Supporting Information

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

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X-ray Data Collection, Structure Solution and Refinement for 4-Y.

A yellow crystal of approximate dimensions 0.280 x 0.296 x 0.329 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were two molecules of the formula-unit present (Z = 4).

At convergence, wR2 = 0.0808 and Goof = 1.071 for 473 variables refined against 10760 data (0.73Å), R1 = 0.0312 for those 9129 data with $I > 2.0\sigma(I)$.

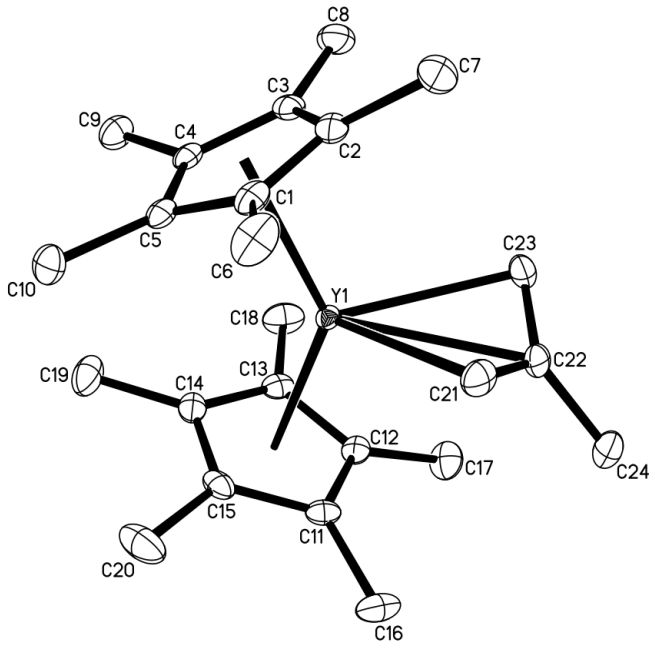

Figure S1. Thermal ellipsoid plot of $[(\eta^5\text{-}C_5Me_5)_2Ln(\eta^3\text{-}CH_2C(CH_3)CH_2)]$, **4-Y**, drawn at the 50% probability level. There are two independent molecules of **4-Y** in the unit cell. The second independent molecule of **4-Y** and hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for **4-Y**.

Empirical formula	$C_{24}H_{37}Y$	
Formula weight	414.44	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 11.0137(17) Å	α= 67.4577(18)°.
	b = 14.194(2) Å	β= 75.8753(19)°.
	c = 15.681(2) Å	γ = 84.5088(19)°.
Volume	2195.6(6) $Å^3$	
Z	4	
Density (calculated)	1.254 Mg/m^3	
Absorption coefficient	2.660 mm^{-1}	
F(000)	880	
Crystal color	yellow	
Crystal size	0.329 x 0.296 x 0.280 mm^3	
Theta range for data collection	1.680 to 29.060°	
Index ranges	$-14 \le h \le 14$, $-19 \le k \le 18$, $-21 \le l \le 21$	
Reflections collected	27139	
Independent reflections	10760 [R(int) = 0.0203]	
Completeness to theta = 25.500°	99.7 %	
Absorption correction	Numerical	
Max. and min. transmission	0.6306 and 0.5168	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10760 / 0 / 473	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I) = 9129 data]	R1 = 0.0312, wR2 = 0.0772	
R indices (all data, 0.73Å)	R1 = 0.0398, wR2 = 0.0808	
Largest diff. peak and hole	0.699 and -0.718 $e.Å^{-3}$	

Table S2. Selected bond lengths [Å] and angles [°] for $(C_5Me_5)_2Y(CH_2C(Me)CH_2)$, **4-Y**, and analogous values of $(C_5Me_5)_2Y(CH_2CHCH_2)$, **3-Y**,[15] for comparison.

	4-Y	**3-Y**		**4-Y**	**3-Y**
Y(1)-Cnt1	2.403	2.381	Y(1)-C(21)	2.562(2)	2.582(2)
Y(1)-Cnt2	2.365	2.362	Y(1)-C(22)	2.7021(2)	2.601(2)
Y(1)-C(1)	2.6855(2)	2.665(2)	Y(1)-C(23)	2.570(2)	2.582(2)
Y(1)-C(2)	2.7075(2)	2.709(2)	C(21)-C(22)	1.401(3)	1.392(3)
Y(1)-C(3)	2.6814(2)	2.670(2)	C(22)-C(23)	1.403(3)	1.391(3)
Y(1)-C(4)	2.6850(2)	2.651(2)	C(22)-C(24)	1.514(3)	
Y(1)-C(5)	2.6814(2)	2.648(2)			
Y(1)-C(11)	2.6685(2)	2.674(2)	Cnt1-Y(1)-Cnt2	135.7	138.8
Y(1)-C(12)	2.6804(2)	2.673(2)	C(21)-C(22)-C(23)	123.24(2)	125.9(2)
Y(1)-C(13)	2.6381(2)	2.6378(2)	C(22)-Y(1)-C(2)	92.06(6)	94.33(7)
Y(1)-C(14)	2.6553(2)	2.640(2)	C(24)-C(22)-Y(1)	132.78(1)	
Y(1)-C(15)	2.6285(2)	2.636(2)	C(23)-C(22)-C(24)	118.48(2)	
C(1)-C(2)	1.419(3)	1.419(3)	C(23)-C(22)-C(24)	118.00(2)	
C(2)-C(3)	1.421(3)	1.414(3)			
C(3)-C(4)	1.416(3)	1.419(3)			
C(4)-C(5)	1.420(3)	1.421(3)			
C(1)-C(5)	1.419(3)	1.418(3)			
C(11)-C(12)	1.416(3)	1.420(3)			
C(12)-C(13)	1.421(3)	1.417(3)			
C(13)-C(14)	1.419(3)	1.416(3)			
C(14)-C(15)	1.418(3)	1.419(3)			
C(11)-C(15)	1.422(3)	1.418(3)			

Table S2 shows that the metal-C_5Me_5 ring centroid distances and angles of **4-Y** are similar to those of **3-Y**.[15] The Y-C21 and Y-C23 distances to the outer carbons of the allyl ligands in the two structures are similar and fall into a narrow range, 2.562(2) - 2.582(2) Å. The Y-C(22) distances to the middle carbon of the allyl ligand differ with the 2.702(2) Å distance of the methyl substituted carbon in **4-Y** significantly longer than the 2.601(2) Å in **3-Y**.

X-ray Data Collection, Structure Solution and Refinement for 5-Y(tol).

A colorless crystal of approximate dimensions 0.264 x 0.072 x 0.070 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[6] program package was used to determine the unit-cell parameters and for data collection (120 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[7] and SADABS[8] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The systematic absences were consistent with the tetragonal space group $P\bar{4}2_1c$ which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. The molecule was located on a two-fold rotation axis. Hydrogen atoms were included using a riding model. There were high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals, although it was probable that hexane solvent was present. The SQUEEZE routine in the PLATON[9] program package was used to account for the electrons in the solvent accessible voids.

At convergence, wR2 = 0.0633 and Goof = 1.051 for 205 variables refined against 4554 data (0.78 Å), R1 = 0.0286 for those 4107 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter.[10]

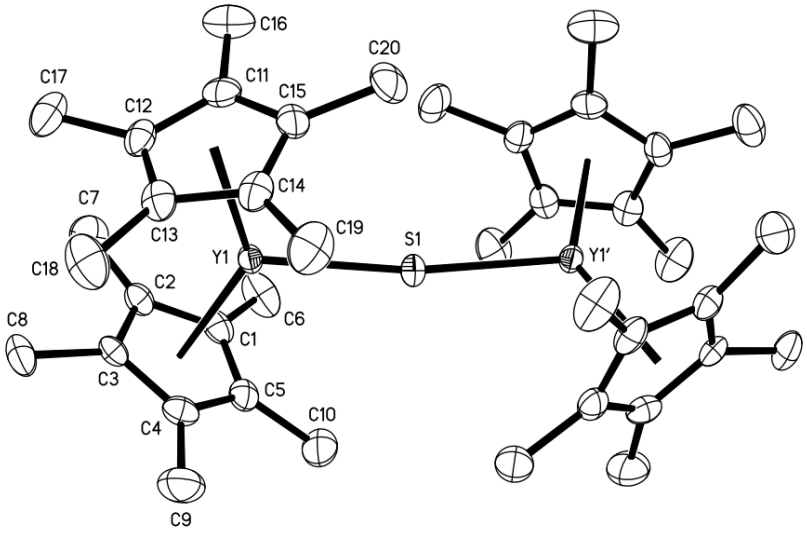

Figure S2. Thermal ellipsoid plot of $[(C_5Me_5)_2Y]_2(\mu\text{-S})$, **5-Y(tol)**, drawn at the 50% probability level. Hydrogen atom are omitted for clarity.

Table S3. Crystal data and structure refinement for **5-Y(tol)**.

Empirical formula	$C_{40}H_{60}SY_2$	
Formula weight	750.76	
Temperature	143(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P\bar{4}2_1c$	
Unit cell dimensions	a = 14.7891(7) Å	α= 90°.
	b = 14.7891(7) Å	β= 90°.
	c = 18.9371(9) Å	γ = 90°.
Volume	4141.9(4) $Å^3$	
Z	4	
Density (calculated)	1.204 Mg/m^3	
Absorption coefficient	2.861 mm^{-1}	
F(000)	1576	
Crystal color	colorless	
Crystal size	0.264 x 0.072 x 0.070 mm^3	
Theta range for data collection	1.747 to 27.091°	
Index ranges	$-18 \le h \le 18$, $-18 \le k \le 18$, $-23 \le l \le 24$	
Reflections collected	31743	
Independent reflections	4554 [R(int) = 0.0489]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8974 and 0.5618	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4554 / 0 / 205	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I) = 4107 data]	R1 = 0.0286, wR2 = 0.0611	
R indices (all data, 0.78 Å)	R1 = 0.0357, wR2 = 0.0633	
Absolute structure parameter	-0.022(3)	
Largest diff. peak and hole	0.469 and -0.181 $e.Å^{-3}$	

X-ray Data Collection, Structure Solution and Refinement for 5-Lu(tol).

A yellow crystal of approximate dimensions 0.124 x 0.134 x 0.398 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The systematic absences were consistent with the hexagonal space group $P\bar{4}2_1c$ which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. The molecule was located on a two-fold rotation axis. Hydrogen atoms were included using a riding model. There were high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals, although it was probable that hexane or toluene solvent was present. The SQUEEZE routine in the PLATON[9] program package was used to account for the electrons in the solvent accessible voids.

At convergence, wR2 = 0.0334 and Goof = 1.093 for 205 variables refined against 5330 data (0.73 Å), R1 = 0.0141 for those 5208 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter.[10]

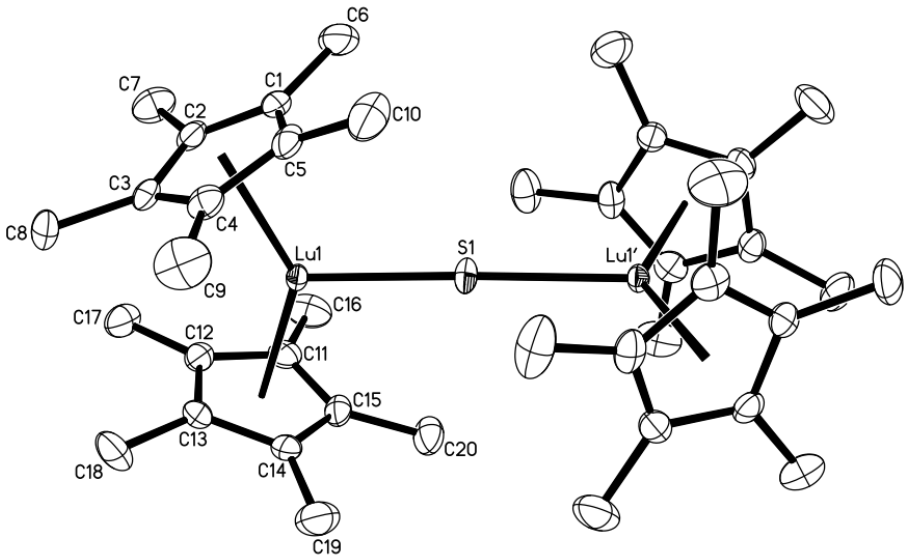

Figure S3. Thermal ellipsoid plot of $[(C_5Me_5)_2Lu]_2(\mu\text{-}S)$, **5-Lu(tol)**, drawn at the 50% probability level. Hydrogen atom are omitted for clarity.

Table S4. Crystal data and structure refinement for **5-Lu(tol)**.

Empirical formula	$C_{40}\ H_{60}\ Lu_2\ S$	
Formula weight	922.88	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P\bar{4}\,2_1c$	
Unit cell dimensions	a = 14.6701(7) Å	α= 90°.
	b = 14.6701(7) Å	β= 90°.
	c = 18.9233(9) Å	γ = 90°.
Volume	4072.5(4) Å^3	
Z	4	
Density (calculated)	1.505 Mg/m^3	
Absorption coefficient	4.894 mm^{-1}	
F(000)	1832	
Crystal color	yellow	
Crystal size	0.398 x 0.134 x 0.124 mm^3	
Theta range for data collection	1.756 to 29.200°	
Index ranges	$-20 \le h \le 20$, $-20 \le k \le 20$, $-25 \le l \le 25$	
Reflections collected	49601	
Independent reflections	5330 [R(int) = 0.0244]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.6345 and 0.3881	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5330 / 0 / 205	
Goodness-of-fit on F^2	1.093	
Final R indices [I>2sigma(I) = 5208 data]	R1 = 0.0141, wR2 = 0.0331	
R indices (all data, 0.73Å)	R1 = 0.0148, wR2 = 0.0334	
Absolute structure parameter	0.002(3)	
Largest diff. peak and hole	0.889 and -0.262 e.Å^{-3}	

Table S5. Selected bond lengths [Å] and angles [°] for **5-Y(tol)** and **5-Lu(tol)**.

	5-Y(tol)	**5-Lu(tol)**		**5-Y(tol)**	**5-Lu(tol)**
Ln(1)-Cnt1	2.341	2.288	Ln(1)-S(1)-Ln(1)'	171.91(6)	173.27(5)
Ln(1)-Cnt2	2.351	2.297	S(1)-Ln(1)-Cnt1	111.0	111.0
Ln(1)-S(1)	2.5433(3)	2.5026(2)	S(1)-Ln(1)-Cnt2	110.7	110.8
Ln(1)-C(1)	2.622(3)	2.581(3)	Cnt1-Ln(1)-Cnt2	138.3	138.2
Ln(1)-C(2)	2.634(3)	2.589(3)			
Ln(1)-C(3)	2.646(3)	2.600(3)			
Ln(1)-C(4)	2.620(4)	2.567(3)			
Ln(1)-C(5)	2.638(3)	2.594(3)			
Ln(1)-C(11)	2.641(3)	2.590(3)			
Ln(1)-C(12)	2.648(4)	2.604(3)			
Ln(1)-C(13)	2.638(3)	2.588(3)			
Ln(1)-C(14)	2.618(4)	2.576(3)			
Ln(1)-C(15)	2.660(3)	2.612(3)			
C(1)-C(2)	1.416(5)	1.419(4)			
C(2)-C(3)	1.418(5)	1.423(4)			
C(3)-C(4)	1.409(5)	1.413(4)			
C(4)-C(5)	1.419(5)	1.424(5)			
C(1)-C(5)	1.411(5)	1.407(5)			
C(11)-C(12)	1.416(5)	1.422(5)			
C(12)-C(13)	1.426(5)	1.415(4)			
C(13)-C(14)	1.410(5)	1.419(4)			
C(14)-C(15)	1.412(5)	1.410(4)			
C(11)-C(15)	1.413(5)	1.423(4)			

X-ray Data Collection, Structure Solution and Refinement for 5-Lu(hex).

A colorless crystal of approximate dimensions 0.198 x 0.166 x 0.096 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[11] program package and CELL_NOW[12] were used to determine the unit-cell parameters. Data was collected using a 15 sec/frame scan time for a sphere of diffraction data. The raw frame data was processed using SAINT[2] and TWINABS[13] to yield the reflection data file (HKLF5 format)[13]. Subsequent calculations were carried out using the SHELXTL[14] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

At convergence, wR2 = 0.0650 and Goof = 1.035 for 410 variables refined against 9521 data (0.74 Å), R1 = 0.0269 for those 8485 with I > 2.0σ(I). The structure was refined as a thee-component twin, BASF[14] = 0.14471 and 0.02977.

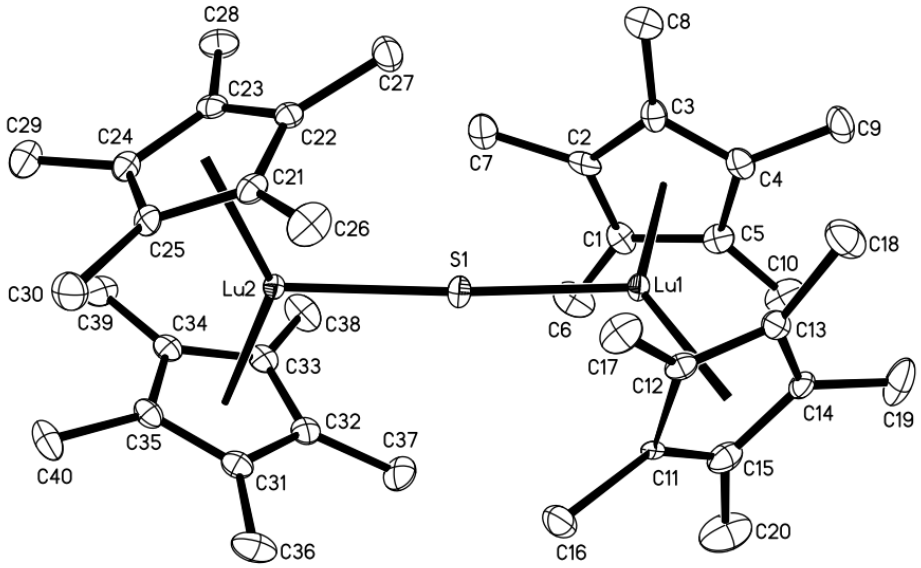

Figure S4. Thermal ellipsoid plot of $[(C_5Me_5)_2Lu]_2(\mu\text{-}S)$, **5-Lu(hex)**, drawn at the 50% probability level. Hydrogen atom are omitted for clarity.

Table S6. Crystal data and structure refinement for **5-Lu(hex)**.

Empirical formula	$C_{40}H_{60}Lu_2S$	
Formula weight	922.88	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.5471(5) Å	α= 77.2811(7)°.
	b = 11.3849(6) Å	β= 76.8625(7)°.
	c = 16.6188(9) Å	γ = 85.1302(7)°.
Volume	1894.36(17) $Å^3$	
Z	2	
Density (calculated)	1.618 Mg/m^3	
Absorption coefficient	5.261 mm^{-1}	
F(000)	916	
Crystal color	colorless	
Crystal size	0.198 x 0.166 x 0.096 mm^3	
Theta range for data collection	1.835 to 28.689°	
Index ranges	$-13 \le h \le 14$, $-14 \le k \le 15$, $0 \le l \le 22$	
Independent reflections	9521	
Completeness to theta = 25.500°	99.9 %	
Absorption correction	Numerical	
Max. and min. transmission	0.431789 and 0.329664	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9521 / 0 / 410	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I) = 8485 data]	R1 = 0.0269, wR2 = 0.0619	
R indices (all data, 0.74 Å)	R1 = 0.0340, wR2 = 0.0650	
Largest diff. peak and hole	1.587 and -0.997 $e.Å^{-3}$	

Table S7. Selected bond lengths [Å] and angles [°] for **5-Lu(hex)**.

	5-Lu(hex)		**5-Lu(hex)**		**5-Lu(hex)**
Lu(1)-Cnt1	2.300	Lu(2)-Cnt3	2.288	S(1)-Lu(1)-Cnt1	111.2
Lu(1)-Cnt2	2.300	Lu(2)-Cnt4	2.297	S(1)-Lu(1)-Cnt2	108.4
Lu(1)-S(1)	2.4868(10)	Lu(2)-S(1)	2.4974(10)	Cnt1-Lu(1)-Cnt2	140.4
Lu(1)-C(1)	2.578(4)	Lu(2)-C(21)	2.591(4)	S(1)-Lu(2)-Cnt3	109.5
Lu(1)-C(2)	2.618(4)	Lu(2)-C(22)	2.599(4)	S(1)-Lu(2)-Cnt4	110.9
Lu(1)-C(3)	2.602(4)	Lu(2)-C(23)	2.567(4)	Cnt3-Lu(2)-Cnt4	139.7
Lu(1)-C(4)	2.613(4)	Lu(2)-C(24)	2.591(4)	Lu(1)-S(1)-Lu(2)	166.68(5)
Lu(1)-C(5)	2.582(4)	Lu(2)-C(25)	2.589(4)		
Lu(1)-C(11)	2.615(4)	Lu(2)-C(31)	2.562(4)		
Lu(1)-C(12)	2.583(4)	Lu(2)-C(32)	2.608(4)		
Lu(1)-C(13)	2.572(4)	Lu(2)-C(33)	2.601(4)		
Lu(1)-C(14)	2.605(4)	Lu(2)-C(34)	2.610(4)		
Lu(1)-C(15)	2.614(4)	Lu(2)-C(35)	2.586(4)		
C(1)-C(2)	1.426(6)	C(21)-C(22)	1.411(5)		
C(2)-C(3)	1.413(6)	C(22)-C(23)	1.428(6)		
C(3)-C(4)	1.427(6)	C(23)-C(24)	1.422(6)		
C(4)-C(5)	1.421(6)	C(24)-C(25)	1.419(6)		
C(1)-C(5)	1.427(6)	C(21)-C(25)	1.424(5)		
C(11)-C(12)	1.423(5)	C(31)-C(32)	1.430(6)		
C(12)-C(13)	1.422(6)	C(32)-C(33)	1.417(6)		
C(13)-C(14)	1.420(6)	C(33)-C(34)	1.419(6)		
C(14)-C(15)	1.415(6)	C(34)-C(35)	1.425(6)		
C(11)-C(15)	1.415(6)	C(31)-C(35)	1.422(6)		

Computational Details. The initial structure optimizations of **3-Lu**, **3-Y**, and **4-Y**, starting from the available crystal data,[15] were performed using the TPSSh[16] hybrid meta-GGA functional. Split valence basis sets with polarization functions on non-hydrogen atoms (SV(P)) were used for light atoms and the triple-zeta valence basis sets with two sets of polarization functions (def2-TZVP) for Y and Lu.[17,18] TPSSh was chosen due to its established performance for transition metal compounds, reductive Ln chemistry, and Ln photochemistry.[19-22] Relativistic small-core pseudopotentials[23] were employed for Y and Lu. Vibrational frequencies were computed at the TPSSh/SV(P) level, and all ground state structures were confirmed to be minima by the absence of imaginary modes.[24] A further optimization using larger triple-zeta valence basis sets (def2-TZVP[18]) for all atoms was then performed. The differences in bond lengths between the SV(P) and the TZVP structures were typically 0.02 Å or less. Fine quadrature grids (size m4)[25] were used throughout. SCF energies and density matrices were converged to 10^{-7} a.u. All calculations were performed using the Turbomole quantum chemistry software.[26] All molecular orbital plots were computed with SV(P) basis sets using contour values of 0.06. Molecular orbital plots of the HOMO and LUMO of **4-Y** are shown in Figure S6. Theoretical, zero temperature gas-phase UV-visible spectra were generated from time dependent density functional theory (TDDFT) excitation energy calculations.[27] The excitation energies and oscillator strengths for selected transitions of **3-Lu**, **3-Y** and **4-Y** are given in Table S10.

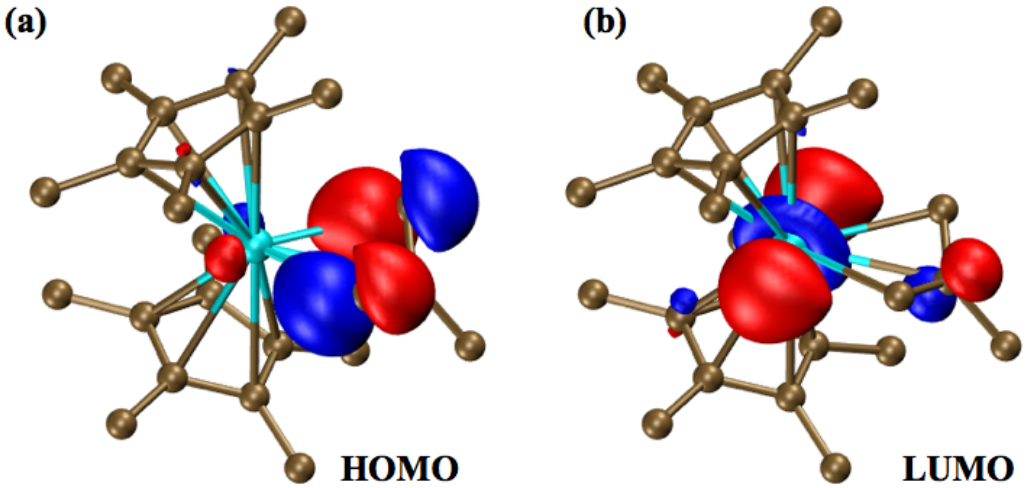

Figure S5. Molecular orbital plots of (a) the HOMO and (b) the LUMO of **4-Y**, using a contour value of 0.06.

Table S8. Computed excitation energies using TPSSH and SV(P) basis sets. Ground state SCF energies and one-electron density matrix were converged to 10^{-7}.

Compound	Wavelength (nm)	Oscillator Strength (a.u.)	Dominant Contributions		
			occupied	virtual	% comp
3-Y	391	0.014	92a (HOMO)	93a (LUMO)	89.4
	369	0.021	91a (HOMO−1)	93a (LUMO)	91.8
	346	0.003	90a (HOMO−2)	93a (LUMO)	99.1
	344	0.005	89a (HOMO−3)	93a (LUMO)	98.3
3-Lu	389	0.005	108a (HOMO)	109a (LUMO)	91
	361	0.010	107a (HOMO−1)	109a (LUMO)	94.5
	358	0.021	106a (HOMO−2)	109a (LUMO)	91.2
	338	0.002	104a (HOMO−4)	109a (LUMO)	70.6
			105a (HOMO−3)	109a (LUMO)	28.6
	336	0.006	105a (HOMO−3)	109a (LUMO)	70.5
			104a (HOMO−4)	109a (LUMO)	28.7
4-Y	389	0.018	96a (HOMO)	97a (LUMO)	93.1
	362	0.011	95a (HOMO−1)	97a (LUMO)	68.9
			94a (HOMO−2)	97a (LUMO)	26.9
	357	0.002	94a (HOMO−2)	97a (LUMO)	70.2
			95a (HOMO−1)	97a (LUMO)	28.9
	335	0.004	93a (HOMO−3)	97a (LUMO)	73.3
			92a (HOMO−4)	97a (LUMO)	25.9

Elemental Analysis Attempts for 5-Ln

5-Y Calcd for $C_{40}H_{60}SY_2$: C, 63.99; H, 8.06.
Found: 1) C, 63.14; H, 8.26
2) C, 65.11; H, 8.79
3) C, 65.62; H, 8.71
4) C, 65.01; H, 8.83
5) C, 64.68; H, 8.10
6) C, 66.68; H, 8.91
7) C, 64.72; H, 8.41
8) C, 64.51; H, 8.50

5-Lu Anal. Calcd for $C_{40}H_{60}SLu_2$: C 52.06 H 6.55.
Found: 1) C 54.72 H 6.84
2) C 54.17 H 6.96
3) C 54.11 H 6.71
4) C 54.08 H 6.29
5) C 53.75 H 6.32.

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Definitions:

$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

$Goof = S = [\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.