namely $(C_5Me_5)_2Y(\eta^3-CH_2CMeCH_2)$ (4-Y), was synthesized from (methylallyl)magnesium chloride and $(C_5Me_5)_2YCl_2K(THF)^{17}$ and was fully characterized. The X-ray crystal structure (Figure 1) is similar to that of 3-Y, as detailed in the Supporting Information.



Figure 1. Thermal ellipsoid plot of $(\eta^5-C_5Me_5)_2Y[(\eta^3-CH_2CMeCH_2)$ (4-Y) drawn at the 50% probability level. The second independent molecule of 4-Y in the unit cell and hydrogen atoms are omitted for clarity.

UV-visible absorption spectra were taken of 3-Y, 3-Lu, and 4-Y (Figure 2) to determine how they compared with that of photoactive 1-Ln. The spectra of the allyl complexes are similar to those of 1-Y and 1-Lu¹ in that they contain two broad absorptions, with the lowest energy absorption being near the 405 nm emission of the medium-pressure mercury vapor lamp used for irradiation.



Figure 2. UV–vis spectra of $(C_5Me_5)_2Y(\eta^3-C_3H_5)$ (**3-Lu**; dotted blue line), $(C_5Me_5)_2Y(\eta^3-C_3H_5)$ (**3-Y**; dashed red line), and $(C_5Me_5)_2Y(\eta^3-CH_2C(Me)CH_2)$ (**4-Y**; solid green line).

Photoactivated Reduction of Dinitrogen. Photolysis of solutions of **3-Y**, **3-Lu**, and **4-Y** in benzene under dinitrogen produced the $(N=N)^{2-}$ complexes $[(C_5Me_5)_2Ln]_2(\mu-\eta^2:\eta^2-N_2)$ (Ln = Y (**2-Y**), Lu (**2-Lu**)), which were identified by ¹H NMR spectroscopy²⁴ (eq 1). Only in the case of **2-Lu** was the



reaction quantitative in 24 h. For 3-Y and 4-Y, conversions of only 40–45% were observed in 24 h with the N_2 reduction product 2-Y being the only metallocene product by ¹H NMR spectroscopy. Using cyclooctane as an internal standard, it appeared that 4-Y generated approximately 50% more 2-Y than 3-Y in the same time period.

Gas chromatography/mass spectrometry (GC/MS) analysis of the gas present in the headspace above a large-scale irradiation of 3-Y under N2 in methylcyclohexane gave a molecular ion peak that matched the m/z value and retention time of a standard sample of propene. The analogous experiment in toluene- d_8 gave a peak with an m/z value that was 1 mass unit higher, as is appropriate for propene-d. Analogous photolysis of 4-Y in methylcyclohexane gave a peak at the m/z value of isobutene, and the corresponding reaction in toluene- d_8 gave a peak 1 mass unit higher. These results are consistent with formation of propene and isobutene by hydrogen abstraction from solvent by photolytically generated allyl and methylallyl radicals.^{39,40} No evidence for dimers of allyl and methylallyl radicals was observed. Hydrogen abstraction from solvent would be expected to be prevalent, since there is a much higher concentration of solvent in comparison to the radical concentration.

Photopolymerization of Isoprene. Photolysis of 3-Y and 3-Lu in neat isoprene that had been vacuum-transferred into the reaction vessel generated a viscous white product. ¹H NMR and ¹³C NMR analysis⁴¹ in CDCl₃ indicated the presence of polyisoprene in the form of cis-1,4-, trans-1,4-, and 3,4-isomers, with the 3,4-isomer being predominant. Gel permeation chromatography (GPC) analysis of the molecular weight of the material indicated that the polymer had a low molecular weight with M_n and M_w values under 6000. The blank reaction

Article

of 3-Y with neat isoprene without irradation showed no polymerization.

Photoreduction of Sulfur. Irradiation of **3-Y** and **3-Lu** under argon in toluene in the presence of elemental sulfur, S_8 , led to the formation of the bridging $(S)^{2-}$ complexes $[(C_5Me_5)_2Ln]_2(\mu$ -S) (5) (eq 2) (Figure 3). X-ray crystallog-



Figure 3. Thermal ellipsoid plots of $[(C_5Me_5)_2Lu]_2(\mu-S)$ (5-Lu) crystallized from (a) hexane (5-Lu(hex)) and (b) toluene (5-Lu(tol)) drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

raphy revealed an unusual feature of the lutetium product: **5-Lu** crystallized in two different forms depending on the crystallization solvent, hexane vs toluene, even though neither solvent cocrystallized in either structure. As shown in Table 1, when **5-Lu** was crystallized from toluene, crystals of **5-Lu(tol)** formed in the $P\overline{4}2_1c$ space group and were isomorphous with **5-Y(tol)**, also crystallized from toluene. When **5-Lu** was crystallized from hexane, crystals of **5-Lu(hex)** were isolated in space group $P\overline{1}$.



All three crystalline materials, **5**-Y(tol), **5**-Lu(tol), and **5**-Lu(hex), have bimetallic structures with similar bond lengths after accounting for the difference in the eight-coordinate ionic radii of Y (1.019 Å) and Lu (0.977 Å),⁴² as shown in Table 2. Bond angles are also similar in the three complexes except for the Ln–S–Ln angles. Complexes **5**-Y(tol) and **5**-Lu(tol) have Ln–S–Ln angles of 171.91(6) and 173.27(5)°, respectively, but the Ln–S–Ln angle in **5**-Lu(hex) is 166.68(5)°. Since the linearity of such angles is sometimes used to argue for multiple

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of 5-Y and 5-Lu (Crystallized from both Toluene and Hexane)

	5-Y(tol)	5-Lu(tol)	5-Lu(hex)
Ln(1)-Cnt1	2.341	2.288	2.300
Ln(1)-Cnt2	2.351	2.297	2.300
Ln(2)-Cnt3			2.288
Ln(2)-Cnt4			2.297
Ln(1)-S(1)	2.5433(3)	2.5026(2)	2.4868(10)
Ln(2)-S(1)			2.4974(10)
Ln-S-Ln	171.91(6)	173.27(5)	166.68(5)
Cnt1-Ln(1)-Cnt2	138.3	138.2	140.4
Cnt3-Ln(2)-Cnt4			139.7
S(1)-Ln(1)-Cnt1	111.0	111.0	111.2
S(1)-Ln(1)-Cnt2	110.7	110.8	108.4
S(1)-Ln(2)-Cnt3			109.5
S(1)-Ln(2)-Cnt4			110.9

Downloaded by STOCKHOLM UNIV on September 8, 2015 | http://pubs.acs.org Publication Date (Web): August 26, 2015 | doi: 10.1021/acs.organomet.5b00613 bonding and covalency, it is significant that for **5-Lu** the value of this angle can vary significantly depending on the solvent of crystallization.

Density Functional Theory (DFT) Calculations. DFT calculations on $(C_5Me_5)_2Ln(\eta^3-C_3H_5)$ (**3-Ln**; Ln = Lu, Y) indicate that the HOMO has electron density located on the allyl ligand while the LUMO resembles a d_z^2 orbital of the metal center (Figure 4). Time-dependent DFT (TDDFT) calcu-



Figure 4. Molecular orbital plots of (a) the HOMO and (b) the LUMO for 3-Lu, using a contour value of 0.06.

lations^{37,38} were performed to compare with the UV-vis spectra of 3-Ln. Excitations near 360 and 390 nm were predicted for 3-Lu and excitations near 370 and 390 nm were predicted for 3-Y. These excitation energies match the experimental spectra, but the oscillator strength for the lowenergy excitation (389 nm) for 3-Lu is not as large as would be expected in comparison to the experimental spectrum. Table S8 in the Supporting Information summarizes the excitation energies and oscillator strengths. The lowest energy absorption for both 3-Y and 3-Lu is the HOMO-LUMO ligand to metal charge transfer (LMCT) from the η^3 -allyl ligand to a d_{z²} orbital. This is analogous to the first two excitations of 1-Y and 1-Lu, which were also predicted to be LMCT transitions from the η^3 ligand to a d_{r^2} orbital that led to the observed photoreduction chemistry.¹ The next excitations for 3-Y and 3-Lu under 300 nm are all predicted to be LMCT from the $(\eta^5 - C_s Me_s)^-$ ligands to the d_{z^2} orbital, which is also analogous to the calculations of 1-Ln.

Further DFT studies of the methylallyl complex 4-Y reveal a HOMO and LUMO similar to those seen for both 3-Y and 3-Lu (Figure S6 in the Supporting Information). TDDFT predicts excitations near 360 and 390 nm similar to those found for 3-Y. The oscillator strength of the excitation for 4-Y near 390 nm is slightly larger than that for 3-Y, while the oscillator strength of the excitation for 4-Y near 360 nm is almost half that for 3-Y. This trend matches the observed differences in the experimental UV–vis spectra.

DISCUSSION

The allyl complexes $(C_5Me_5)_2Y(\eta^3-C_3H_5)$ (3-Y), $(C_5Me_5)_2Lu(\eta^3-C_3H_5)$ (3-Lu), and $(C_5Me_5)_2Y(\eta^3-CH_2C(Me)CH_2)$ (4-Y) are similar to the photochemically active compounds $(C_5Me_5)_2Ln(\eta^3-C_5Me_4H)$ (1-Ln) and $(C_5Me_5)(C_5Me_4H)_2Ln$ in Scheme 1 in terms of their yellow color, their UV-vis spectra, and their overall structures, which include two $(\eta^5-C_5Me_5)^-$ rings and one η^3 ligand. As such, they were good candidates to undergo the photochemistry observed in Scheme 1. As shown in eq 1, each of the allyl complexes can be photoactivated to reduce dinitrogen to $(N=N)^{2^-}$.

DFT calculations suggest that the source of the photoactivity is a LMCT band near 390 nm arising from a transition between the HOMO of the allyl complexes, which is localized on the allyl ligand, and the LUMO, which is mainly d_{z^2} in character. The calculations suggest that this would generate an allyl radical and the excited-state Y^{2+} species " $(C_5Me_5)_2Y$ ", which should be capable of reducing dinitrogen on the basis of data on the recently discovered Y^{2+} complexes.^{43,44} Identification of propene and isobutene by GC/MS in the headspace over the photolysis solution is consistent with formation of allyl radicals followed by hydrogen abstraction.^{39,40} Reactions done in toluene- d_8 that generate propene-d and isobutene-d are consistent with radical abstraction from solvent. This result is parallel to the postulated pathway of photolysis of the $(C_5Me_5)_{3-x}(C_5Me_4H)_xLn$ complexes, which have $(C_5Me_4H)_2$ byproducts from formation of C_5Me_4H radicals.¹

Irradiation of **3-Y** and **3-Lu** in neat isoprene led to the formation of low-molecular-weight polyisoprene. NMR evidence showed that a mixture of *cis*-1,4-, *trans*-1,4-, and 3,4-polyisoprene had formed, with the 3,4-isomer being predominant. This is consistent with radical polymerization of isoprene, as opposed to rare-earth-metal-based coordination polymerization, which can give specific isomers.^{45–51} Although selective polymerization was not observed in this case, the photopolymerization of isoprene is rare.^{25–28}

Complexes 3-Y and 3-Lu also can be photoactivated to reduce S_8 to form the bridging sulfide complexes 5-Y and 5-Lu (eq 2). While the reduction is not as challenging as that of dinitrogen (S to S²⁻ is only -0.476 V vs SCE⁵²), this reduction suggests that this photochemical rare-earth-metal process is not restricted to just the reduction of dinitrogen. To our knowledge, this is just the third example of S_8 being reduced to (S)²⁻ or (S₂)²⁻ by a trivalent rare-earth-metal complex.²⁹⁻³¹

Structural analysis of the sulfide-bridged complexes provided another example of the variability of organometallic rare-earthmetal structures on the basis of crystallization conditions. $[(C_5Me_5)_2Lu]_2(\mu$ -S) (5-Lu) was found to crystallize from hexane with a Lu-S-Lu angle more linear, 173.27(5)°, than the $166.68(5)^{\circ}$ angle found in crystals obtained from toluene. Similar situations have recently been reported for (C₅Me₅)₂Y- $(NC_4Me_4)^{53}$ and $[(C_5Me_5)_2DyH]_2^{54}$ where different crystallization methods led to different structures of the same complex. Evidently, in some combinations of ligands and metals, the energy surface is very shallow and several structures are possible. This emphasizes the dangers of drawing conclusions from a single structural feature in a single structure of a crystal. For example, it could be argued that the more linear $171.91(6)^{\circ}$ angle in 5-Y in comparison to the $166.68(5)^{\circ}$ angle in 5-Lu(hex) was due to enhanced covalency with yttrium, since it is a transition metal. However, 5-Lu(tol) has a $173.27(5)^{\circ}$ angle that is even closer to linear than that in the vttrium structure.

CONCLUSION

These studies have shown that productive rare-earth-metalbased photochemistry is not limited to complexes containing the unusual $(\eta^3 \cdot C_5 Me_4 H)^-$ ligand or to heteroleptic tris-(cyclopentadienyl) species. In fact, photochemical reduction of dinitrogen is possible with a common class of rare-earth-metal metallocenes, the $(C_5 Me_5)_2 Ln(C_3 H_5)$ allyl complexes, which are frequently used as precursors to a variety of bis-(cyclopentadienyl) rare-earth-metal compounds. The results not only show that powerful reductions such as N₂ to (N= N)²⁻ can be accomplished with this synthetically accessible class of complexes, but also suggest that a wider range of rareearth-metal compounds may be photochemically active. Photolytic methods should be more generally considered with the rare-earth metals not only for reduction, but also for photopolymerization, as demonstrated here with isoprene.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00613. These data can also be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif (CCDC file nos. 1411848– 1411851, respectively).

Computational details, converged calculated structures for 3-Y, 3-Lu, and 4-Y, and selected bond distances for 4-Y, 5-Y(tol), 5-Lu(tol), and 5-Lu(hex) (PDF)

Cartesian coordinates for calculated structures (XYZ)

Crystallographic data (CIF) for 4-Y, 5-Y(tol), 5-Lu(tol), and 5-Lu(hex) (CIF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail for F.F.: filipp.furche@uci.edu. *E-mail for W.J.E.: wevans@uci.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

For support of this research, we thank the U.S. National Science Foundation for the experimental studies under grant CHE-1265396 (W.J.E.) and the Department of Energy for the theoretical studies under grant DE-SC0008694 (F.F.). We also thank Dr. John Greaves and Dr. Beniam Berhane at the University of California, Irvine Mass Spectrometry Facility, for assistance with mass spectrometry, Professor A. S. Borovik for assistance with UV–vis spectroscopy, Jordan F. Corbey for help with crystallography, Dr. Margaret Flook for polymer analysis, and Ryan R. Langeslay for experimental assistance.

REFERENCES

(1) Fieser, M. E.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. J. Am. Chem. Soc. **2013**, 135, 3804–3807.

(2) Carnall, W. T. In *Handbook on the Physics and Chemistry of Rare Earths*; Bünzli, J.-C. G., Pecharsky, V. K., Eds.; Elsevier: Amsterdam, 1979; Vol. 43, p 171.

- (3) Bünzli, J.-C. G. Acc. Chem. Res. 2006, 39, 53-61.
- (4) Vogler, A.; Kunkely, H. Inorg. Chim. Acta 2006, 359, 4130-4138.

(5) Leonard, J. P.; Nolan, C. B.; Stomeo, F.; Gunnlaugsson, T. In *Photochemistry and Photophysics of Coordination Compounds II*; Balzani, V., Campagna, S., Eds.; Springer: Berlin, 2007; Vol. 281, p 1.

(6) Lanthanide Luminescencence; Photophysical, Analytical and Biological Aspects, 1st ed.; Hänninen, P., Härmä, H., Eds.; Springer: New York, 2011; Vol. 1.

(7) Zinnen, H. A.; Pluth, J. J.; Evans, W. J. J. Chem. Soc., Chem. Commun. 1980, 810–812.

(8) Ogawa, A.; Ohya, S.; Doi, M.; Sumino, Y.; Sonoda, N.; Hirao, T. *Tetrahedron Lett.* **1998**, *39*, 6341–6342.

(9) Sumino, Y.; Harato, N.; Tomisaka, Y.; Ogawa, A. Tetrahedron 2003, 59, 10499–10508.

(10) Kalina, D. G.; Marks, T. J.; Wachter, W. A. J. Am. Chem. Soc. 1977, 99, 3877-3879.

(11) Bruno, J. W.; Kalina, D. G.; Mintz, E. A.; Marks, T. J. J. Am. Chem. Soc. 1982, 104, 1860–1869.

- (12) Thomson, R. K.; Cantat, T.; Scott, B. L.; Morris, D. E.; Batista,
 E. R.; Kiplinger, J. L. Nat. Chem. 2010, 2, 723–729.
 - (13) Gardner, B. M.; Patel, D.; Lewis, W.; Blake, A. J.; Liddle, S. T. Angew. Chem., Int. Ed. 2011, 50, 10440-10443.
 - (14) Margulieux, G. W.; Semproni, S. P.; Chirik, P. J. Angew. Chem., Int. Ed. 2014, 53, 9189–9192.
 - (15) Fieser, M. E. Ph.D. Thesis, University of California, Irvine, CA, 2015.
 - (16) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. J. Am. Chem. Soc. 1990, 112, 2314–2324.
 - (17) Evans, W. J.; Kozimor, S. A.; Brady, J. C.; Davis, B. L.; Nyce, G. W.; Seibel, C. A.; Ziller, J. W.; Doedens, R. J. *Organometallics* **2005**, *24*, 2269–2278.
 - (18) Demir, S.; Zadrozny, J. M.; Nippe, M.; Long, J. R. J. Am. Chem. Soc. 2012, 134, 18546–18549.
 - (19) Demir, S.; Mueller, T. J.; Ziller, J. W.; Evans, W. J. Angew. Chem., Int. Ed. 2011, 50, 515–518.
 - (20) Mueller, T. J.; Fieser, M. E.; Ziller, J. W.; Evans, W. J. Chem. Sci. 2011, 2, 1992–1996.
 - (21) Evans, W. J.; Seibel, C. A.; Ziller, J. W. J. Am. Chem. Soc. 1998, 120, 6745–6752.
 - (22) Evans, W. J.; Davis, B. L.; Champagne, T. M.; Ziller, J. W. Proc. Natl. Acad. Sci. U. S. A. **2006**, 103, 12678–12683.
 - (23) Hamaed, H.; Lo, A. Y. H.; Lee, D. S.; Evans, W. J.; Schurko, R.
 W. J. Am. Chem. Soc. 2006, 128, 12638–12639.
 - (24) Schmiege, B. M.; Ziller, J. W.; Evans, W. J. Inorg. Chem. 2010, 49, 10506-10511.
 - (25) Tang, D. K.; Ho, S. Y. J. Polym. Sci., Polym. Chem. Ed. 1984, 22, 1357–1363.
 - (26) Salman, S. R.; Al-Jarrah, M. M. F. Polym.-Plast. Technol. Eng. 1989, 28, 1009–1014.
 - (27) Derouet, D.; Thuc, C. N. H. J. Rubber Research 2008, 11, 78–96.
 (28) Gobran, R. H.; Berenbaum, M. B.; Tobolsky, A. V. J. Polym. Sci.
 - **1960**, *46*, 431–440.
 - (29) Corbey, J. F.; Fang, M.; Ziller, J. W.; Evans, W. J. Inorg. Chem. 2015, 54, 801–807.
 - (30) Li, Y.; Pi, C.; Zhang, J.; Zhou, X.; Chen, Z.; Weng, L. Organometallics 2005, 24, 1982–1988.
 - (31) Zhang, Z.; Zhang, L.; Li, Y.; Hong, L.; Chen, Z.; Zhou, X. Inorg. Chem. 2010, 49, 5715–5722.
 - (32) Evans, W. J.; Kozimor, S. A.; Ziller, J. W.; Kaltsoyannis, N. J. Am. Chem. Soc. 2004, 126, 14533–14547.
 - (33) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. J. Chem. Phys. **2003**, 119, 12129–12137.
 - (34) Andrae, D.; Hauessermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123–141.
 - (35) Weigend, F.; Ahlrichs, R. Phys. Chem. Chem. Phys. 2005, 7, 3297–3305.
 - (36) Furche, F.; Ahlrichs, R.; Hättig, C.; Klopper, W.; Sierka, M.; Weigend, F. WIREs Comput. Mol. Sci. 2014, 4, 91–100.
 - (37) Bauernschmitt, R.; Ahlrichs, R. Chem. Phys. Lett. 1996, 256, 454–464.
 - (38) Bates, J. E.; Furche, F. J. Chem. Phys. 2012, 137, 164105.
 - (39) Gordon, A. S.; Smith, S. R.; McNesby, J. R. J. Am. Chem. Soc. 1959, 81, 5059–5061.
 - (40) Chen, Y.; Tschuikow-Roux, E. J. Phys. Chem. 1993, 97, 3742-3749.
 - (41) Tanaka, Y.; Takeuchi, Y.; Kobayashi, M.; Tadokoro, H. J. Polym. Sci. Part A-2 1971, 9, 43–57.
 - (42) Shannon, R. D. Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. 1976, 32, 751–767.
 - (43) Fang, M.; Lee, D. S.; Ziller, J. W.; Doedens, R. J.; Bates, J. E.; Furche, F.; Evans, W. J. J. Am. Chem. Soc. 2011, 133, 3784–3787.
 - (44) MacDonald, M. R.; Ziller, J. W.; Evans, W. J. J. Am. Chem. Soc. **2011**, 133, 15914–15917.

(45) Kaita, S.; Doi, Y.; Kaneko, K.; Horiuchi, A. C.; Wakatsuki, Y. *Macromolecules* **2004**, *37*, 5860–5862.

(46) Zhang, L.; Luo, Y.; Hou, Z. J. Am. Chem. Soc. 2005, 127, 14562–14563.

F

(47) Rodrigues, I.; Mihalcea, I.; Volkringer, C.; Loiseau, T.; Visseaux, M. Inorg. Chem. **2012**, *51*, 483–490.

- (48) Jian, Z.; Cui, D.; Hou, Z. Chem. Eur. J. 2012, 18, 2674–2684.
 (49) Li, L.; Wu, C.; Liu, D.; Li, S.; Cui, D. Organometallics 2013, 32, 3203–3209.
- (50) Jende, L. N.; Hollfelder, C. O.; Maichle-Mössmer, C.; Anwander, R. Organometallics **2015**, 34, 32–41 and references therein. (51) Zhang, G.; Wei, Y.; Guo, L.; Zhu, X.; Wang, S.; Zhou, S.; Mu, X. Chem. - Eur. J. **2015**, 21, 2519–2526.

(52) CRC Handbook of Chemistry and Physics, 64th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1983–1984; p D-159.

(53) Webster, C. L.; Bates, J. E.; Fang, M.; Ziller, J. W.; Furche, F.; Evans, W. J. *Inorg. Chem.* **2013**, *52*, 3565–3572.

(54) Liu, S.; Gao, S.; Ziller, J. W.; Evans, W. J. Dalton Trans. 2014, 43, 15526–15531.