(C $_5$ Me $_5$)/enolamido lutetium dinitrogen complex promoted by the

deprotonation on amidinate ligand

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1. Experiment Section

All manipulations of air- and moisture-sensitive materials were performed under a nitrogen atmosphere by using standard Schlenk line techniques and a dinitrogen-filled Vigor glovebox. All the solvents were purified from a MBraun solvent purification system (SPS-800) or the FLEANO solvent purification system and dried over fresh Na chips and molecular sieves in the glovebox overnight before use. ¹H and ¹³C spectra were recorded with a Bruker Avance III 400 MHz NMR spectrometer with reference to the solvent resonances. IR spectra were obtained on a Bruker ALPHA II FTIR spectrometer in the 400-4000 cm⁻¹ region using a KBr pellet. UV–vis spectrum was recorded with Agilent Cary 60 spectrophotometer. Elemental analyses were carried out with an Elementar Vario microcube. Raman spectra were recorded using a Thermo Scientific DXRxi Raman Imaging Microscope. A laser at 532 nm with 5 mW power was used as the excitation source.

Complex **1** was prepared according to our previously published procedure.¹ The other chemicals were commercially available and used without further purification.

$[{Cp*{H_2C=C(N^iPr)_2}Lu}_2(\mu^2-\eta^2:\eta^2-N_2)K][K(crypt)] (2)$

Complex **1** (134.7 mg, 0.1 mmol) was dissolved in 20 mL THF/Et₂O (v/v = 1:3). Then, potassium metal (39.1 mg, 0.1 mmol) was added. After stirring 6 h at room temperature, the black mixture turned light brown. Volatiles were removed under vacuum, and the residue was washed thrice with n-hexene (10 mL). The light brown solid left was dissolved in 10 mL THF. Laying 20 mL *n*-hexane on the top of the THF solution. After 12 h, light brown crystals of complex **2** suitable for single crystal X-ray diffraction were obtained with a crystallization yield of 45% (62.3 mg, 0.045 mmol). IR(KBr, cm⁻¹): 2953, 2856, 2820, 1521, 1444, 1391, 1354, 1293, 1165, 1132, 1107, 1079, 1006, 950, 901, 750, 715, 497, 467. Anal. Calcd. for C₅₄H₈₈K₂Lu₂N₈O₆: C, 47.22; H, 6.46; N, 8.16. Found: C, 47.91; H, 6.79; N, 7.49. Multiple samples gave low nitrogen values, and it is possible that N₂ is lost before combustion is complete^{2, 3}.

$[{Cp*K{H_2C=C(N'Pr)_2}Cp*Lu}_2(\mu^2-\eta^2:\eta^2-N_2)][K(crypt)]_2 (3)$

Complex 1 (134.7 mg, 0.1 mmol) was dissolved in 20 mL THF/Et₂O (v/v = 1:3). Then, potassium metal (1 eq. K: 40.0 mg, .0.1 mmol; 2 eq. K: 80.2 mg, 0.2 mmol) was added. After 10 h of stirring at

room temperature, the black solution turned colorless. Volatiles were removed under vacuum, and the residue was washed with *n*-hexene (10 mL) thrice. The off-white solid left was dissolved in 10 mL THF. Laying 20 mL *n*-hexane on the top of the THF solution. After 12 h, colorless block crystals of complex **3** suitable for single crystal X-ray diffraction were obtained (1 eq. K: crystallization yield of 13%, 29.3 mg, 0.013 mmol; 2 eq. K: crystallization yield of 31%, 69.8 mg, 0.031 mmol).

¹H NMR (298 K, 400 MHz, THF-*d*₈): δ 1.12-1.14 (d, *J* = 5.8 Hz, 12 H, Me in ^{*i*}Pr), 1.22-1.23 (d, *J* = 6.2 Hz, 12 H, Me in ^{*i*}Pr), 1.88 (s, 30 H, Cp*), 1.92 (s, 30 H, Cp*), 1.99 (s, 4 H, C*H*₂), 2.48-2.50 (m, 24 H, crypt), 3.17-3.23 (m, 4H, C*H* in ^{*i*}Pr), 3.46-3.48 (m, 24 H, crypt), 3.51 (s, 24 H, crypt). ¹³C NMR (298 K, 125 MHz, THF-*d*₈): δ 166.4, 113.8, 105.6, 71.5, 68.7, 54.9, 47.5, 42.2, 26.7, 26.6, 12.1, 11.8. IR(KBr, cm⁻¹): 2952, 2887, 2855, 1518, 1476, 1445, 1390, 1356, 1291, 1168, 1131, 1107, 1076, 1006, 950, 901, 827, 566, 526, 432. Anal. Calcd. for C₁₀₀H₁₈₀K₄Lu₂N₁₀O₁₄: C, 53.31; H, 8.05; N, 6.22. Found: C, 53.89; H, 8.61; N, 5.29. Multiple samples gave low nitrogen values, and it is possible that N₂ is lost before combustion is complete^{2, 3}.

2. NMR spectra



Figure S2. ¹³C NMR spectrum of 3 (298 K, 101 MHz, THF-*d*₈).

3. IR spectra



Figure S4. IR spectrum of 3.

4. Raman Spectra



Figure S5. Raman spectra of 14 N-3 and 15 N-3.

5. UV-vis spectrum of 3



Figure S6. Uv-vis spectrum of complex 3.

6. Crystallographic Investigations

Single crystals of compounds **2** and **3** suitable for X-ray analysis were obtained as described in the experimental details and covered in mineral oil (Aldrich) and mounted on a glass fiber or a mylar loop. The crystal was transferred directly to the cold stream of a Rigaku XtaLAB PRO 007HF(Mo) diffractometer at 180 K.

All structures were solved by using the program SHEL XS/T^{4, 5} using Olex2⁶. The remaining nonhydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F^2 by using the program SHEL XL⁴, ⁵. In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 2379597-2379598. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.



Figure S7. Dimeric structure of **2** in the solid state. Hydrogen atoms, [K(crypt)] fragment and isopropyl groups in enolamido ligands are omitted for clarity.



Figure S8. Molecular structure of **2** (Up: left part; Below: right part) in the solid-state. Hydrogen atoms and [K(crypt)] fragment are omitted for clarity. Ellipsoids displayed at 50% probability.

Empirical formula	$C_{108}H_{196}K_4Lu_4N_{16}O_{12}$
Formula weight	2767.08
Temperature/K	179.99(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	49.9594(7)
<i>b</i> /Å	25.6494(5)
c/Å	20.3764(5)
$\alpha/^{\circ}$	90
$eta / ^{\circ}$	96.014(2)
$\gamma/^{\circ}$	90
Volume/Å ³	25967.2(9)
Z	8
$ ho_{ m calc} g/cm^3$	1.416
μ/mm^{-1}	3.200
<i>F</i> (000)	11296.0
Crystal size/mm ³	0.26 imes 0.23 imes 0.2
Radiation	Mo Ka ($\lambda = 0.71073$)
2Θ range for data collection/°	4.016 to 56.852
Index ranges	$-66 \le h \le 60, -33 \le k \le 33, -21 \le l \le 26$
Reflections collected	87148
Independent reflections	31107 [$R_{\text{int}} = 0.0452, R_{\text{sigma}} = 0.0622$]
Data/restraints/parameters	31107/2333/1675
Goodness-of-fit on F^2	1.057
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0465, wR_2 = 0.1113$
Final R indexes [all data]	$R_1 = 0.0695, wR_2 = 0.1198$
Largest diff. peak/hole / e Å $^{\text{-}3}$	1.84/-1.57

 Table S1. Crystal data and structure refinement for 2.



Figure S9. Molecular structure of **3** in the solid-state. Hydrogen atoms, two [K(crypt)] fragments and THF molecule are omitted for clarity. Ellipsoids displayed at 50% probability.

Empirical formula	$C_{100}H_{180}K_4Lu_2N_{10}O_{14}$
Formula weight	2252.87
Temperature/K	179.99(10)
Crystal system	triclinic
Space group	<i>P</i> -1
a/Å	12.4692(3)
<i>b</i> /Å	16.0421(4)
c/Å	16.7103(4)
$\alpha/^{\circ}$	113.745(2)
$eta / ^{\circ}$	95.077(2)
γ/°	102.135(2)
Volume/Å ³	2934.74(13)
Z	1
$ ho_{ m calc} g/cm^3$	1.275
μ/mm^{-1}	1.871
<i>F</i> (000)	1180.0
Crystal size/mm ³	$0.23 \times 0.21 \times 0.18$
Radiation	MoKa ($\lambda = 0.71073$)
2Θ range for data collection/°	4.736 to 60.422
Index ranges	$-15 \le h \le 17, -22 \le k \le 22, -23 \le l \le 23$
Reflections collected	61077
Independent reflections	15258 [$R_{int} = 0.0318$, $R_{sigma} = 0.0281$]
Data/restraints/parameters	15258/305/639
Goodness-of-fit on F ²	1.047
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0282, wR_2 = 0.0687$
Final R indexes [all data]	$R_1 = 0.0372, wR_2 = 0.0727$
Largest diff. peak/hole / e Å ⁻³	1.14/-0.75

 Table S2. Crystal data and structure refinement for 3.

			ⁱ Pr N 2⊝
Bond lengths	2	N3-N4 1.285(5)	C49-C50 1.376(7)
(Å)	(left)	Lu1-N3 2.282(4)	C58-C57 1.367(7)
		Lu2-N3 2.281(4)	
		Lu1-N4 2.278(4)	
		Lu2-N4 2.268(4)	
	2	N9-N10 1.329(6)	C73-C74 1.373(7)
	(right)	Lu4-N9 2.253(4)	C65-C66 1.358(7)
		Lu4-N10 2.250(4)	
		Lu3-N9 2.252(5)	
		Lu3-N10 2.253(4)	
	3	N1-N1' 1.273(4)	C17-C18 1.373(4)
		Lu1-N1 2.2537(17)	
		Lu1-N1' 2.2482(18)	
Bond angles	2	N4-Lu2-N3 32.8(1)	
(°)	(left)	N4-Lu1-N3 32.8(1)	
		Lu2-N3-Lu1 143.2(2)	
		Lu2-N4-Lu1 144.6(2)	
	2	N9-Lu3-N10 34.3(2)	
	(right)	N10-Lu4-N9 34.3(2)	
		Lu3-N9-Lu4 139.5(2)	
		Lu4-N10-Lu3 139.7(2)	
	3	Lu1-N1-Lu1' 147.16(9)	
		N1-Lu1-N1' 32.84(9)	

Table S3. Selected bond lengths (Å) and angles (°) in complexes 2 and 3.

Symmetry code: ': 1+x, y, 1+z.

	υ	1
	N-N bond length (Å)	Raman (cm ⁻¹)
Lu-(N ₂) ²⁻ complexes		
$[(Cp^*)_2Lu]_2(\mu-\eta^2:\eta^2-N_2)^7$	1.111-1.239	1406
$[(Cp^*)(C_5Me_4H)Lu]_2(\mu-\eta^2:\eta^2-N_2)^8$	1.275(4)	-
$[{(Me_3Si)_2N}_2(THF)Lu]_2(\mu-\eta^2:\eta^2-N_2)^9$	1.285(4)	1451 ¹⁰
$[(C_5Me_4H)_2(THF)Lu]_2(\mu-\eta^2:\eta^2-N_2)^{11}$	1.243(12)	-
$[\{(Cp^*)\{MeC(N^iPr)_2\}Lu\}_2(\mu-\eta^2:\eta^2-N_2)]^1$	1.303(5)	1371
$[\{Cp^*\{H_2C=C(N^iPr)_2\}Lu\}_2(\mu^2-\eta^2:\eta^2-N_2)K][K(crypt)](2)$	1.285(5) 1.329(6)	-
$[\{Cp^{*}K\{H_{2}C=C(N^{i}Pr)_{2}\}Cp^{*}Lu\}_{2}(\mu^{2}-\eta^{2}:\eta^{2}-N_{2})][K(crypt)]_{2}(3)$	1.273(4)	1426
Lu-(N ₂) ³⁻ complexes		
{[(Me ₃ Si) ₂ N] ₂ Lu(THF)} ₂ (μ - η ² : η ² -N ₂)[K(THF) ₆] ¹⁰	1.414(8)	979
$[\{(Cp^*)\{MeC(N^iPr)_2\}Lu\}_2(\mu-\eta^2:\eta^2-N_2)][K(crypt)]^1$	1.449(4)	903

Table S4. N-N bond length and Raman spectra data of reported lutetium dinitrogen complex

7. DFT calculation

Calculations were performed using ORCA 5.0.4 and ORCA 6.0.0.^{12, 13} Geometric structures were optimized at the TPSSh/def2-SVP level of theory, incorporating dispersion corrections with the Becke-Johnson damping scheme (D3BJ). To simplify the calculations, we optimized the structures of the anionic part of complex 1, the dianionic part of complex 2, the anionic part of one unit of complex 2, and the dianionic part of complex 3, all using closed-shell calculations. We also attempted a broken-symmetry calculation for complex 3, which produced the same result as the closed-shell system. The optimized geometric structures were uploaded separately as .xyz files.

Multiwfn software was employed based on the optimized structures.¹⁴ We conducted an Atoms-In-Molecules (AIM) analysis on one unit of the anionic part of complex **2** using Multiwfn. Bond critical points (BCPs) with (3, -1) topology were identified. The results indicate interactions between the potassium ion (K) and the carbon and nitrogen atoms of the enolamido group, as well as the coordinated N₂ unit. Notably, the Laplacian of the electron density at these BCPs is positive, and the energy density, H(r), is slightly positive, suggesting that the interactions between K and the surrounding atoms are predominantly ionic.¹⁵

Fuzzy bond order (FBO) analysis, a widely recognized bond order index developed by Mayer and Salvador, was applied to complexes **1-3**.¹⁶ The FBO values for the NN bond were determined to be 1.14, 1.66, and 1.65 in complexes **1**, **2**, and **3**, respectively.

Tabel S5. Hirshield charge analysis of complexes 1-5			
		Charge Value	
1	N ₂ unit	-0.66	
1	Lu	0.38	
2	N ₂ unit	-0.36	
2	Lu	0.39	
2	N ₂ unit	-0.34	
3	Lu	0.38	

 Tabel S5. Hirshfeld charge analysis of complexes 1-3



Figure S10. The Atoms-In-Molecules (AIM) analysis of complex **2** (Orange balls: bond critical point(BCP); Blue ball: nitrogen atom; Grey ball: carbon atom; Pink ball: potassium atom; Green ball: lutetium atom).

8. Reference

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