Supporting Information

Insertion of Ketenimines into the Ln–C σ-Bond of Organolanthanides: A New Strategy for Synthesis of 1-Aza-allyl Lanthanide Complexes

Zhengxing Zhang,[†] Xiuli Bu,[†] Jie Zhang,[†] Ruiting Liu,[†] Xigeng Zhou,*[,†,‡] Linhong Weng[†]

Department of Chemistry, Molecular Catalysis and Innovative Material Laboratory, Fudan University, Shanghai 200433, People's Republic of China, and State Key Laboratory of Organometallic Chemistry, Shanghai 200032, People's Republic of China

X-ray structure determination details for 1-4. Suitable single crystals of compounds **1**-**4** were sealed under N_2 in thin-walled glass capillaries for X-ray structural analysis. X-ray diffraction data were collected on a SMART APEX CCD diffractometer (graphite-monochromated Mo*K*α radiation, Φ-ω scan technique, λ = 0.71073 Å). The intensity data were integrated by means of the SAINT program.[1] SADABS[2] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against F^2 using all reflections with the aid of the SHELXTL package.[3] All non-hydrogen atoms were found from the difference Fourier syntheses. The hydrogen atom on the β-carbon of aza-allyl ligands was located in a difference Fourier map, and was refined. All remaining hydrogen atoms were assigned in idealized positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker Smart program. Crystallographic parameters for compounds **1**-**4** along with details of the data collection and refinement are collected in Table 1-5.

References

(1) *SAINTPlus Data Reduction and Correction Program* v. 6.02 a; Bruker AXS: Madison, WI, 2000.

(2) Sheldrick, G. M. *SADABS*, A Program for Empirical Absorption Correction; University of Go¨ttingen: Go¨ttingen, Germany, 1998.

(3) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Go¨ttingen: Go¨ttingen, Germany, 1997.

Table 1. Crystal and Data Collection Parameters of Complexes **1-Ln**

	1-Y	**1-Er**	**1-Yb**
Formula	$C_{29}H_{32}NY$	$C_{29}H_{32}NEr$	$C_{29}H_{32}NYb$
Molecular weight	483.47	561.82	567.60
Crystal color	orange red	red	deep red
Crystal dimens (mm)	0.20 x 0.15 x 0.12	0.20 x 0.15 x 0.12	0.20 x 0.15 x 0.10
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n	P2(1)/n
Unit cell dimensions			
a (Å)	20.750(11)	20.675(8)	20.688(10)
b (Å)	10.820(6)	10.789(4)	10.760(5)
c (Å)	23.573(12)	23.493(9)	23.461(11)
β (deg)	112.204(6)	112.187(4)	112.248(6)
V (Å^3)	4900(4)	4853(3)	4834(4)
Z	8	8	8
Dc (g.cm^{-3})	1.311	1.538	1.560
μ (mm^{-1})	2.396	3.474	3.885
F (000)	2016	2248	2264
Radiation (λ =0.710730Å)	Mo-K_α	Mo-K_α	Mo-K_α
Temperature (K)	293.2	293.2	293.2
Scan type	ω-2θ	ω-2θ	ω-2θ
θ range (deg)	1.66 to 25.01	1.66 to 25.01	1.66 to 25.00
h,k,l range	$-24\leq h\leq 24$	$-22\leq h\leq 24$	$-24\leq h\leq 22$
	$-12\leq k\leq 6$	$-12\leq k\leq 12$	$-12\leq k\leq 12$
	$-28\leq l\leq 25$	$-27\leq l\leq 15$	$-27\leq l\leq 25$
No. of reflections measured	19481	19548	19540
No. of unique reflections	8618 (R_{int} = 0.1115)	8542 (R_{int} = 0.0521)	8506 (R_{int} = 0.0785)
Completeness to θ	99.8 % (θ = 25.01)	99.9 % (θ = 25.01)	99.8 % (θ = 25.00)
Max. and min. Transmission	0.7620 and 0.6458	0.6806 and 0.5433	0.6973 and 0.5104
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8618 / 0 / 559	8542 / 0 / 560	8506 / 0 / 560
Goodness-of-fit on F^2	1.018	0.909	0.924
Final R indices [I>2σ (I)]	R_1 = 0.0594	R_1 = 0.0354	R_1 = 0.0446
	wR_2 = 0.0710	wR_2 = 0.0748	wR_2 = 0.0984
R indices (all data)	R_1 = 0.1639	R_1 = 0.0620	R_1 = 0.0819
	wR_2 = 0.0789	wR_2 = 0.0809	wR_2 = 0.1076
Largest diff. peak and hole (e·Å^{-3})	0.662 and -0.743	1.808 and -0.697	1.695 and -1.506

Table 2. Crystal and Data Collection Parameters of Complexes **2-Ln**

	2-Y	**2-Yb**
Formula	$C_{34}H_{34}NY$	$C_{34}H_{34}NYb$
Molecular weight	545.53	629.66
Crystal color	yellow	red
Crystal dimens (mm)	0.15 x 0.12 x 0.08	0.20 x 0.06 x 0.05
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbca	Pbca
Unit cell dimensions		
a (Å)	25.255(9)	25.065(7)
b (Å)	9.392(4)	9.369(3)
c (Å)	26.426(10)	26.260(8)
β (deg)	90	90
V (Å^3)	6268(4)	6167(3)
Z	8	8
Dc (g.cm^{-3})	1.156	1.356
μ (mm^{-1})	1.880	3.053
F (000)	2272	2520
Radiation (λ =0.710730Å)	Mo-K_α	Mo-K_α
Temperature (K)	293.2	293.2
Scan type	ω-2θ	ω-2θ
θ range (deg)	1.54 to 25.01	1.55 to 25.01
h,k,l range	$-30 \le h \le 20$	$-29 \le h \le 29$
	$-11 \le k \le 11$	$-11 \le k \le 10$
	$-29 \le l \le 31$	$-31 \le l \le 24$
No. of reflections measured	24609	24164
No. of unique reflections	5522 (R_{int} = 0.1811)	5423 (R_{int} = 0.0764)
Completeness to θ	100.0 % (θ = 25.01)	99.9 % (θ = 25.01)
Max. and min. Transmission	0.8641 and 0.7657	0.6417 and 0.5541
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5522 / 0 / 325	5423 / 0 / 325
Goodness-of-fit on F^2	0.913	1.005
Final R indices [I>2σ (I)]	R_1 = 0.0676	R_1 = 0.0382
	wR_2 = 0.1207	wR_2 = 0.0821
R indices (all data)	R_1 = 0.1901	R_1 = 0.0804
	wR_2 = 0.1325	wR_2 = 0.0858
Largest diff. peak and hole (e·Å^{-3})	1.113 and -0.326	0.981 and -0.550

Table 3. Crystal and Data Collection Parameters of Complexes **2-Ln·THF**

	2-Y·THF	**2-Er·THF**	**2-Yb·THF**
Formula	$C_{38}H_{42}NOY$	$C_{38}H_{42}NOEr$	$C_{38}H_{42}NOYb$
Molecular weight	617.64	695.99	701.77
Crystal color	orange yellow	orange	dark red
Crystal dimens (mm)	0.15 x 0.12 x 0.08	0.15 x 0.10 x 0.06	0.22 x 0.18 x 0.16
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n	P2(1)/n
Unit cell dimensions			
a (Å)	13.637(4)	13.628(4)	13.603(5)
b (Å)	9.134(3)	9.119(3)	9.132(4)
c (Å)	25.475(8)	25.399(8)	25.305(10)
β (deg)	98.862(5)	98.926(5)	99.003(5)
V (Å^3)	3135.2(17)	3118.1(16)	3105(2)
Z	4	4	4
Dc (g.cm^{-3})	1.309	1.483	1.501
μ (mm^{-1})	1.890	2.722	3.043
F (000)	1296	1412	1420
Radiation (λ =0.710730Å)	Mo-K_α	Mo-K_α	Mo-K_α
Temperature (K)	293.2	293.2	293.2
Scan type	ω-2θ	ω-2θ	ω-2θ
θ range (deg)	1.60 to 25.01	1.60 to 25.01	1.60 to 25.01
h,k,l range	$-16\leq h\leq 12$ $-10\leq k\leq 10$ $-30\leq l\leq 30$	$-16\leq h\leq 10$ $-10\leq k\leq 10$ $-29\leq l\leq 30$	$-15\leq h\leq 16$ $-10\leq k\leq 10$ $-23\leq l\leq 30$
No. of reflections measured	12601	12579	12480
No. of unique reflections	5510 (R_{int} = 0.1248)	5474 (R_{int} = 0.0739)	5448 (R_{int} = 0.0564)
Completeness to θ	99.7 % (θ = 25.01)	99.6 % (θ = 25.01)	99.6 % (θ = 25.00)
Max. and min. Transmission	0.8635 and 0.7647	0.8537 and 0.6856	0.6417 and 0.5541
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5510 / 7 / 345	5474 / 7 / 345	5448 / 7 / 345
Goodness-of-fit on F^2	1.004	0.985	1.002
Final R indices [I>2σ(I)]	R_1 = 0.0729 wR_2 = 0.1586	R_1 = 0.0465 wR_2 = 0.0824	R_1 = 0.0474 wR_2 = 0.1276
R indices (all data)	R_1 = 0.1542 wR_2 = 0.1906	R_1 = 0.0800 wR_2 = 0.0868	R_1 = 0.0651 wR_2 = 0.1344
Largest diff. peak and hole (e·Å^{-3})	1.547 and -0.552	1.643 and -0.737	2.189 and -0.966

Table 4. Crystal and Data Collection Parameters of Complexes **3-Ln**

	3-Er	**3-Yb**	**3-Y(THF)**
Formula	$C_{23}H_{28}NEr$	$C_{23}H_{28}NYb$	$C_{27}H_{36}NOY$
Molecular weight	485.72	491.50	479.48
Crystal color	orange	green	pale yellow
Crystal dimens (mm)	0.08 x 0.05 x 0.04	0.20 x 0.12 x 0.10	0.42 x 0.20 x 0.18
Crystal system	Orthorhombic	Tetragonal	Monoclinic
Space group	Pbca	P-42(1)c	P2(1)/n
Unit cell dimensions			
a (Å)	27.581(10)	22.078(5)	13.126(6)
b (Å)	8.893(3)	22.078(5)	8.896(4)
c (Å)	33.879(13)	8.932(3)	20.839(9)
β (deg)	90	90	96.019(7)
V (Å^3)	8309(5)	4354(2)	2420.0(19)
Z	16	8	4
Dc (g.cm^{-3})	1.553	1.500	1.316
μ (mm^{-1})	4.044	4.300	2.427
F (000)	3856	1944	1008
Radiation (λ =0.710730Å)	Mo-K_α	Mo-K_α	Mo-K_α
Temperature (K)	293.2	293.2	293.2
Scan type	ω-2θ	ω-2θ	ω-2θ
θ range (deg)	1.20 to 25.01	1.30 to 25.01	1.75 to 25.01
h,k,l range	$-29\leq h\leq 32$	$-26\leq h\leq 19$	$-15\leq h\leq 15$
	$-10\leq k\leq 10$	$-26\leq k\leq 26$	$-9\leq k\leq 10$
	$-32\leq l\leq 40$	$-10\leq l\leq 10$	$-21\leq l\leq 24$
No. of reflections measured	27545	17788	9727
No. of unique reflections	7317 (R_{int} = 0.1687)	3844 (R_{int} = 0.1430)	4258 (R_{int} = 0.1067)
Completeness to θ	99.8 % (θ = 25.01)	99.9 % (θ = 25.01)	99.7 % (θ = 25.01)
Max. and min. Transmission	0.8550 and 0.7380	0.6730 and 0.4801	0.6691 and 0.4288
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7317 / 25 / 457	3844 / 5 / 184	4258 / 1 / 274
Goodness-of-fit on F^2	0.892	0.954	0.968
Final R indices [I>2σ (I)]	R_1 = 0.0694	R_1 = 0.0550	R_1 = 0.0593
	wR_2 = 0.0849	wR_2 = 0.1222	wR_2 = 0.0680
R indices (all data)	R_1 = 0.1664	R_1 = 0.1142	R_1 = 0.1436
	wR_2 = 0.0996	wR_2 = 0.1355	wR_2 = 0.0756
Largest diff. peak and hole (e·Å^{-3})	2.895 and -1.399	1.706 and -0.524	0.741 and -0.881

Table 5. Crystal and Data Collection Parameters of Complexes **4-Ln**

	4-Yb	**4-Y(THF)**
Formula	$C_{28}H_{30}NYb$	$C_{32}H_{38}NOY$
Molecular weight	553.57	541.54
Crystal color	dark green	pale yellow
Crystal dimens (mm)	0.20 x 0.12 x 0.10	0.12 x 0.10 x 0.08
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/n	P-1
Unit cell dimensions		
a (Å)	10.039(3)	10.576(4)
b (Å)	18.244(6)	11.590(4)
c (Å)	13.750(5)	12.272(5)
α (deg)	90	109.547(4)
β (deg)	110.457(4)	96.541(5)
γ (deg)	90	97.659(5)
V (Å^3)	2359.6(14)	1384.5(9)
Z	4	2
Dc (g.cm^{-3})	1.558	1.299
μ (mm^{-1})	3.977	2.130
F (000)	1100	568
Radiation (λ =0.710730Å)	Mo-K_α	Mo-K_α
Temperature (K)	293.2	293.2
Scan type	ω-2θ	ω-2θ
θ range (deg)	1.94 to 25.01	1.79 to 25.00
h,k,l range	$-11 \le h \le 7$	$-12 \le h \le 12$
	$-21 \le k \le 21$	$-8 \le k \le 13$
	$-16 \le l \le 16$	$-14 \le l \le 14$
No. of reflections measured	9637	5756
No. of unique reflections	4160 (R_{int} = 0.0415)	4787 (R_{int} = 0.0537)
Completeness to θ	99.9 % (θ = 25.01)	98.0 % (θ = 25.00)
Max. and min. Transmission	0.7415 and 0.5869	0.8481 and 0.7841
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4160 / 1 / 274	4787 / 1 / 319
Goodness-of-fit on F^2	0.991	1.042
Final R indices [I>2σ (I)]	R_1 = 0.0315	R_1 = 0.0479
	wR_2 = 0.0576	wR_2 = 0.0931
R indices (all data)	R_1 = 0.0465	R_1 = 0.0735
	wR_2 = 0.0602	wR_2 = 0.0987
Largest diff. peak and hole (e·Å^{-3})	0.772 and -1.304	0.520 and -0.648