Electronic Supplementary Material (ESI) for Chemical Science.

Comparison of tetravalent cerium and terbium ions in a conserved, homoleptic imidophosphorane ligand field

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Table of Contents

General Considerations

Unless otherwise noted, all reagents were obtained from commercial suppliers and the syntheses and manipulations were conducted under argon with exclusion of oxygen and water using Schlenk techniques or in an inert atmosphere box (Vigor) under a dinitrogen (<0.1 ppm O_2/H_2O) atmosphere. The glovebox is equipped with two -35 ˚C freezers. All glassware and cannulae were stored in an oven overnight (>8 h) at a temperature of ca. 160 ˚C. Celite and molecular sieves were dried under vacuum at a temperature >250 ˚C for a minimum of 24 h. C_6D_6 was stored over 3 Å molecular sieves and then vacuum-transferred from purple sodium/benzophenone prior to use. Diethyl ether, *n*-pentane, *n*-hexane, benzene, toluene, tetrahydrofuran, and 1,2-dimethoxyethane were purged with UHP-grade argon (Airgas) and passed through columns containing Q-5 and molecular sieves in a solvent purification system (JC Meyer Solvent Systems). All solvents in the glovebox were stored in bottles over 3 Å molecular sieves. Methanol was dried by refluxing over magnesium turnings activated with iodine for 12 h and then distilled and stored over 3 Å molecular sieves.

The starting materials $CeI_3(THF)_4$, $[(CH_2N^tBu)_2(Et_2N)P{=}NK]$, **1-Tb(PN*)**, **2-Tb(PN*)**, and potassium benzyl were prepared according to literature procedures.[1-3] Potassium *t*-butoxide was sublimed prior to use. NMR spectra were obtained on a Bruker Advance III 400 MHz spectrometer at 298 K, unless otherwise noted. ^1H, ^{13}C, and ^{31}P NMR chemical shifts are reported in δ, parts per million. ^1H NMR are referenced to the residual ^1H resonances of the solvent. ^{13}C NMR are referenced to the ^{13}C resonance of the deuterated solvent.[4] Peak position is listed, followed by peak multiplicity, integration value, and proton assignment, where applicable. Multiplicity and shape are indicated by the following abbreviations: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); td (triplet of doublets); m (multiplet); br (broad). Infrared (IR) samples were taken on a Bruker ALPHA FTIR spectrometer from 400 to 4000 cm^{-1}. IR samples were prepared as Nujol mulls sandwiched between two KBr plates. The peaks are listed in wavenumber [cm^{-1}] and intensity using the following abbreviations: vw (very weak); w (weak); m (medium); s (strong); vs (very strong); br (broad). UV/visible/NIR spectroscopy was performed in Teflon-valve sealed quartz cuvettes with a 1 cm path length on a Hitachi UH4150 UV-vis-NIR scanning spectrophotometer between 2400-200 nm. Elemental analyses were determined at Robertson Microlit Laboratories (Ledgewood, NJ).

Synthetic Methods

Preparation of [K][Ce(NP(1,2-*bis*-^{t}Bu-diamidoethane)(NEt$_2$))$_4$], 1-Ce(PN*). Inside a glovebox, 2 mL of diethyl ether was added to a 20 mL scintillation vial charged with a glass stir bar and $CeI_3(THF)_4$ (0.185 g, 0.230 mmol). $[(CH_2N^tBu)_2(Et_2N)P{=}NK]$ (0.300 g, 0.919 mmol) was added as a solution in diethyl ether (3 mL) and the reaction mixture was stirred overnight. Then the mixture was filtered through a fine porosity frit packed with Celite. The filtrate was concentrated *in vacuo* to give a yellow solid. The residue was triturated five times with 1 mL *n*-pentane and then taken up in 3 mL hexanes and filtered through a pipet filter packed with Celite and a glass fiber filter paper. The yellow solution was concentrated *in vacuo* and placed into a -35° C freezer. Overnight yellow crystals formed which were isolated by decantation and residual volatiles were removed *in vacuo* to afford the title compound (0.191 g, 62 %). ^1H NMR (400.13 MHz, C_6D_6): 4.98 (s, 8 H),

4.08 (s, 8H), 1.69 (s, 72 H), -1.29 (s, 24 H), -1.60 (s, 12 H)z. ^{31}P NMR (161.98 MHz, C_6D_6): 108.03 (s). ^{13}C NMR (100.61 MHz, C_6D_6): 53.20 (s), 43.36 (d), 34.26 (s), 28.89 (s), 11.27 (s). IR: ν [cm^{-1}] = 1478 (w), 1356 (m), 1344 (m), 1266 (m), 1249 (s), 1210 (s), 1195 (s), 1157 (s), 1152 (m), 1092 (s), 1053 (s), 1028 (m), 975 (m), 929 (m), 866 (m), 796 (m), 778 (m), 691 (m), 628 (w), 618 (w). Elemental analysis found(calculated): C, 53.11(52.63), H, 10.00(10.12), N, 15.40(15.84). One hexane molecule within the lattice is found by EA in agreement with the ^{1}H NMR. XRD quality crystals were grown from a concentrated solution of **1-Ce(PN*)** hexanes at -35 °C.

Preparation of [Ce(NP(1,2-*bis*-^{t}Bu-diamidoethane)(NEt$_2$))$_4$], 2-Ce(PN*). Inside a glovebox, **1** (0.13 g, 0.099 mmol) was dissolved in 2 mL diethyl ether in a 20 mL scintillation vial charged with a stir bar. AgI (0.026 g, 0.11 mmol) was added to the scintillation vial as a suspension in diethyl ether (3 mL). Upon addition, the yellow solution turned a deep red/orange and the reaction mixture was stirred for 20 min. A fine grey powder and a white precipitate were formed during the course of the reaction. The mixture was filtered through a pipet filter packed with Celite and glass fiber filter paper and then volatiles were removed *in vacuo*. The residue was triturated 3 times with 1 mL *n*-pentane. The residue was then taken up in *n*-pentane, filtered through a pipet filter packed with Celite and glass fiber filter paper, concentrated *in vacuo*, and placed into a -35 °C fridge. Overnight red/orange crystals formed which were isolated by decantation and residual volatiles were removed *in vacuo* to afford the title compound (0.098 g, 77 %). ^{1}H NMR (400.13 MHz, C_6D_6): 3.36 (q, 4 H), 3.10 (m, 2 H), 2.89 (m, 2 H), 1.56 (s, 18 H), 1.22 (t, 6 H). ^{31}P NMR (161.98 MHz, C_6D_6): -24.89 (s).^{13}C NMR (100.61 MHz, C_6D_6): 52.17 (s), 40.74 (s), 39.65 (s), 30.01 (s), 13.68 (s). IR: ν [cm^{-1}] = 1476 (w), 1387 (m), 1358 (m), 1346 (w), 1268 (m), 1251 (m), 1227 (s), 1210 (s), 1196 (s), 1152 (m), 1131 (w), 1094 (s), 1074 (w), 1055 (m), 1026 (s), 980 (m), 934 (m), 923 (w), 868 (m), 798 (x), 777 (w), 700 (m), 635 (m). Elemental analysis found(calculated): C, 50.53(52.15), H, 9.55(10.00), N, 16.87(17.38). Carbon was consistently low on multiple burns. XRD quality crystals were grown from a concentrated solution of **2-Ce(PN*)** in *n*-pentane at -35 °C.

NMR Spectroscopy

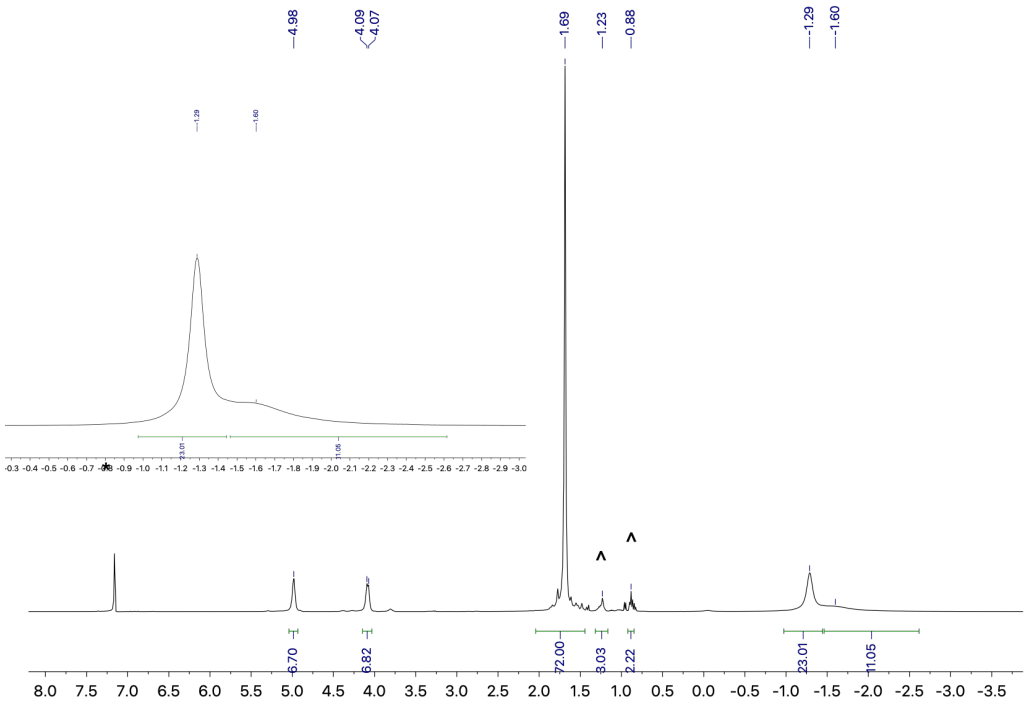

Figure S1. ^{1}H NMR of **1-Ce(PN*)** in C_6D_6 when crystallized from hexanes. Peak of C_6D_5H is noted as *. Residual hexanes is denoted by ^.

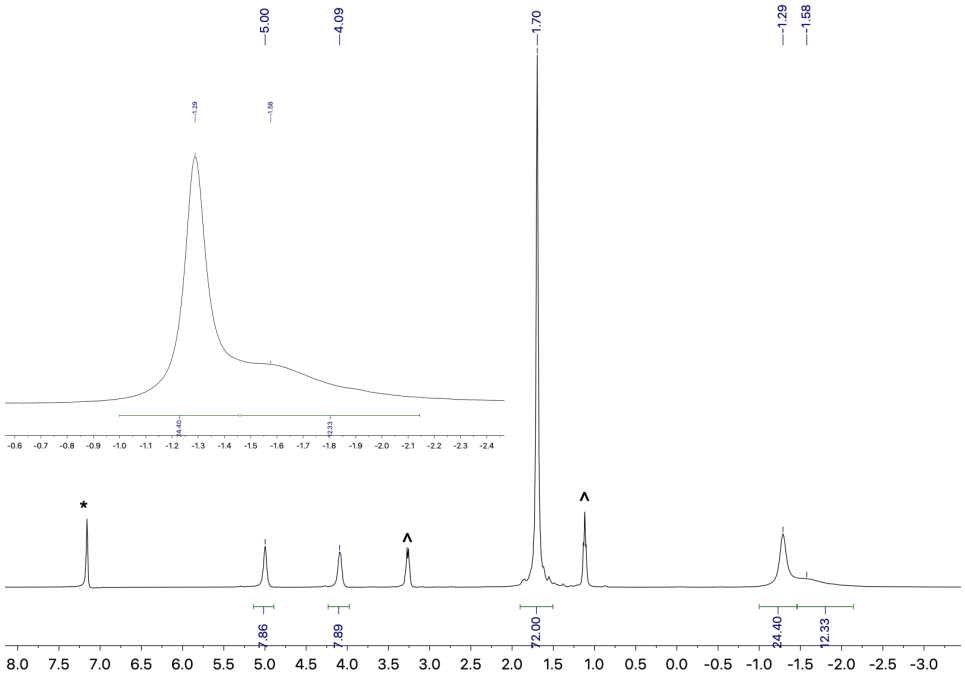

Figure S2. ^{1}H NMR of **1-Ce(PN*)** in C_6D_6 when crystallized from diethyl ether. Peak of C_6D_5H is noted as *. Residual diethyl ether is denoted by ^.

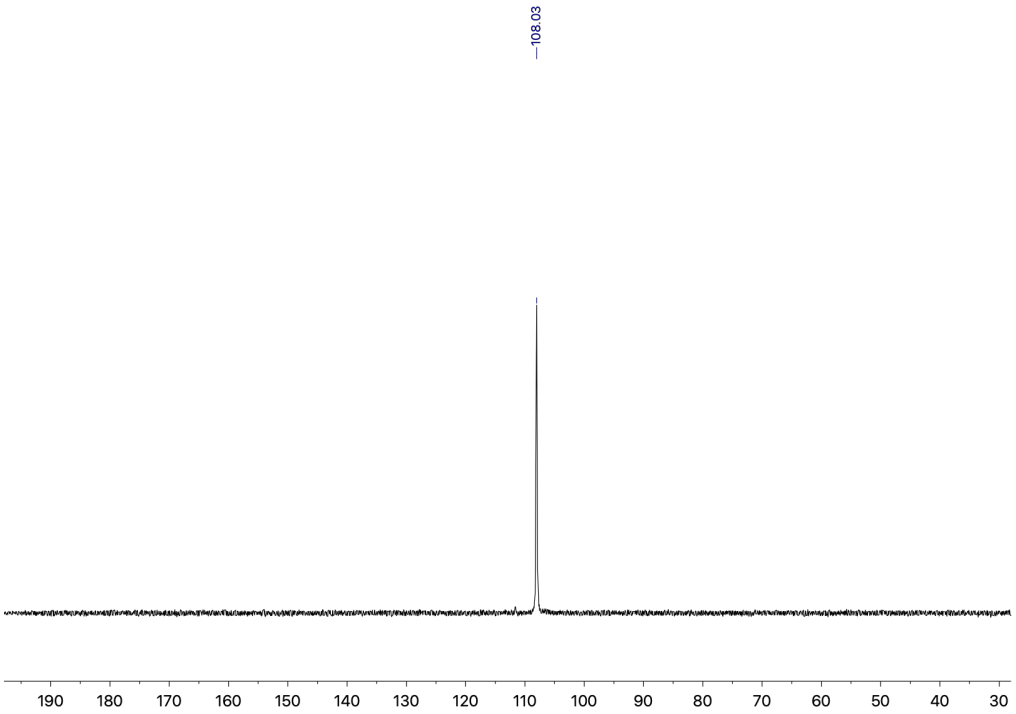

Figure S3. $^{31}P\{^{1}H\}$ NMR of **1-Ce(PN*)** in C_6D_6 when crystallized from diethyl ether.

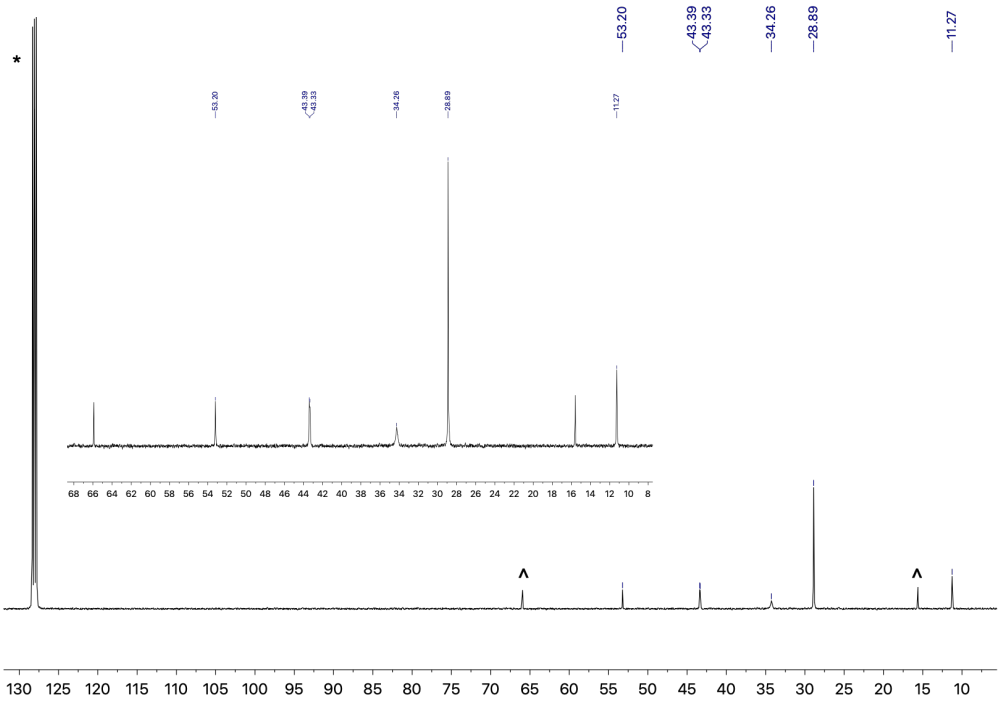

Figure S4. $^{13}C\{^{1}H\}$ NMR of **1-Ce(PN*)** in C_6D_6 when crystallized from diethyl ether. Peak of C_6D_5H is noted as *. Residual diethyl ether is denoted by ^.

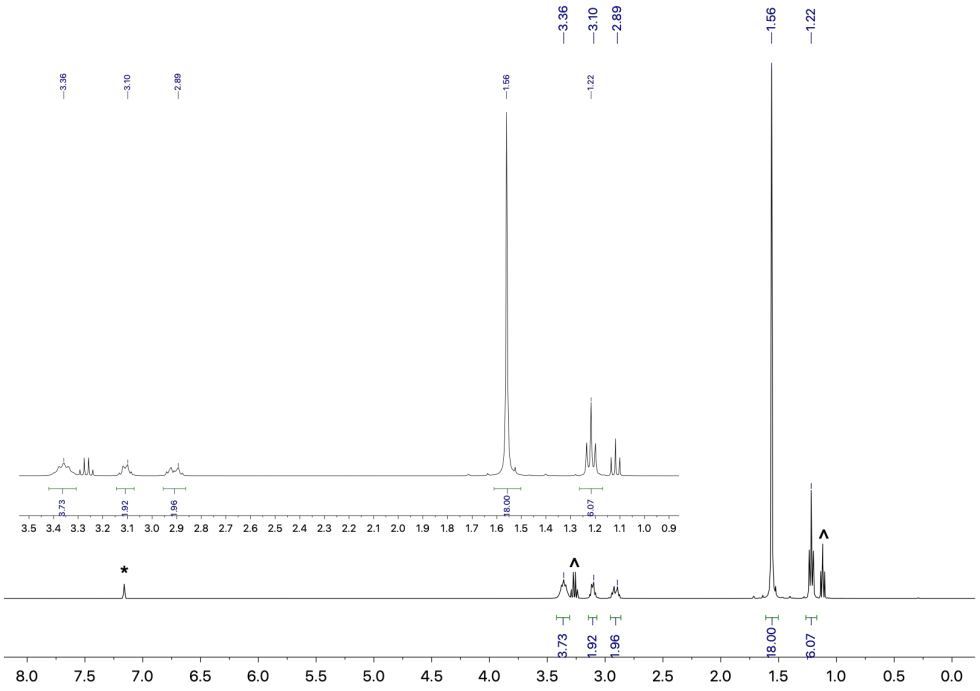

Figure S5. ^{1}H NMR of **2-Ce(PN*)** in C_6D_6. Peak of C_6D_5H is noted as *. Residual diethyl ether is denoted by ^.

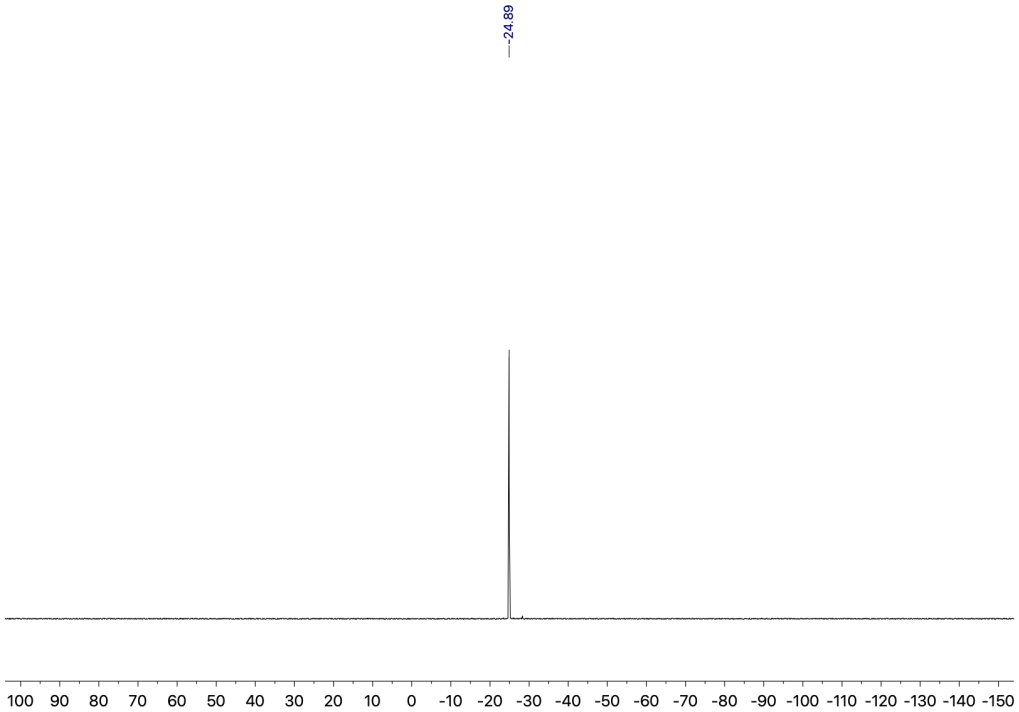

Figure S6. $^{31}P\{^{1}H\}$ NMR of **2-Ce(PN*)** in C_6D_6.

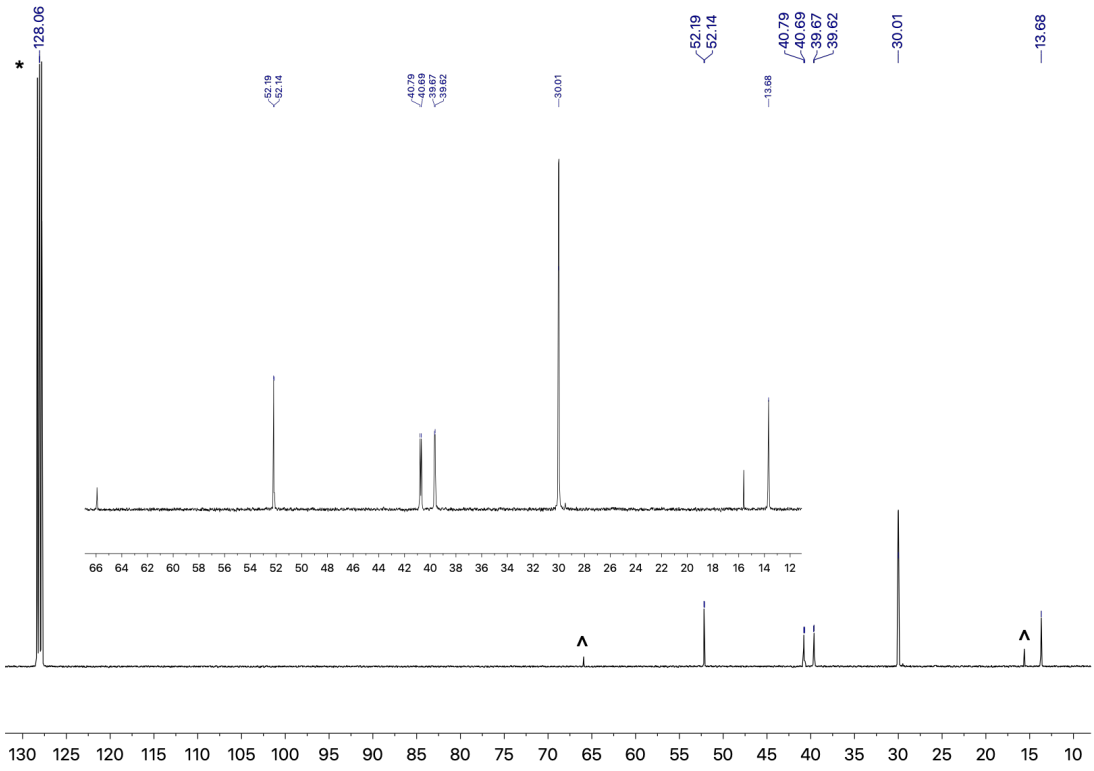

Figure S7. $^{13}C\{^{1}H\}$ NMR of **2-Ce(PN*)** in C_6D_6. Peak of C_6D_5H is noted as *. Residual diethyl ether is denoted by ^.

Crystallographic Analyses

Crystals suitable for X-ray diffraction were covered in paratone oil in a glove box and transferred to the diffractometer in a 20 mL capped vial. Crystals were mounted on a loop with paratone oil on a Bruker D8 VENTURE diffractometer. The crystals were cooled and kept at *T* = 100(2) K during data collections (except for 3 – following description – which was collected at *T* = 180(2) K). The structures were solved with the ShelXT structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface.[5, 6] The model was refined with version 2014/7 of XL using Least Squares minimization.[7]

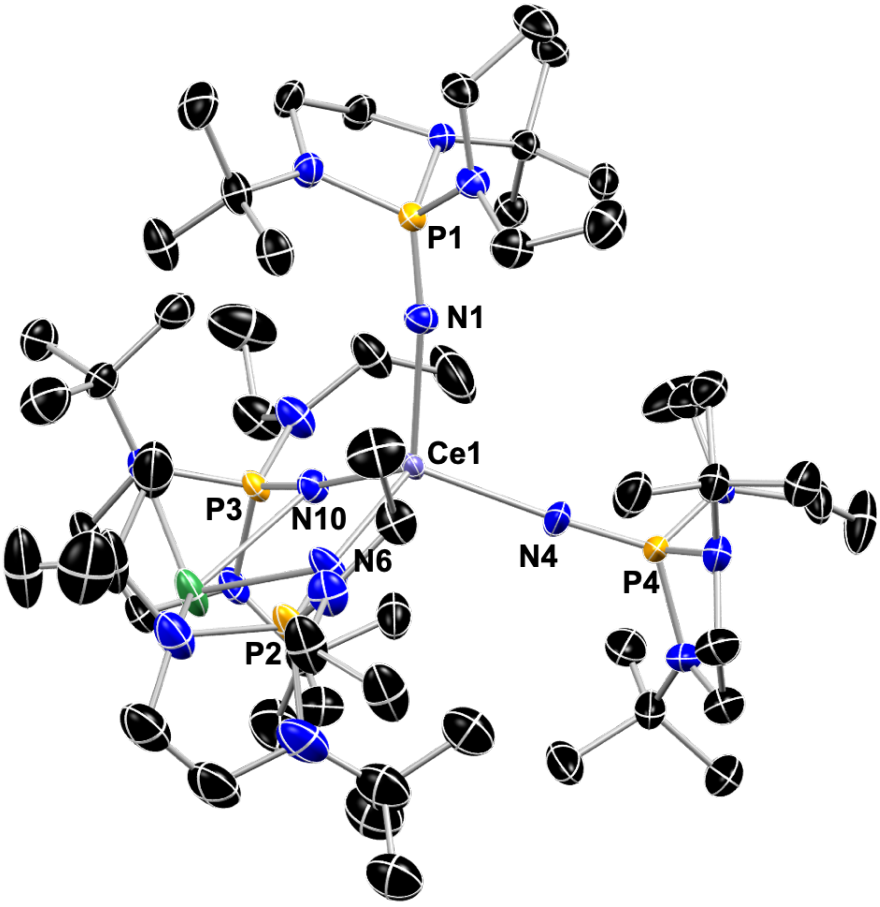

Figure S8. Molecular structure of **1-Ce(PN*)** at with thermal ellipsoids shown at 50% probability. H atoms are omitted for clarity.

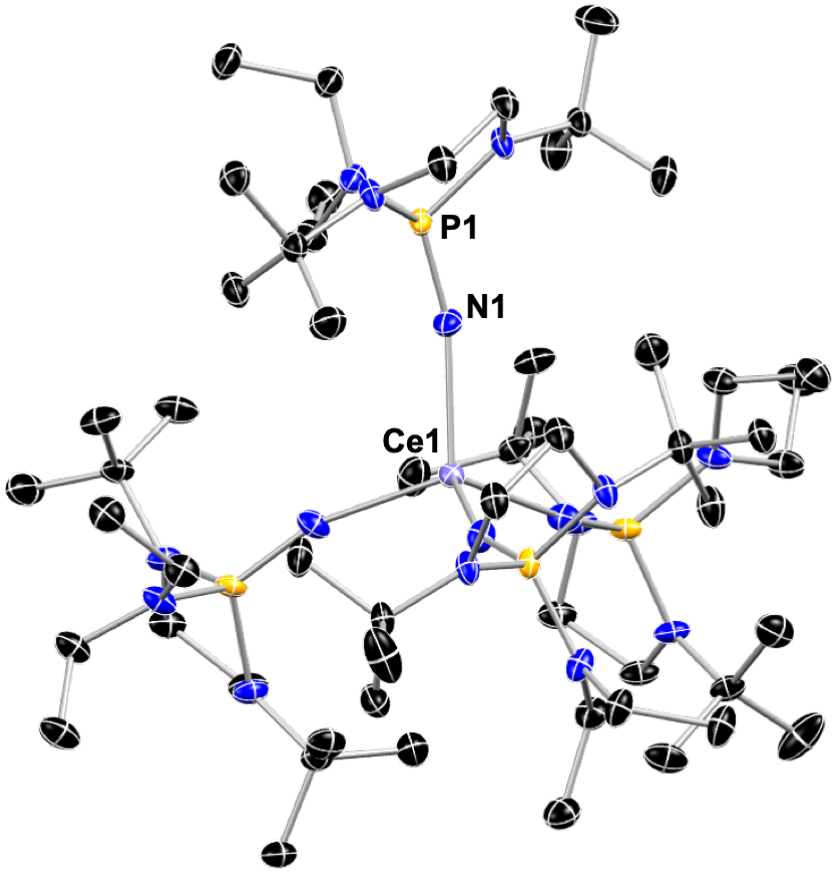

Figure S9. Molecular structure of **2-Ce(PN*)** at with thermal ellipsoids shown at 50% probability. H atoms are omitted for clarity.

Table S1. Crystallographic Data

	1-Ce(PN)*	*2-Ce(PN*)*
Empirical Formula	$C_{56}H_{128}KN_{16}P_4$	$C_{56}H_{128}CeN_{16}P_4$
Formula Weight	1328.84	1289.74
Temperature (K)	100(2)	100(2)
Crystal System	triclinic	tetragonal
Space Group	P-1	I-4
a/Å	13.160(2)	13.3276(10)
b/Å	13.956(3)	13.3276(10)
c/Å	23.750(5)	21.0511(17)
α/°	74.835(8)	90
β/°	81.559(8)	90
γ/°	65.275(7)	90
Volume/Å3	3820.6(13)	3764.5(6)
Z	2	2
Z'	1	0.25
ρ(g/cm3)	1.155	1.138
μ(mm-1)	0.776	0.732
F(000)	1428	1388
Crystal Size/mm3	0.32 x 0.28 x 0.23	0.355 x 0.326 x 0.301
Radiation	MoKα (λ=0.71073)	MoKα (λ=0.71073)
2θ range for data collection(°)	2.138 to 29.130	2.896 to 36.303
Index Ranges	*-22 ≤ h ≤ 22, -23 ≤ k ≤23, -40≤ l ≤ 40	*-22 ≤ h ≤ 22, -22 ≤ k ≤ 22, -35 ≤ l ≤ 35
Reflections Collected	66228	44868
Independent Reflections	20511 [R_{int} = 0.0625, R_{sigma} = 0.0633]	9035 [R_{int} = 0.0331, R_{sigma} = 0.0303]
Data/Restraints/Parameters	66228/266/745	44868/0/183
Goodness-of-Fit on F2	1.046	1.048
Final R Indexes [I>=2σ (I)]	R_1=0.0465, wR_2=0.1145	R_1=0.0263, wR_2=0.0689
Final R Indexes [all data]	R_1=0.0534, wR_2=0.1195	R_1=0.0266, wR_2=0.0692
Largest Diff. Peak/Hole/ (e Å3)	1.696/-1.274	1.256/-0.535
Flack Parameter	-	0.189(8)
Completeness to 2θ	99.8	99.5

Table S2: Bond Lengths in Å for **1-Ce(PN*)**.

Atom	Atom	Length/Å
Ce1	N6	2.381(2)
Ce1	N10	2.372(2)
Ce1	N1	2.322(2)
Ce1	N14	2.303(3)
P3	N10	1.530(2)
P3	N13	1.673(3)
P3	N11	1.710(3)
P3	N12	1.715(3)
P1	N5	1.692(2)
P1	N1	1.533(2)
P1	N2	1.719(2)
P1	N4	1.696(3)
P2	N6	1.532(2)
P2	N9	1.680(3)
P2	N7	1.707(4)
P2	N8	1.733(3)
P4	N14	1.528(3)
P4	N16	1.682(3)
P4	N15	1.726(3)
P4	N44	1.694(3)
N5	C10	1.471(4)
N5	C12	1.453(4)
N9	C24	1.466(4)
N9	C26	1.469(4)
N2	C3	1.489(3)
N2	C4	1.461(4)
N13	C38	1.458(4)
N13	C40	1.474(4)
C3	C1	1.539(4)
C3	C2	1.538(4)
C3	C0AA	1.531(4)
N11	C34	1.484(4)
N11	C28	1.444(4)
N7	C20	1.451(6)
N7	C14	1.484(5)
N16	C53	1.451(4)
N16	C55	1.460(4)
N15	C49	1.466(5)
N15	C42	1.471(5)
N4	C6	1.482(4)
N4	C5	1.449(4)
N12	C30	1.483(5)
N12	C29	1.442(4)

Atom	Atom	Length/Å
N8	C16	1.482(6)
N8	C15	1.454(5)
C4	C5	1.522(4)
C34	C35	1.530(4)
C34	C36	1.533(4)
C34	C37	1.531(5)
C54	C53	1.501(4)
C24	C25	1.516(5)
C10	C11	1.525(4)
N44	C43	1.462(5)
N44	C45	1.470(5)
C6	C7	1.535(5)
C6	C8	1.524(5)
C6	C9	1.532(5)
C38	C39	1.474(4)
C12	C13	1.510(5)
C43	C42	1.512(7)
C40	C41	1.477(4)
C31	C30	1.515(5)
C49	C50	1.542(5)
C49	C51	1.548(5)
C49	C52	1.533(5)
C27	C26	1.520(5)
C30	C32	1.570(6)
C30	C33	1.504(5)
C28	C29	1.491(5)
C17	C16	1.504(6)
C55	C56	1.471(6)
C20	C21	1.521(6)
C20	C22	1.534(7)
C20	C23	1.551(6)
C16	C18	1.547(6)
C16	C19	1.544(7)
C45	C46	1.526(7)
C45	C47	1.544(5)
C45	C48	1.534(5)
C14	C15	1.460(7)

Table S3: Bond Angles in ° for **1-Ce(PN*)**.

Atom	Atom	Atom	Angle/°
N10	Ce1	N6	92.00(9)
N1	Ce1	N6	114.52(9)
N1	Ce1	N10	114.49(8)

Atom	Atom	Atom	Angle/°
N14	Ce1	N6	112.61(10)
N14	Ce1	N10	112.92(11)
N14	Ce1	N1	109.49(10)
N10	P3	N13	114.04(14)
N10	P3	N11	116.09(14)
N10	P3	N12	120.17(14)
N13	P3	N11	108.77(15)
N13	P3	N12	104.00(15)
N11	P3	N12	91.02(13)
N5	P1	N2	102.12(12)
N5	P1	N4	106.41(13)
N1	P1	N5	113.41(13)
N1	P1	N2	121.32(13)
N1	P1	N4	119.44(13)
N4	P1	N2	90.77(12)
N6	P2	N9	113.46(14)
N6	P2	N7	121.02(18)
N6	P2	N8	115.08(16)
N9	P2	N7	105.06(17)
N9	P2	N8	108.60(16)
N7	P2	N8	91.09(18)
N14	P4	N16	112.80(15)
N14	P4	N15	120.67(17)
N14	P4	N44	120.76(16)
N16	P4	N15	104.99(14)
N16	P4	N44	103.37(16)
N44	P4	N15	90.95(16)
P2	N6	Ce1	165.51(16)
P3	N10	Ce1	170.80(15)
C10	N5	P1	120.5(2)
C12	N5	P1	120.0(2)
C12	N5	C10	115.9(2)
C24	N9	P2	121.7(2)
C24	N9	C26	115.5(3)
C26	N9	P2	121.9(3)
P1	N1	Ce1	167.53(15)
P4	N14	Ce1	168.8(2)
C3	N2	P1	122.78(18)
C4	N2	P1	107.79(18)
C4	N2	C3	115.6(2)
C38	N13	P3	121.6(2)
C38	N13	C40	117.5(3)
C40	N13	P3	120.9(2)
N2	C3	C1	110.0(2)
N2	C3	C2	111.8(2)

Atom	Atom	Atom	Angle/°
N2	C3	C0AA	108.6(2)
C2	C3	C1	108.3(2)
C0AA	C3	C1	108.3(2)
C0AA	C3	C2	109.8(2)
C34	N11	P3	125.6(2)
C28	N11	P3	114.0(2)
C28	N11	C34	118.2(3)
C20	N7	P2	123.9(3)
C20	N7	C14	117.2(4)
C14	N7	P2	110.5(3)
C53	N16	P4	119.2(2)
C53	N16	C55	116.3(3)
C55	N16	P4	120.9(2)
C49	N15	P4	122.9(2)
C49	N15	C42	114.6(3)
C42	N15	P4	110.8(3)
C6	N4	P1	127.9(2)
C5	N4	P1	114.16(19)
C5	N4	C6	117.9(2)
C30	N12	P3	122.0(2)
C29	N12	P3	113.1(2)
C29	N12	C30	118.0(3)
C16	N8	P2	124.3(3)
C15	N8	P2	111.9(3)
C15	N8	C16	116.6(3)
N2	C4	C5	104.1(2)
N11	C34	C35	110.8(3)
N11	C34	C36	110.8(3)
N11	C34	C37	108.6(3)
C35	C34	C36	108.5(3)
C35	C34	C37	109.2(3)
C37	C34	C36	108.9(3)
N9	C24	C25	114.7(3)
N5	C10	C11	115.3(3)
C43	N44	P4	112.6(3)
C43	N44	C45	119.3(3)
C45	N44	P4	125.5(3)
N4	C6	C7	109.8(3)
N4	C6	C8	110.6(3)
N4	C6	C9	108.9(3)
C8	C6	C7	108.9(3)
C8	C6	C9	109.5(3)
C9	C6	C7	109.2(3)
N4	C5	C4	104.7(2)
N13	C38	C39	116.1(3)

Atom	Atom	Atom	Angle/°
N16	C53	C54	116.5(3)
N5	C12	C13	114.7(3)
N44	C43	C42	109.8(3)
N13	C40	C41	114.2(3)
N15	C49	C50	111.9(3)
N15	C49	C51	109.4(3)
N15	C49	C52	109.8(3)
C50	C49	C51	109.7(4)
C52	C49	C50	109.1(3)
C52	C49	C51	106.8(3)
N12	C30	C31	110.6(3)
N12	C30	C32	109.8(3)
N12	C30	C33	110.7(3)
C31	C30	C32	106.2(3)
C33	C30	C31	109.9(4)
C33	C30	C32	109.5(4)
N11	C28	C29	107.1(3)
N16	C55	C56	114.7(3)
N7	C20	C21	111.8(4)
N7	C20	C22	111.0(4)
N7	C20	C23	109.0(4)
C21	C20	C22	109.0(4)
C21	C20	C23	107.6(4)
C22	C20	C23	108.2(4)
N8	C16	C17	111.2(3)
N8	C16	C18	109.6(5)
N8	C16	C19	112.7(4)
C17	C16	C18	106.8(4)
C17	C16	C19	109.5(5)
C19	C16	C18	106.8(4)
N44	C45	C46	111.0(3)
N44	C45	C47	109.7(4)
N44	C45	C48	109.1(3)
C46	C45	C47	109.0(3)
C46	C45	C48	108.2(4)
C48	C45	C47	109.8(3)
C15	C14	N7	106.5(4)
N12	C29	C28	107.6(3)
N8	C15	C14	104.8(4)
N9	C26	C27	115.2(3)
N15	C42	C43	103.4(4)

Table S4: Bond Lengths in Å for **2-Ce(PN*)**.

Atom	Atom	Length/Å
Ce1	N1[1]	2.2370(17)
Ce1	N1[2]	2.2370(17)
Ce1	N1	2.2370(17)
Ce1	N1[3]	2.2370(17)
P1	N4	1.6751(17)
P1	N2	1.6796(16)
P1	N1	1.5567(17)
P1	N3	1.6935(16)
N4	C11	1.465(4)
N4	C13	1.461(3)
N2	C7	1.475(2)
N2	C1	1.457(2)
N3	C3	1.492(3)
N3	C2	1.461(3)
C11	C12	1.526(3)
C7	C8	1.526(3)
C7	C9	1.523(3)
C7	C10	1.537(3)
C3	C4	1.538(3)
C3	C5	1.529(3)
C3	C6	1.546(3)
C2	C1	1.536(3)
C13	C14	1.531(3)

[1]1-x,1-y,+z; [2]+y,1-x,1-z; [3]1-y,+x,1-z

Table S5: Bond Angles in ° for **2-Ce(PN*)**.

Atom	Atom	Atom	Angle/°
N1[1]	Ce1	N1[2]	107.41(4)
N1[2]	Ce1	N1[3]	113.68(9)
N1[1]	Ce1	N1[3]	107.41(4)
N1[3]	Ce1	N1	107.41(4)
N1[2]	Ce1	N1	107.41(4)
N1[1]	Ce1	N1	113.68(9)
N4	P1	N2	104.97(9)
N4	P1	N3	106.07(9)
N2	P1	N3	91.70(8)
N1	P1	N4	112.44(9)
N1	P1	N2	119.76(9)
N1	P1	N3	119.23(10)
C11	N4	P1	122.23(13)
C13	N4	P1	120.48(13)
C13	N4	C11	117.24(15)
C7	N2	P1	126.85(12)
C1	N2	P1	114.16(13)
C1	N2	C7	118.11(14)
P1	N1	Ce1	163.02(11)
C3	N3	P1	124.09(13)
C2	N3	P1	108.93(12)
C2	N3	C3	115.81(16)
N4	C11	C12	113.97(17)
N2	C7	C8	108.83(16)
N2	C7	C9	111.48(16)
N2	C7	C10	109.53(18)
C8	C7	C10	110.8(2)
C9	C7	C8	108.2(2)
C9	C7	C10	107.94(17)
N3	C3	C4	107.58(16)
N3	C3	C5	110.43(17)
N3	C3	C6	112.13(17)
C4	C3	C6	110.07(18)
C5	C3	C4	107.84(17)
C5	C3	C6	108.69(19)
N3	C2	C1	104.51(16)
N2	C1	C2	105.41(15)
N4	C13	C14	115.01(19)

[1]1-x,1-y,+z; [2]1-y,+x,1-z; [3]+y,1-x,1-z

Voronoi-Dirichlet Polyhedral Analysis

Table 6. Analysis of the Voronoi polyhedron of **2-Ce(PN*)**

Traditional coordination number = 4

Rsd:1.555 Å
CN=12:0:4 NV=28 V=**15.743**/71.045 S=36.674 Cpac=0.376 Ccov=2.282

G3=0.0867 (the degree of asymmetry)

	Atom	x	y	z	Dist.	SAng.	Valence 4(SAng/100%)
1	N	0.402	0.601	0.442	2.244	19.53	0.7812
2	N	0.399	0.402	0.558	2.244	19.53	0.7812
3	N	0.598	0.399	0.442	2.244	19.53	0.7812
4	N	0.601	0.598	0.558	2.244	19.53	0.7812
5	H	0.45	0.731	0.565	3.44	1.91	0.0764
6	H	0.55	0.269	0.565	3.44	1.91	0.0764
7	H	0.269	0.45	0.435	3.44	1.91	0.0764
8	H	0.731	0.55	0.435	3.44	1.91	0.0764
9	H	0.408	0.413	0.355	3.489	2.65	0.106
10	H	0.587	0.408	0.645	3.489	2.65	0.106
11	H	0.413	0.592	0.645	3.489	2.65	0.106
12	H	0.592	0.587	0.355	3.489	2.65	0.106
*13	H	0.741	0.38	0.517	3.618	0.91	0.0364
*14	H	0.259	0.62	0.517	3.618	0.91	0.0364
*15	H	0.38	0.259	0.483	3.618	0.91	0.0364
*16	H	0.62	0.741	0.483	3.618	0.91	0.0364

Table S7. Analysis of the Voronoi polyhedron of **2-Tb(PN*)**

Traditional coordination number = 4

Rsd:1.487 Å

CN=12:0:4 NV=28 V=**13.769**/58.134 S=34.618 Cpac=0.355 Ccov=2.479

G3=0.0890 (the degree of asymmetry)

	ATOM	X	Y	Z	DIST.	SANG.	VALENCE 4(SANG/100%)
1	N	0.592	0.406	0.444	2.106	21	0.84
2	N	0.408	0.594	0.444	2.106	21	0.84
3	N	0.594	0.592	0.556	2.106	21	0.84
4	N	0.406	0.408	0.556	2.106	21	0.84
5	H	0.561	0.726	0.434	3.407	1.64	0.0656
6	H	0.439	0.274	0.434	3.407	1.64	0.0656
7	H	0.726	0.439	0.566	3.407	1.64	0.0656
8	H	0.274	0.561	0.566	3.407	1.64	0.0656
*** 9**	H	0.738	0.616	0.481	3.54	0.79	0.0316
***10**	H	0.262	0.384	0.481	3.54	0.79	0.0316
***11**	H	0.384	0.738	0.519	3.54	0.79	0.0316
***12**	H	0.616	0.262	0.519	3.54	0.79	0.0316
13	H	0.598	0.589	0.354	3.545	1.57	0.0628
14	H	0.402	0.411	0.354	3.545	1.57	0.0628
15	H	0.589	0.402	0.646	3.545	1.57	0.0628
16	H	0.411	0.598	0.646	3.545	1.57	0.0628

Electronic Absorption Spectra

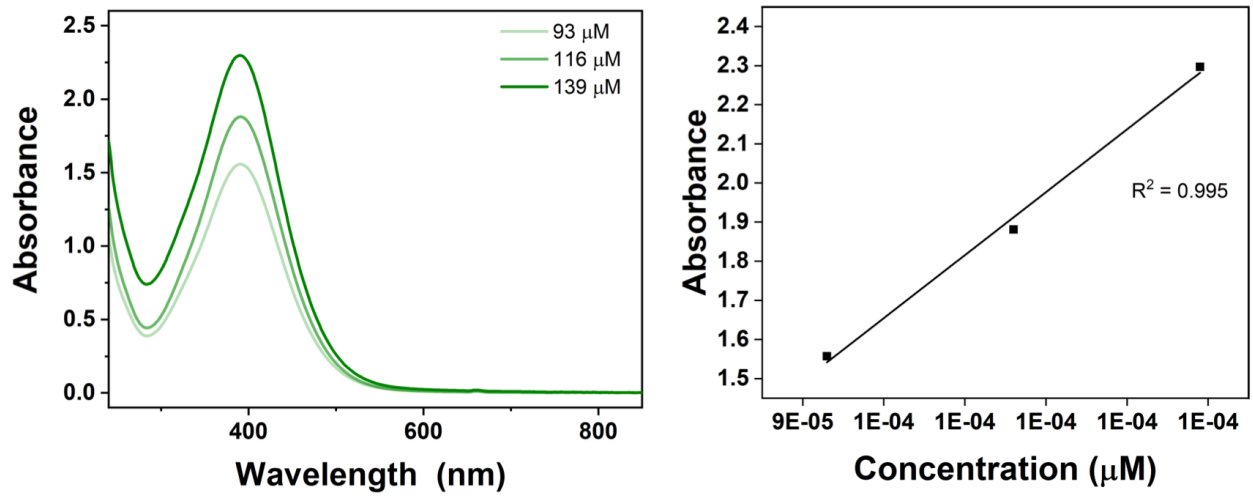

Figure S10. (left) UV-vis-NIR spectra of **2-Ce(PN*)** in THF. (right) Linear regression of absorbance at 391 nm maximum where ε= 16,100 cm^{-1} M^{-1}.

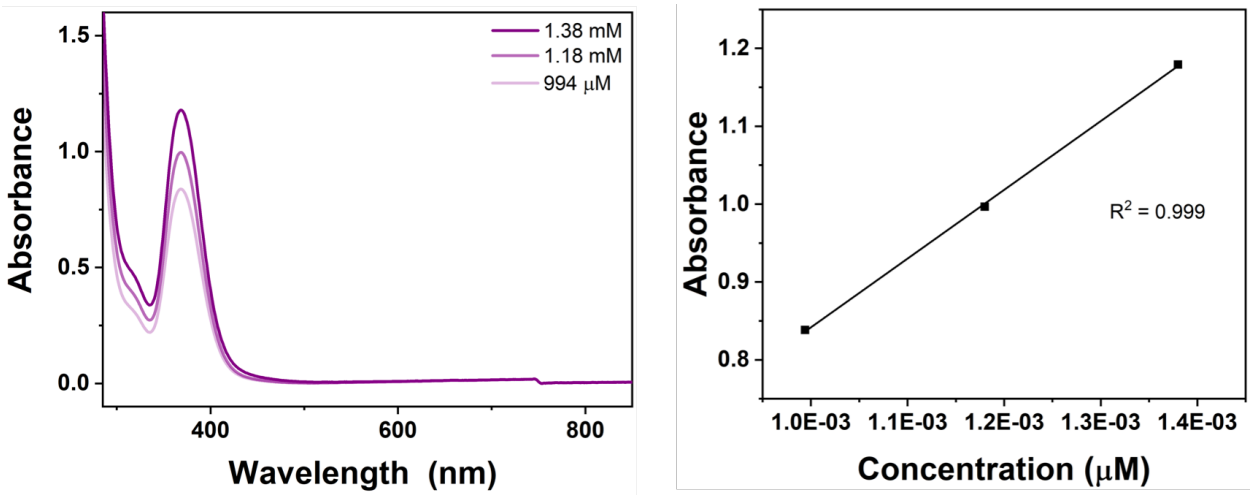

Figure S11. (left) UV-vis-NIR spectra of **1-Ce(PN*)** in THF. (right) Linear regression of absorbance at 369 nm maximum where ε= 883 cm^{-1} M^{-1}.

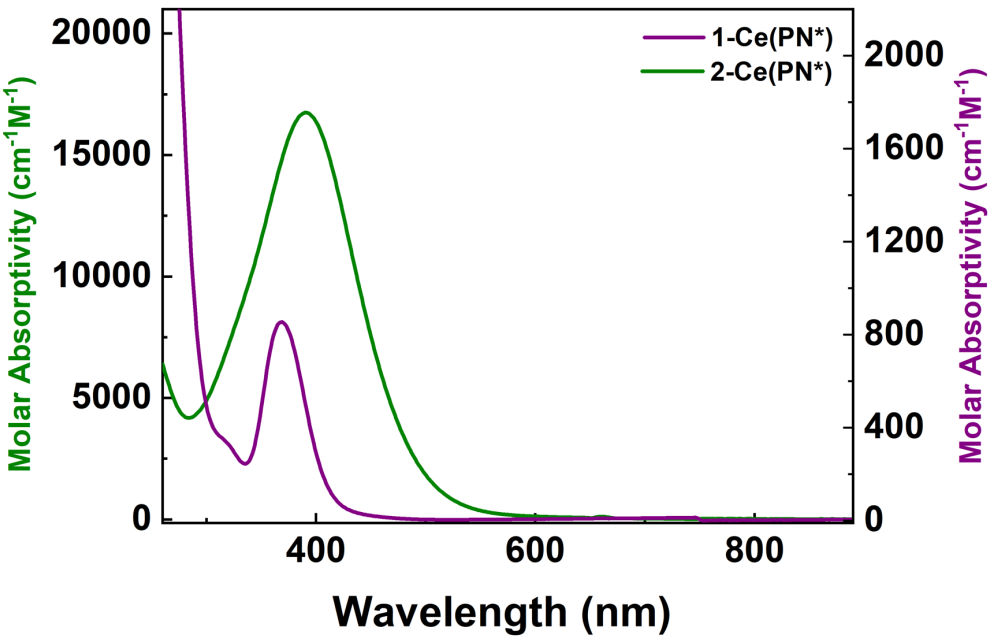

Figure S12. UV-vis-NIR spectra of **1-Ce(PN*)** (*right axis*) and **2-Ce(PN*)** (*left axis*) in THF.

Electrochemistry

Electrochemical measurements were performed on a Pine Wave Driver 20 Bipotentiostat/Galvanostat. Measurements were performed inside a N_2 atmosphere glovebox in a 20 mL electrochemical cell with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl pseudo reference electrode. Electrodes were polished before each use. Measurements were performed in a positive feedback IR compensation mode and referenced versus Fc/Fc^+.

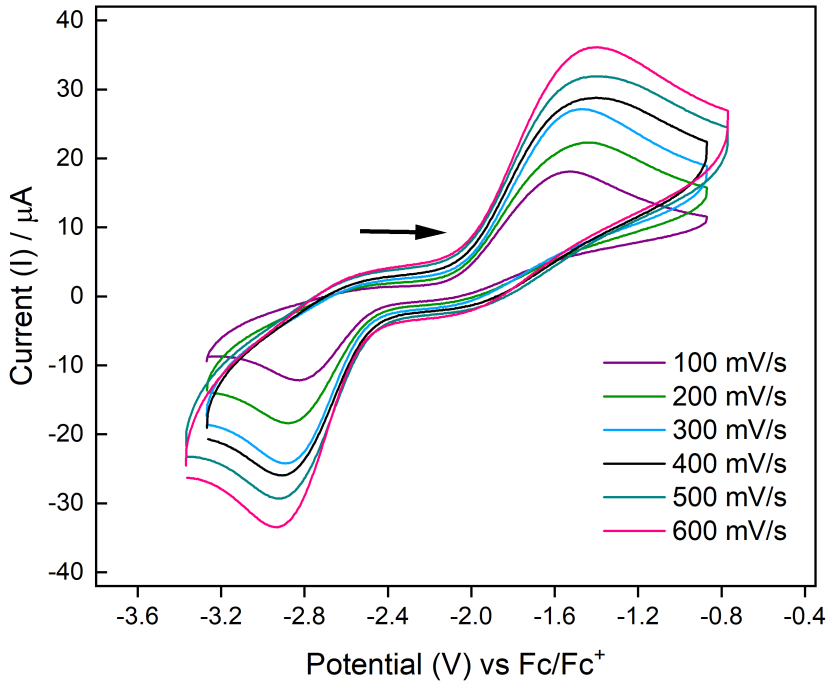

Figure S13. Scan rate dependence of **1-Ce(PN*)** (2.5 mM) vs. Fc/Fc^+ in 0.1 M $[^n(Bu)_4N][PF_6]$ in THF.

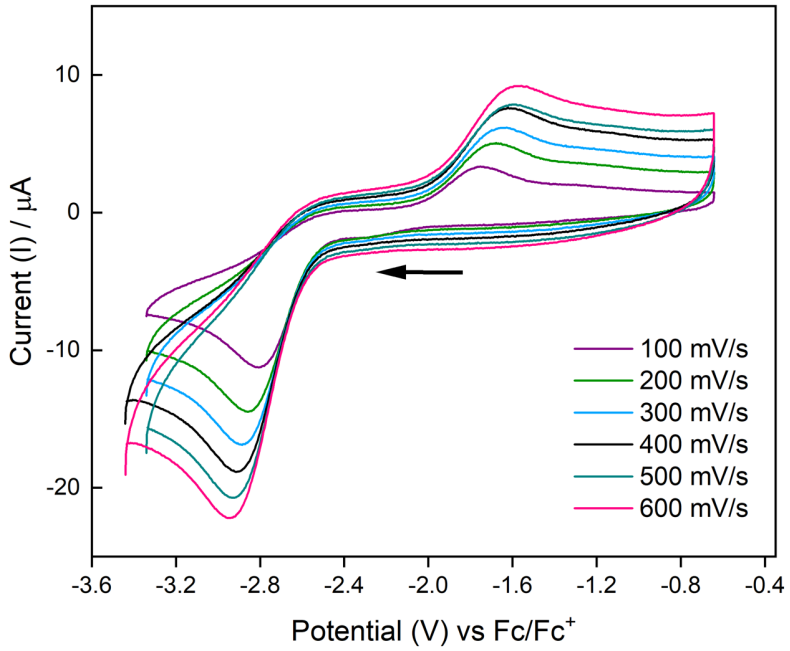

Figure S14. Scan rate dependence of **2-Ce(PN*)** (2.5 mM) vs. Fc/Fc^+ in 0.1 M $[^n(Bu)_4N][PF_6]$ in THF.

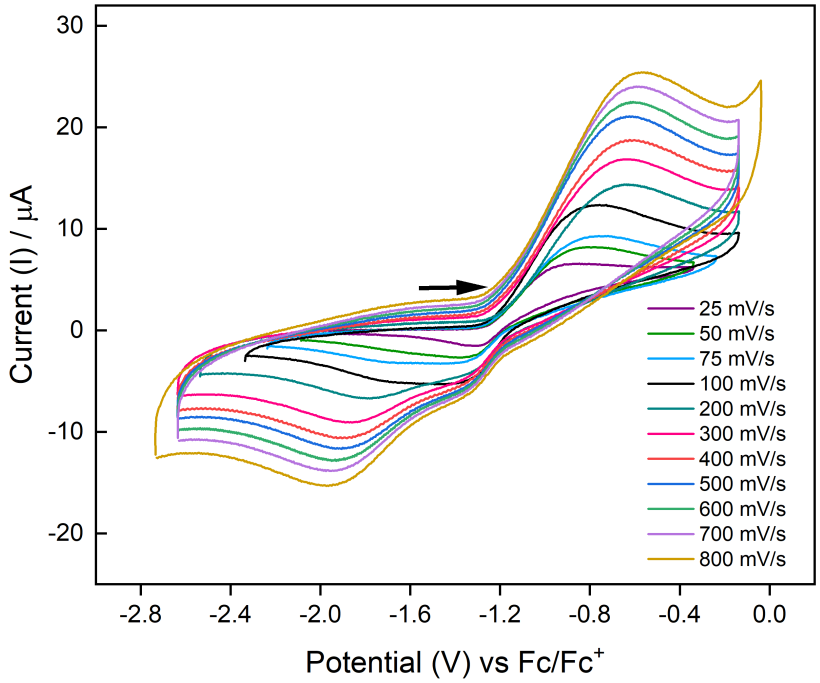

Figure S15. Scan rate dependence of **1-Tb(PN*)** (3 mM) vs. Fc/Fc^+ in 0.1 M $[^n(Bu)_4N][PF_6]$ in THF.

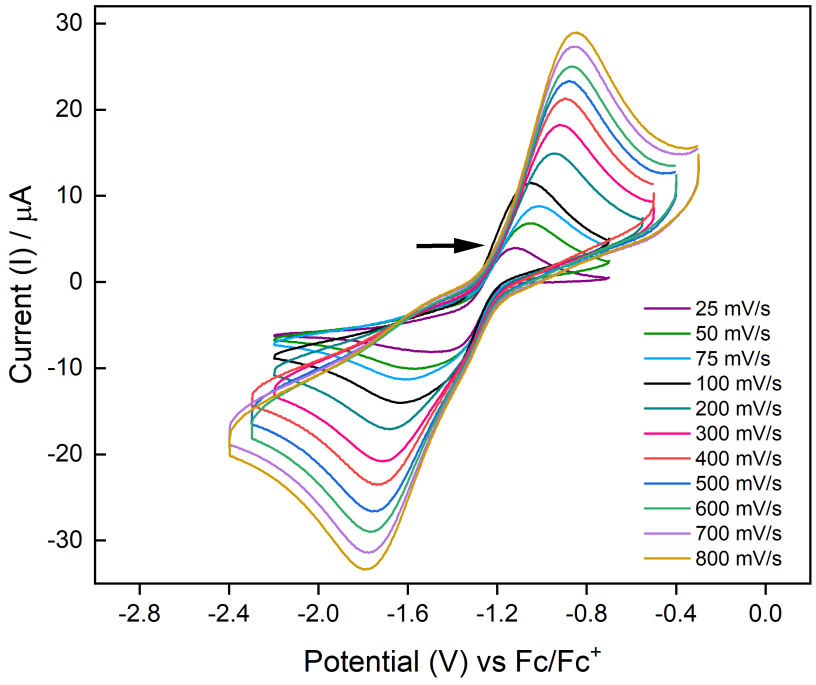

Figure S16. Scan rate dependence of **2-Tb(PN*)** (3 mM) vs. Fc/Fc^+ in 0.1 M $[^n(Bu)_4N][PF_6]$ in THF.

Ce L_3-Edge X-ray Absorption Near Edge Spectroscopy

Cerium samples were prepared in an argon glovebox at Stanford Synchrotron Radiation Lightsource (SSRL) because both Ce^{4+} and Ce^{3+} complexes are air-sensitive. A mixture of the analyte and boron nitride (BN) was weighed, such that the edge jump for the absorbing atom was calculated to be at one absorption length in transmission (~8−12 mg for the cerium samples). The samples were diluted with BN (~10 mg), which had been dried at elevated temperature (250 °C) under vacuum (1×10^{-3} Torr) for 24 h prior to use. Samples were ground with a mortar and pestle.

Solid-state sample holders for the Ce samples consisted of an aluminum plate with a 3×15 mm^2 oval window and screw holes. One side of the plate was covered with 0.5 mm Kapton tape, and the sample was evenly loaded in the window. The powder was then secured by covering the sample with a second piece of 0.5 mm Kapton tape. A second layer of compound was painted onto a third piece of Kapton tape, which was subsequently fixed to the backside of the sample holder. The sample holder was then loaded onto a sample rod, taken out of the glovebox, and transported to the beamline while submerged within a N_2(liq) cooling bath. Once at the beam, the rod with the sample was placed at 45° inside the Oxford He(liq) cryostat, which was precooled at 85 K and attached to the SSRL Beamline 11-2 rail. When the cryostat was closed, the system was put under vacuum and flushed with helium five times. The valve was closed, and the measurements were performed in the cryostat at 10 K.

The solid-state cerium complexes were characterized by metal L_3-edge X-ray measurements. The X-ray absorption measurements were made at SSRL, under dedicated operating conditions (3.0 GeV, 5%, 500 mA using continuous top-off injections) on end station 11-2. With the use of a liquid-nitrogen-cooled double-crystal Si(220) (φ = 0) monochromator that employed collimating and focusing mirrors, a single energy was selected from the incident white beam. For Ce measurements, the beam was fully tuned at 6800 eV, and harmonic rejection was achieved with a Rh-coated mirror. The horizontal slit sizes were 10 mm, and vertical slit sizes were 1 mm in all measurements.

The cryostat was attached to the beamline 11-2 XAS rail (SSRL), which was equipped with three ionization chambers, through which nitrogen gas was continually flowed. One chamber was positioned before the helium beam pass and the cryostat (10 cm) to monitor the incident radiation (I_0). The second chamber was positioned after the cryostat (30 cm) so that sample transmission (I_1) could be evaluated against I_0 and so that the absorption coefficient (μ) could be calculated as $\ln(I_0/I_1)$. The third chamber (I_2; 30 cm) was positioned downstream from I_1 so that the XANES of a calibration foil could be measured against I_1. A potential of 1100 V was applied in series to the ionization chambers. A PIPS detector under argon was placed on one side of the cryostat (4 cm) to detect the fluorescence from the samples. The Ce samples were calibrated in situ to the energy of the first inflection point of the K-edge of chromium foil (5989 eV). Data were acquired in triplicate and averaged. Background subtraction and normalization (at 5800 eV) were performed in Athena.

Curve fitting was performed in IgorPro 7.0 using a modified version of EDG_FIT.[8] Derivative spectra were used as guides to determine the number and positions of the peaks, and edge features were modeled by pseudo-Voigt line shapes and an additional function consisting of arctangent and error function contributions, which was used to model the absorption threshold. Deconvoluted spectral models were performed over several energy ranges. In the spectrum of **2-Ce(PN*)**, four pseudo-Voigts were employed to fit the spectrum: p_1 (the quadrupole-allowed $2p_{3/2} \rightarrow 4f$ transition), p_2 and p_3 and p_4 to model the double-white line feature. In the spectrum of **1-Ce(PN*)**, a single pseudo-Voigt was employed to model the white-line feature. The area under the pseudo-Voigt functions (defined as the intensity) was calculated with the formula ph × fwhm × $^1/_4([\pi/\ln(2)]^{1/2} + \pi)$, where ph = peak height (normalized intensity), fwhm = full-width at half-maximum height (eV), and the value $^1/_4([\pi/\ln(2)]^{1/2} + \pi) \approx 1.318$ is a constant associated with the pseudo-Voigt function. The fits are shown in Figures 4 and summarized in Table S8. Relative parameter error estimates are calculated from the covariance matrix assuming normally distributed variances in the data. The absolute error in n_f is about 0.04 or 10% for **2-Ce(PN*)** and 0.02 or 6 % for **2-Ce(PN)**.

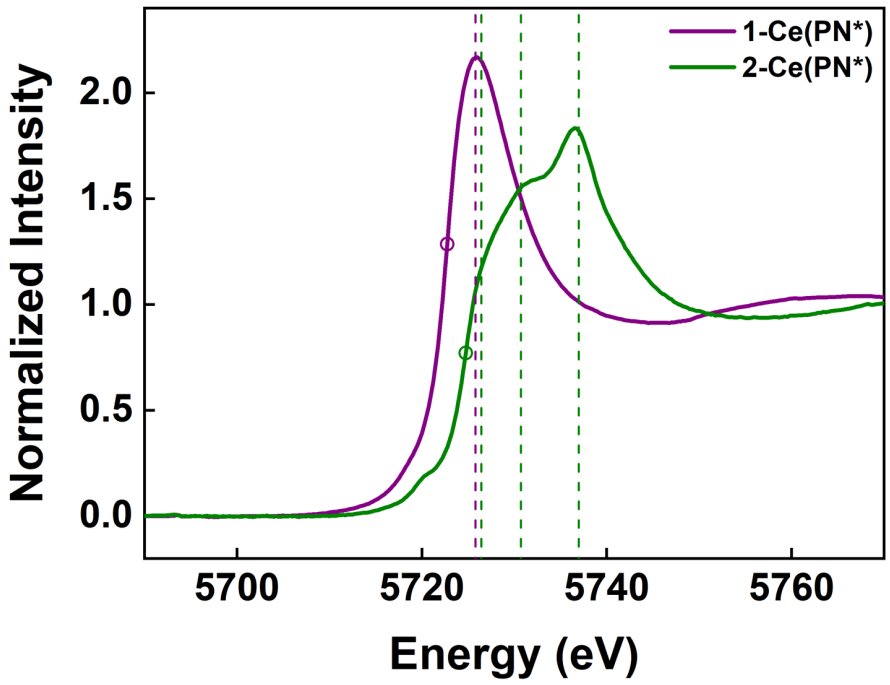

Figure S17. Overlay of L_3-edge XAS spectra of **1-Ce(PN*)** and **2-Ce(PN*)**. Dashed lines correspond to peak energies of the fit. Open circles correspond to the inflection point of the associated spectrum.

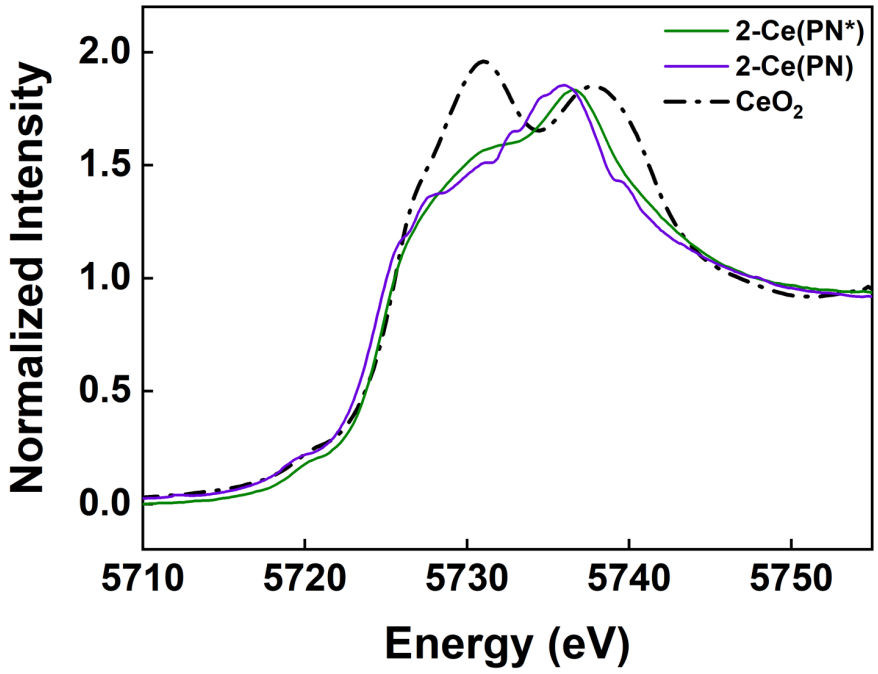

Figure S18. Overlay of L_3-edge XAS spectra of **2-Ce(PN*)** and **2-Ce(PN)** with CeO_2.

Table S8. Summary of fit parameters for Ce L_3-edge XANES of **1-Ce(PN*), 2-Ce(PN*)**, and **2-Ce(PN)**.

Complex	Peak 1 Intensity	Energy (eV)	Peak 2 Intensity	Energy (eV)	Peak 3 Intensity	Energy (eV)	Peak 4 Intensity	Energy (eV)
1-Ce(PN*)	5.72(8)	5725.8(0)	-	-	-	-	-	-
2-Ce(PN*)	0.14(0)	5719.7(0)	3.7(3)	5730.44(9)	9.0(1)	5736.57(6)	2.4(2)	5726.45(8)
2-Ce(PN)	0.14(0)	5719.7(0)	4.83(9)	5728.91(8)	9.59(6)	5735.96(3)	1.13(7)	5725.67(3)

Table S9. Background subtracted and normalized spectrum of Ce L_3-edge XANES of **1-Ce(PN*) and 2-Ce(PN*)**.

1-Ce(PN*)_eV	1-Ce(PN*)_Int	2-Ce(PN*)_eV	2-Ce(PN*)_Int
5683.2495	2.65E-03	5683.2495	3.12E-03
5686.2515	1.66E-03	5686.2515	3.85E-03
5689.249	9.92E-04	5689.249	2.51E-03
5692.25	8.51E-04	5692.25	2.96E-03
5693.2485	2.29E-03	5693.2485	7.14E-03

5693.4995	6.35E-03	5693.999	6.64E-04
5693.751	5.07E-03	5694.2505	7.87E-04
5693.999	-1.41E-03	5694.4985	2.23E-04
5694.2505	-1.27E-03	5694.75	-2.15E-04
5694.4985	-2.84E-04	5695.001	-2.12E-04
5694.75	-2.32E-04	5695.2495	6.36E-04
5695.001	-1.28E-05	5695.501	1.31E-03
5695.2495	2.82E-04	5695.7495	2.29E-04
5695.501	4.37E-04	5696.001	3.36E-04
5695.7495	9.25E-04	5696.2495	-1.16E-03
5696.001	6.76E-04	5696.501	8.88E-04
5696.2495	-2.22E-04	5696.7495	1.75E-03
5696.501	-1.02E-03	5697.001	-1.25E-04
5696.7495	-2.45E-03	5697.2495	-1.03E-03
5697.001	-3.35E-03	5697.501	-7.19E-05
5697.2495	-3.08E-03	5697.7495	9.02E-04
5697.501	-3.54E-03	5698.0015	-5.08E-04
5697.7495	-3.35E-03	5698.25	-1.73E-03
5698.0015	-3.22E-03	5698.499	4.52E-05
5698.25	-2.48E-03	5698.7505	-1.78E-03
5698.499	-2.25E-03	5698.9995	-1.47E-03
5698.7505	-1.60E-03	5699.251	1.00E-03
5698.9995	-1.51E-03	5699.5	-2.65E-03
5699.251	-1.26E-03	5699.749	-1.81E-03
5699.5	-1.98E-04	5700.0005	-1.34E-03
5699.749	-8.25E-04	5700.2495	-2.14E-03
5700.0005	-9.65E-04	5700.4985	-2.94E-03
5700.2495	-1.21E-03	5700.7505	-1.05E-03
5700.4985	-1.18E-04	5700.9995	1.16E-04
5700.7505	9.97E-04	5701.2485	-1.84E-03
5700.9995	9.80E-04	5701.5005	-2.30E-03
5701.2485	5.55E-04	5701.75	-3.31E-03
5701.5005	2.51E-04	5701.999	-2.54E-03
5701.75	2.29E-04	5702.251	1.94E-04
5701.999	4.27E-04	5702.5	-6.28E-04
5702.251	7.64E-04	5702.7495	1.45E-03
5702.5	2.90E-04	5702.9985	9.68E-04
5702.7495	8.57E-06	5703.251	2.80E-03
5702.9985	2.43E-04	5703.5	-5.32E-04
5703.251	7.01E-04	5703.7495	-1.49E-03
5703.5	6.72E-04	5703.999	-1.91E-03
5703.7495	-9.44E-05	5704.251	-1.41E-03
5703.999	5.49E-04	5704.5005	-1.86E-03

5704.251	1.19E-03	5704.75	-2.21E-03
5704.5005	1.87E-03	5704.9995	-1.11E-03
5704.75	2.63E-03	5705.249	-3.84E-04
5704.9995	2.89E-03	5705.5015	-2.58E-04
5705.249	2.71E-03	5705.751	7.70E-04
5705.5015	2.21E-03	5706.0005	-4.33E-04
5705.751	2.69E-03	5706.25	8.43E-04
5706.0005	3.19E-03	5706.5	-1.79E-03
5706.25	3.57E-03	5706.7495	-3.65E-03
5706.5	4.10E-03	5706.999	-1.45E-03
5706.7495	5.29E-03	5707.249	-1.14E-03
5706.999	5.16E-03	5707.4985	-4.35E-04
5707.249	5.23E-03	5707.7515	1.08E-04
5707.4985	6.30E-03	5708.001	-4.43E-04
5707.7515	7.46E-03	5708.251	-6.56E-04
5708.001	7.78E-03	5708.501	-1.36E-04
5708.251	8.96E-03	5708.7505	-1.12E-04
5708.501	9.53E-03	5709.0005	5.38E-04
5708.7505	1.14E-02	5709.2505	1.81E-03
5709.0005	1.18E-02	5709.5005	2.15E-03
5709.2505	1.32E-02	5709.7505	2.67E-03
5709.5005	1.37E-02	5710.0005	1.64E-04
5709.7505	1.52E-02	5710.2505	1.42E-03
5710.0005	1.75E-02	5710.5005	2.54E-03
5710.2505	1.97E-02	5710.7505	2.55E-03
5710.5005	2.07E-02	5711.0005	5.57E-03
5710.7505	2.12E-02	5711.251	5.61E-03
5711.0005	2.37E-02	5711.501	5.81E-03
5711.251	2.56E-02	5711.7515	5.49E-03
5711.501	2.73E-02	5711.9985	7.25E-03
5711.7515	2.90E-02	5712.249	7.93E-03
5711.9985	3.12E-02	5712.499	8.47E-03
5712.249	3.34E-02	5712.7495	1.09E-02
5712.499	3.55E-02	5713	1.24E-02
5712.7495	3.84E-02	5713.25	1.42E-02
5713	4.18E-02	5713.5005	1.44E-02
5713.25	4.52E-02	5713.751	1.59E-02
5713.5005	4.84E-02	5714.0015	1.67E-02
5713.751	5.22E-02	5714.249	1.77E-02
5714.0015	5.58E-02	5714.4995	2.08E-02
5714.249	5.95E-02	5714.75	2.39E-02
5714.4995	6.51E-02	5715.0005	2.67E-02
5714.75	7.08E-02	5715.251	2.85E-02

5715.0005	7.68E-02	5715.499	3.19E-02
5715.251	8.27E-02	5715.7495	3.57E-02
5715.499	8.96E-02	5716	3.94E-02
5715.7495	9.66E-02	5716.251	4.24E-02
5716	0.10383402	5716.4985	4.57E-02
5716.251	0.11413432	5716.7495	5.04E-02
5716.4985	0.12455535	5717	5.60E-02
5716.7495	0.13579548	5717.251	5.92E-02
5717	0.14850344	5717.499	6.48E-02
5717.251	0.16247436	5717.7495	7.04E-02
5717.499	0.17755266	5718.0005	7.85E-02
5717.7495	0.19458837	5718.2515	8.77E-02
5718.0005	0.21268032	5718.4995	9.85E-02
5718.2515	0.23128564	5718.7505	0.10891822
5718.4995	0.24929826	5719.0015	0.12067265
5718.7505	0.2687641	5719.2495	0.13614126
5719.0015	0.28883798	5719.5005	0.15135676
5719.2495	0.31040338	5719.7485	0.16400757
5719.5005	0.3337043	5720	0.17680926
5719.7485	0.36053836	5720.251	0.18886542
5720	0.39181038	5720.499	0.19529987
5720.251	0.42794231	5720.7505	0.20369985
5720.499	0.46924225	5720.9985	0.20925477
5720.7505	0.51755195	5721.25	0.21630917
5720.9985	0.57339361	5721.501	0.22668174
5721.25	0.6388282	5721.7495	0.24296277
5721.501	0.71557928	5722.0005	0.25799012
5721.7495	0.80452362	5722.249	0.27700573
5722.0005	0.90797489	5722.5005	0.29942436
5722.249	1.0238938	5722.749	0.32463717
5722.5005	1.1519956	5723.0005	0.35718157
5722.749	1.2867157	5723.249	0.39566072
5723.0005	1.4248857	5723.5005	0.44063662
5723.249	1.5563728	5723.749	0.4935324
5723.5005	1.6776743	5724.0005	0.55283854
5723.749	1.7840994	5724.249	0.62050483
5724.0005	1.8742857	5724.5005	0.69325633
5724.249	1.9493216	5724.7495	0.7700149
5724.5005	2.0133418	5725.001	0.84915095
5724.7495	2.0637838	5725.25	0.92314315
5725.001	2.105347	5725.5015	0.99363546
5725.25	2.1362882	5725.7505	1.0516659
5725.5015	2.1573992	5725.999	1.1031179

5725.7505	2.1658108	5726.251	1.1457173
5725.999	2.1684876	5726.4995	1.1828396
5726.251	2.1613463	5726.7485	1.2140163
5726.4995	2.1465702	5727.0005	1.2476387
5726.7485	2.1241566	5727.2495	1.2763445
5727.0005	2.0960722	5727.5015	1.3034556
5727.2495	2.0640299	5727.7505	1.3295044
5727.5015	2.0276984	5727.9995	1.3528217
5727.7505	1.9880939	5728.2515	1.3752147
5727.9995	1.9463983	5728.5005	1.3934685
5728.2515	1.9026269	5728.7495	1.4149162
5728.5005	1.8590983	5728.9985	1.4348725
5728.7495	1.8150335	5729.251	1.4556707
5728.9985	1.7718975	5729.5	1.4715633
5729.251	1.7293632	5729.749	1.4911974
5729.5	1.6875268	5730.0015	1.5084643
5729.749	1.646049	5730.2505	1.5261823
5730.0015	1.6073121	5730.5	1.540518
5730.2505	1.5705361	5730.7495	1.5536984
5730.5	1.5347578	5730.9985	1.5653301
5730.7495	1.4986715	5731.251	1.5703985
5730.9985	1.4637827	5731.5005	1.5759938
5731.251	1.4307744	5731.75	1.5831346
5731.5005	1.3989656	5731.999	1.5878108
5731.75	1.367582	5732.2485	1.5887665
5731.999	1.3382282	5732.501	1.5944425
5732.2485	1.3114618	5732.7505	1.598109
5732.501	1.2850923	5733.0005	1.6017071
5732.7505	1.2605792	5733.25	1.6060391
5733.0005	1.2368282	5733.4995	1.61607
5733.25	1.2146546	5733.749	1.6271683
5733.4995	1.19487	5733.999	1.6408635
5733.749	1.1733769	5734.2485	1.6583042
5733.999	1.1567212	5734.501	1.6793309
5734.2485	1.1396084	5734.751	1.7005956
5734.501	1.1237515	5735.001	1.7234287
5734.751	1.1089553	5735.2505	1.7485843
5735.001	1.0944921	5735.5005	1.7717479
5735.2505	1.0815057	5735.7505	1.792858
5735.5005	1.0707278	5736	1.8144767
5735.7505	1.0582023	5736.25	1.8244109
5736	1.0468276	5736.5	1.8341073
5736.25	1.0372156	5736.75	1.8323743

5736.5	1.0287967	5737	1.8191958
5736.75	1.0206358	5737.25	1.7992531
5737	1.0129475	5737.5	1.7697776
5737.25	1.0044548	5737.75	1.7375902
5737.5	0.99695587	5738	1.7034575
5737.75	0.99081294	5738.2505	1.6680259
5738	0.98619137	5738.5005	1.6291572
5738.2505	0.98222581	5738.7505	1.5860473
5738.5005	0.97733681	5739.001	1.5499913
5738.7505	0.97156468	5739.251	1.517352
5739.001	0.96652002	5739.5015	1.4875751
5739.251	0.96036664	5739.7485	1.4584979
5739.5015	0.95491985	5739.999	1.4350642
5739.7485	0.95139285	5740.2495	1.4127596
5739.999	0.94618359	5740.5	1.3906071
5740.2495	0.94448481	5740.75	1.3689916
5740.5	0.9425917	5741.0005	1.3493623
5740.75	0.93922535	5741.251	1.3285499
5741.0005	0.93701326	5741.4985	1.3102175
5741.251	0.93398591	5741.749	1.2910194
5741.4985	0.93184663	5741.9995	1.2681988
5741.749	0.92945966	5742.25	1.2528953
5741.9995	0.92677346	5742.501	1.2360697
5742.25	0.92467216	5742.7515	1.2203757
5742.501	0.92336368	5742.999	1.2029712
5742.7515	0.9223648	5743.25	1.1877813
5742.999	0.92153222	5743.5005	1.1729752
5743.25	0.91966281	5743.7515	1.1568867
5743.5005	0.91814017	5743.999	1.1425274
5743.7515	0.91769488	5744.25	1.1312462
5743.999	0.91672568	5744.5005	1.1177772
5744.25	0.91601136	5744.7515	1.1037429
5744.5005	0.91365655	5744.9995	1.0928488
5744.7515	0.91421425	5745.25	1.0826358
5744.9995	0.9145582	5745.501	1.0716526
5745.25	0.91424466	5745.749	1.0606317
5745.501	0.9142533	5746	1.0521652
5745.749	0.91464182	5746.251	1.0478318
5746	0.91392173	5746.499	1.0388058
5746.251	0.91454635	5746.75	1.0305381
5746.499	0.91406587	5747.0015	1.0248166
5746.75	0.91365421	5747.2495	1.0142853
5747.0015	0.9155851	5747.5005	1.0083188

5747.2495	0.91650238	5747.7485	1.0021878
5747.5005	0.91790153	5748	0.99727257
5747.7485	0.91980537	5748.251	0.99134864
5748	0.92100321	5748.4995	0.98862475
5748.251	0.92263433	5748.7505	0.98426552
5748.4995	0.92379627	5748.999	0.9783734
5748.7505	0.92620598	5749.2505	0.97713027
5748.999	0.92806025	5749.4985	0.97298005
5749.2505	0.93264586	5749.75	0.96984107
5749.4985	0.93630567	5750.0015	0.96930233
5749.75	0.94002883	5750.25	0.96755643
5750.0015	0.94380559	5750.5015	0.96195198
5750.25	0.94726263	5750.75	0.95876402
5750.5015	0.95107668	5751.0015	0.95776789
5750.75	0.95367459	5751.25	0.95294754
5751.0015	0.956037	5751.4985	0.95318942
5751.25	0.95810179	5751.75	0.94818522
5751.4985	0.96101271	5751.9985	0.94906618
5751.75	0.96372762	5752.2505	0.94891995
5751.9985	0.96573173	5752.499	0.94765744
5752.2505	0.96817779	5752.751	0.94553792
5752.499	0.97044785	5752.9995	0.94192983
5752.751	0.97294804	5753.2515	0.94106309
5752.9995	0.97493817	5753.5503	0.94119249
5753.2515	0.97762426	5753.8496	0.93958615
5753.5503	0.97981405	5754.1489	0.93991097
5753.8496	0.9821894	5754.4512	0.9421205
5754.1489	0.98633371	5755.0498	0.93691951
5755.0498	0.99259632	5755.3491	0.93702992
5755.3491	0.99399614	5755.6484	0.9383951
5755.6484	0.99703254	5755.9512	0.94071078
5755.9512	0.99888876	5756.2505	0.93951123
5756.2505	1.0016003	5756.5503	0.93806989
5756.5503	1.004643	5756.8496	0.93723918
5756.8496	1.0070608	5757.1494	0.93815664
5757.1494	1.0090159	5757.4492	0.93787773
5757.4492	1.0112253	5757.7485	0.93897053
5757.7485	1.0136636	5758.0513	0.94134941
5758.0513	1.0153469	5758.3511	0.94143252
5758.3511	1.0172764	5758.6509	0.93940317
5758.6509	1.019868	5758.9512	0.94068819
5758.9512	1.0204139	5759.251	0.94358766
5759.251	1.0230343	5759.5508	0.94269464

5759.5508	1.0250764	5759.8506	0.9486328
5759.8506	1.0285815	5760.4507	0.94786574
5760.4507	1.0292761	5760.751	0.95005984
5760.751	1.0287634	5761.0508	0.95009834
5761.0508	1.0290174	5761.3511	0.95116048
5761.3511	1.0301857	5761.6514	0.95102245
5761.6514	1.0306915	5761.9487	0.95276156
5761.9487	1.0319724	5762.249	0.95525666
5762.249	1.0328338	5762.5493	0.95640276
5762.5493	1.0325025	5762.8496	0.96084648
5762.8496	1.0346535	5763.1499	0.96174587
5763.1499	1.0349363	5763.4502	0.9649249
5763.4502	1.0335668	5763.751	0.96401936
5763.751	1.034801	5764.0513	0.96767969
5764.0513	1.0364022	5764.3491	0.97019822
5764.3491	1.0358545	5764.6494	0.97140696
5764.6494	1.0363082	5764.9502	0.97251749
5764.9502	1.0374519	5765.251	0.9746628
5765.251	1.0374047	5765.5488	0.97542375
5765.5488	1.0385394	5765.8491	0.97812274
5765.8491	1.0393154	5766.1499	0.97966672
5766.1499	1.0400976	5766.4512	0.98255885
5766.4512	1.0403953	5766.749	0.98632846
5766.749	1.0401995	5767.0498	0.99032525
5767.0498	1.0407096	5767.3506	0.99205162
5768.5488	1.0401419	5768.2505	1.003912
5768.8501	1.0383283	5768.5488	0.99901155
5769.1509	1.0377155	5768.8501	0.99924672
5769.4492	1.0367928	5769.1509	1.0028183
5769.7505	1.0356292	5769.4492	1.0038818
5770.0488	1.0351531	5769.7505	1.0045667
5770.3501	1.034794	5770.0488	1.0070531
5770.6484	1.035267	5770.3501	1.0090288
5770.9497	1.0348852	5770.6484	1.0098663
5771.2515	1.034146	5770.9497	1.0124682
5771.5498	1.0339811	5771.2515	1.0151343
5771.8516	1.0335664	5771.5498	1.0186348
5772.1499	1.0329804	5771.8516	1.022456
5772.4487	1.0325355	5772.1499	1.0246915
5772.75	1.0308669	5772.4487	1.0254631
5773.0488	1.0303997	5772.75	1.0244056
5773.3506	1.0305247	5773.0488	1.0274819
5773.6494	1.0294178	5773.3506	1.0282808

5773.9512	1.0283931	5773.6494	1.0281998
5774.25	1.0276891	5773.9512	1.0282372
5774.5488	1.0272794	5774.25	1.0277894
5774.8506	1.0255627	5774.5488	1.0288991
5775.1494	1.0252467	5774.8506	1.030992
5775.4487	1.0237506	5775.1494	1.0329897
5775.7505	1.0216009	5775.4487	1.0328875
5776.0498	1.0209841	5775.7505	1.0336257
5776.3486	1.01974	5776.0498	1.0371612
5776.6509	1.0176107	5776.3486	1.0400709
5776.9502	1.0165193	5776.6509	1.0397269
5777.2495	1.015565	5776.9502	1.0414801
5777.5483	1.0141402	5777.2495	1.0418765
5777.8506	1.0130645	5777.5483	1.0415606
5778.1499	1.0116593	5777.8506	1.0419346
5778.4497	1.0110339	5778.1499	1.0443363
5778.749	1.0101179	5778.4497	1.0442002
5779.0513	1.0083344	5778.749	1.0450805
5779.3506	1.0078124	5779.0513	1.0472048
5779.6504	1.0067082	5779.3506	1.0478325
5779.9497	1.0050348	5779.6504	1.0484969
5780.2495	1.0041376	5779.9497	1.0480429
5780.5493	1.0031064	5780.2495	1.0472429
5780.8486	1.0017887	5780.5493	1.0480266
5781.1514	1.0000974	5780.8486	1.0486895
5781.4512	1.0003593	5781.1514	1.0462349
5781.751	0.99926779	5781.4512	1.0464473
5782.0508	0.99878576	5781.751	1.0476653
5782.3506	1.0006753	5782.0508	1.0480702
5782.6504	1.0023065	5782.3506	1.0489488
5782.9507	1.0023152	5782.6504	1.0513366
5783.2505	1.0017284	5782.9507	1.0527049
5784.1509	0.99722595	5783.2505	1.0526126
5784.4507	0.9910238	5784.4507	1.0487938
5784.751	0.98543898	5784.751	1.0420476
5785.0513	0.98384669	5785.0513	1.0403512
5785.3516	0.98185586	5785.3516	1.0401415
5785.6489	0.98032314	5785.6489	1.039398
5785.9492	0.97855042	5785.9492	1.0387995
5786.2495	0.97723029	5786.2495	1.0395527
5786.5498	0.97554698	5786.5498	1.040617
5786.8501	0.9752628	5786.8501	1.0387896
5787.1509	0.9759202	5787.1509	1.0401194

5787.4512	0.97494114	5787.4512	1.0383752
5787.7485	0.97364735	5787.7485	1.0371354
5788.0493	0.97263302	5788.0493	1.0363914
5788.3501	0.97099975	5788.3501	1.03506
5788.6504	0.97058174	5788.6504	1.034114
5788.9512	0.96934719	5788.9512	1.032279
5789.249	0.96886413	5789.249	1.031356
5789.5498	0.9684696	5789.5498	1.0297
5789.8506	0.96679276	5789.8506	1.0279689
5790.1514	0.96638215	5790.1514	1.0284333
5790.4492	0.96515372	5790.4492	1.0294287
5790.7505	0.96526622	5790.7505	1.0269529
5791.0513	0.96345893	5791.0513	1.0243493
5791.3491	0.962237	5791.3491	1.0224569
5791.6504	0.96205314	5791.6504	1.0215353
5791.9512	0.96159548	5791.9512	1.0183487
5792.2495	0.96049659	5792.2495	1.018323
5792.5508	0.9592804	5792.5508	1.0146096
5792.8486	0.95799404	5792.8486	1.0115107
5793.1499	0.95886417	5793.1499	1.0101919
5793.2495	0.95901692	5793.2495	1.0083385
5796.249	0.95416622	5796.249	0.99055838
5799.2495	0.95648522	5799.2495	0.97409543
5805.249	0.97746987	5805.249	0.94652943
5808.249	0.99386431	5808.249	0.94090219
5811.249	1.0059163	5811.249	0.94251972
5814.2505	1.0136208	5814.2505	0.94563891
5817.249	1.016057	5817.249	0.95161319
5820.2485	1.012669	5820.2485	0.95625878
5823.249	1.0061934	5823.249	0.9631415
5826.25	1.0002071	5826.25	0.97230713
5829.2485	0.99637754	5829.2485	0.97774847
5832.251	0.9919393	5832.251	0.98090247
5835.251	0.9919281	5835.251	0.98022915
5838.249	0.99388496	5838.249	0.97621691
5844.2495	1.0005635	5844.2495	0.97205793
5847.249	1.0084242	5847.249	0.97241125
5850.2495	1.0117976	5850.2495	0.9755623
5853.251	1.0105927	5853.251	0.98366764
5856.2495	1.0051741	5856.2495	0.99224304
5859.249	0.99953019	5859.249	0.99336327
5862.249	0.99311069	5862.249	0.98320646
5865.2495	0.987317	5865.2495	0.97682497

5868.2505	0.98379769	5868.2505	0.97279239
5871.2495	0.98258	5871.2495	0.96823263
5874.249	0.98329876	5874.249	0.96675475
5877.249	0.98699492	5877.249	0.96270628
5880.2495	0.9914745	5880.2495	0.96038226
5883.2505	0.9967433	5883.2505	0.9573894
5886.2495	1.0037953	5886.2495	0.95444982
5889.2485	1.0083374	5889.2485	0.9547269
5892.2515	1.0122342	5892.2515	0.95794666
5895.2485	1.0139345	5895.2485	0.96174294
5898.2495	1.0150752	5898.2495	0.96851978

Theoretical Details

All the calculations were carried out with the PBE0[9] hybrid functional as implemented in the Gaussian 16 software package revision B.01.[10] ECP28MWB[11] small core quasi-relativistic pseudopotential and ECP28MWB_ANO[12] basis set were used to describe Ce, and the remaining atoms were described with the all-electron Pople basis set 6-311G(d).[13] The geometries of compounds **1-Ce(PN*)** (excluding the K^+ counter ion) and **2-Ce(PN*)** were optimized in gas phase without any constraints. Harmonic frequency calculations were performed to confirm that the optimized structures were stationary points on the potential energy surface. The computed structural metrics are in good agreement with the XRD data, with Ce−N and N−P bond distances, as well as Ce−N−P and N−Ce−N valence angles within 2.0%, 0.3%, 3.3%, and 0.4% of the experimental ones, respectively, providing confidence to the theoretical model (Table S10). In all calculations, spin contamination was found to be less than 0.2% with $\langle S^2 \rangle$ values being close to the corresponding values of the considered spin states, *i.e.* doublet for **1-Ce(PN*)** (C_1 point group symmetry) and singlet for **2-Ce(PN*)** (S_4 point group symmetry). Wavefunctions of the studied species were found to be stable indicating that the calculations converged to the ground electronic state. Time-dependent DFT calculations (TD-DFT) of up to 150 excited states were carried out to simulate the experimental UV-vis spectrum of both complexes. The computed UV-vis spectra were plotted broadening the calculated excitation lines with Gaussian-type peaks using 0.1 eV half-width at half height (Fig. 6 of the main text) and 0.3 eV half-width at half height (Fig. S21). Natural transition orbitals (NTOs),[14] which most of the time can yield a single electron-hole representations of the electronic excitations, were employed to interpret the calculated excitation spectra. To gain more insight into electronic structure of these complexes, chemical bonding analyses were performed using Natural Bond Orbital[15, 16] (NBO6) method. The GaussView 6[17] was used for molecular orbitals visualization of the NBO results. Chemissian 4.60[18] was used to plot molecular orbital energy level diagrams and the computed TD-DFT spectra.

Table S10. Experimental (exp) vs. optimized (opt) Ce–N and N–P bond lengths (Å) and Ce–N–P, N–Ce–N valence angles (º) of complexes **1-Ce(PN*)** and **2-Ce(PN*)**.

	1 (exp)	**1** (opt)	**2** (exp)	**2** (opt)
avg. Ce–N (K^+ capped)	2.377	2.350	2.237	2.193
avg. Ce–N (terminal)	2.313			
avg. N_{imido}–P (K^+ capped)	1.531	1.535	1.557	1.558
avg. N_{imido}–P (terminal)	1.531			
avg. Ce–N–P (K^+ capped)	168.2	173.0	163.0	168.3
avg. Ce–N–P (terminal)	168.2			
avg. N–Ce–N	109.3	109.5	109.5	109.1

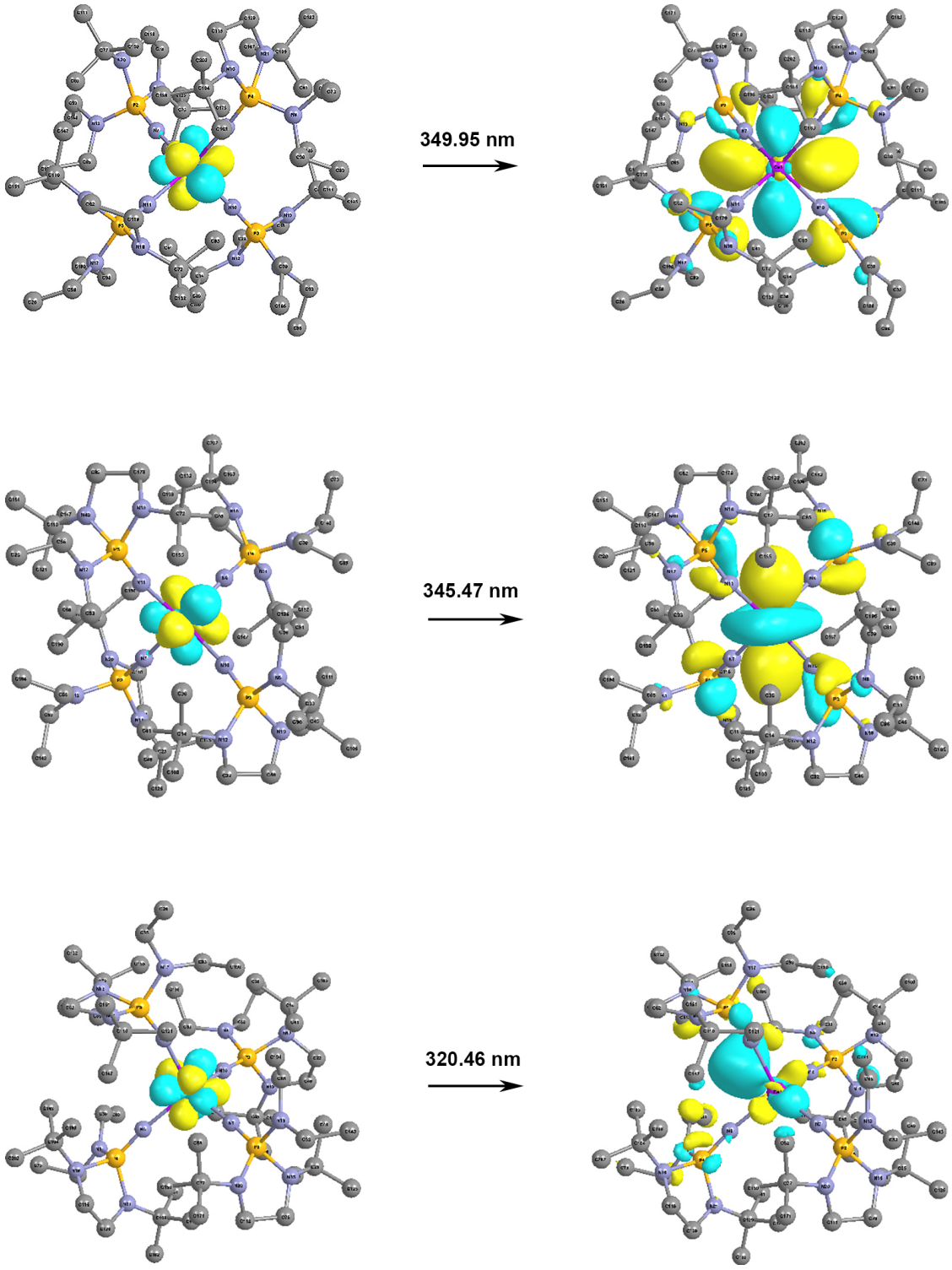

Figure S19. Dominant NTO pairs ("hole" (on the left) → "particle" (on the right)) corresponding to the f-d transitions at a particular energy (nm) of complex **1-Ce(PN*)**.

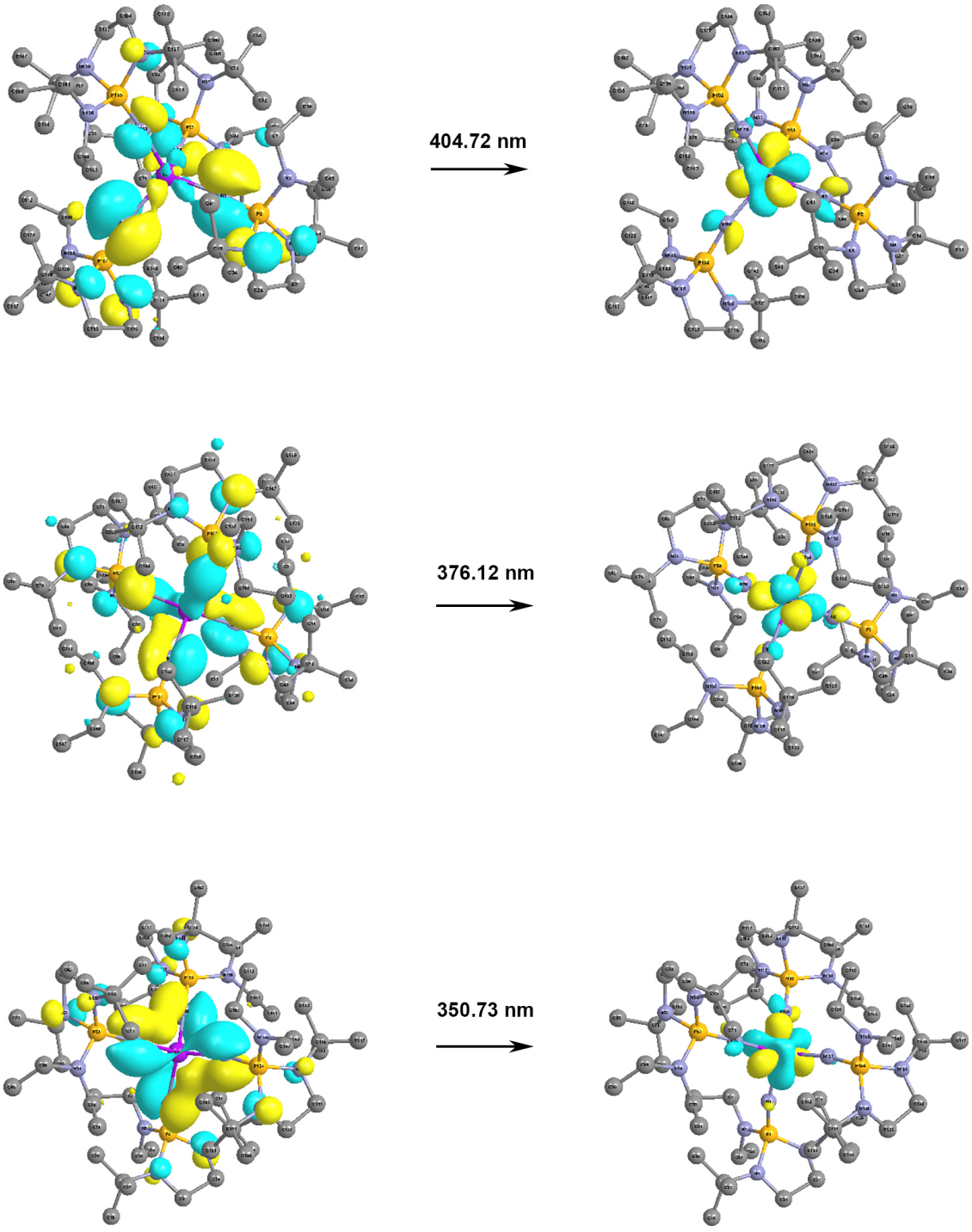

Figure S20. Dominant NTO pairs ("hole" (on the left) → "particle" (on the right)) corresponding to the three LMCT transitions with the highest oscillator strength values within the ~330-480 nm range of complex **2-Ce(PN*)**.

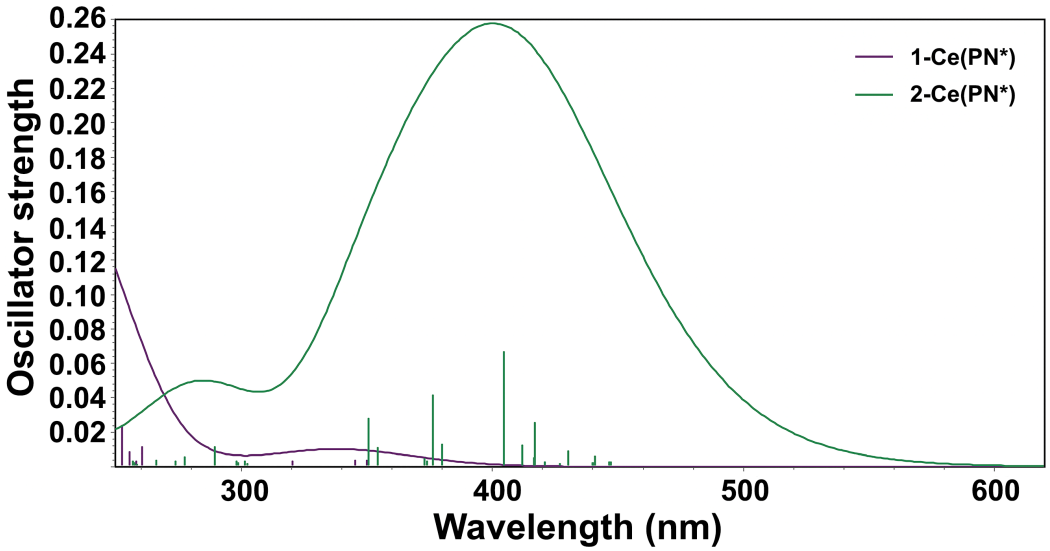

Figure S21. Computed TD-DFT spectra of **1-Ce(PN*)** (*purple*) and **2-Ce(PN*)** (*green*) using 0.3 eV half-width at half height. Vertical bars depict theoretical oscillator strength of single-electron excitations.

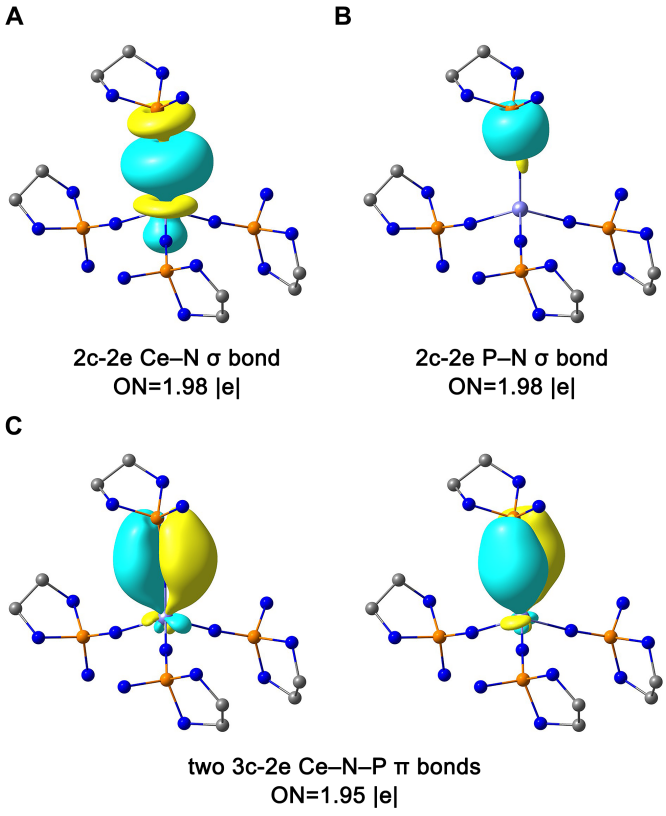

Figure S22. Bonding analysis of the Ce–N–P interactions in **2-Ce(PN*)**. (A) Two-center two-electron Ce–N σ bond. (B) Two-center two-electron P–N σ bond. (C, D) Three-center two-electron Ce–N–P π bonds. ON denotes occupation number. Side groups of the ligands (^{t}Bu, Et_2) are omitted for simplicity. An equivalent set of bonds is identified for other three ligands.

Table S11. ON values (|e|) of the Ce–N σ bonds, N–P σ bonds, Ce–N–P π bonds, and 1c-1e α NBO (unpaired f electron on Ce) in **1-Ce(PN*)** and **2-Ce(PN*)**.

Bonds	Ce–N σ bond	N–P σ bond	Ce–N–P π bonds	1c-1e α NBO
1-Ce(PN*)	1.97	1.99	1.94	1.00
2-Ce(PN*)	1.98	1.98	1.95	N/A

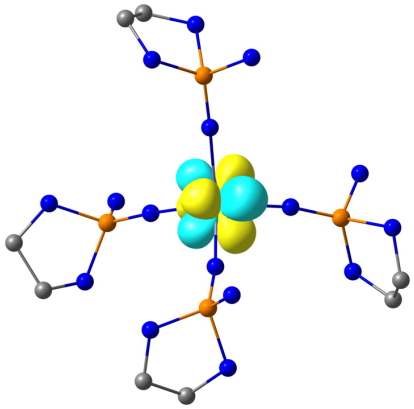

Figure S23. Unpaired Ce 4f electron identified as 1c-1e NBO on Ce with ON=1.00 |e| in **1-Ce(PN*)**. Side groups of the ligands (^{t}Bu, Et_2) are omitted for simplicity.

Table S12. Bond polarization (%) of the NBOs shown in Figure S22.

Bonds	Ce–N σ bond		N–P σ bond		Ce–N–P π bonds		
	Ce	N	N	P	Ce	N	P
1-Ce(PN*)	5.82	94.18	69.94	30.06	1.32	96.48	2.20
2-Ce(PN*)	10.43	89.57	70.17	29.83	4.37	94.02	1.61

Table S13. Ce hybrids (%) of the Ce-containing NBOs.

Bonds	1-Ce(PN*)				2-Ce(PN*)			
	s	p	d	f	s	p	d	f
Ce–N σ bond	0.96	0.70	69.71	28.40	0.28	0.32	64.42	34.82
Ce–N–P π bonds	0.67	4.48	27.19	63.69	0.05	3.41	26.87	65.68
1c-1e α NBO on Ce	0.00	0.00	0.42	99.58	N/A			

Table S14. Cartesian coordinates of **1-Ce(PN*)** (excluding K^+ counterion) and **2-Ce(PN*)**.

1-Ce(PN*)				2-Ce(PN*)			
Ce	0.02123400	-0.03481900	-0.01965200	Ce	0.00000000	0.00000000	0.00000000
P	0.32307100	3.17842500	-2.19083500	P	-2.37617400	1.77746600	2.26440000
P	3.32399600	-2.06284900	-0.27052200	N	-3.82165800	2.21659700	1.51330500
P	-0.60478600	1.13621600	3.61560700	N	-1.95488300	3.09674800	3.25379600
P	-3.03116300	-2.17314300	-1.04140200	N	-1.33921900	1.20269200	1.25338700
N	-0.41724000	0.57498600	2.19856600	N	-2.83835200	0.85276500	3.63964100
N	0.22138300	1.87356600	-1.38585000	C	-4.10561900	1.88505900	0.12982100
N	3.33299000	-3.60172100	0.48476300	H	-4.86188300	1.08768800	0.07427000
N	-0.06690200	0.08270500	4.84350200	H	-3.18721400	1.46551400	-0.28554900
N	2.01148100	-1.29170900	-0.07609800	C	-4.56754300	3.06811900	-0.70955400
N	-1.75296500	-1.36261200	-0.79079800	H	-4.72495000	2.74996900	-1.74388100
N	3.94205400	-2.43378400	-1.85815100	H	-3.82487800	3.86865300	-0.71279900
N	-0.12420100	3.01080000	-3.82671700	H	-5.51408100	3.48775300	-0.35559400
C	3.02728000	-2.82106700	-2.95368600	C	-1.50436000	4.43495000	2.84101900
N	1.80115300	4.06793300	-2.23412700	C	-2.25588700	5.50396700	3.64196600
N	-2.16969200	1.67184600	4.17994400	H	-3.33701400	5.40060400	3.51289100
N	-3.00591200	-3.01602200	-2.53501400	H	-1.96744100	6.50048200	3.29537900
N	-3.59010200	-3.37171100	0.09782800	H	-2.03281600	5.45472900	4.71152700
N	4.84164800	-1.36711300	0.16120100	C	-3.18161700	-0.58244300	3.58829200
N	-0.53633100	4.62182700	-1.73571900	C	-1.77957500	4.66956600	1.35959800
N	0.08002900	2.64169400	4.07807600	H	-1.33531400	3.88664700	0.74239000
C	4.96292200	-1.45690700	-2.19271000	H	-1.34705100	5.62814100	1.05871200
H	4.53648400	-0.48542400	-2.48703500	H	-2.85110200	4.70281800	1.15763000
H	5.59412800	-1.81110900	-3.01330300	C	-2.07658500	1.30567500	4.78980000
C	3.13311200	3.46440200	-2.34779700	H	-1.04737300	0.91498600	4.79041300
C	-4.51806200	-3.97707700	-4.28349300	H	-2.55508700	0.99795400	5.72338400
H	-4.84239100	-2.98288700	-4.60399500	C	0.00000000	4.57142900	3.09011800
H	-5.36122800	-4.66666700	-4.40285700	H	0.25335100	4.40645000	4.14161800
H	-3.72875800	-4.30842400	-4.96382600	H	0.35161300	5.57265400	2.82007600
C	0.19778900	-1.31055700	4.54919600	H	0.54041500	3.83650200	2.49206400
H	0.20404300	-1.39542400	3.46009500	C	-2.05606100	2.81563800	4.67042800
H	-0.62136500	-1.95568500	4.90967900	H	-2.97586000	3.24207500	5.10201200
C	4.57005600	-4.34627500	0.62607900	H	-1.20712600	3.23166200	5.22385300
H	4.61695000	-4.75024700	1.64926400	C	-4.20929300	-0.87326100	4.68751800
H	5.41030700	-3.65019500	0.54186200	H	-3.80581000	-0.70482300	5.68976400
C	2.00141300	-3.82905100	-2.43870700	H	-4.52655400	-1.91935700	4.64049500
H	2.49114100	-4.70889000	-2.01805800	H	-5.09177300	-0.23987900	4.56597500
H	1.35834300	-4.14812200	-3.26452000	C	-4.85775400	2.89892500	2.26909100

H	1.36833200	-3.38604000	-1.66747700
N	-4.58385600	-1.43868500	-1.02996100
C	2.29003500	-1.61608300	-3.54841500
H	1.73002300	-1.09555700	-2.76946000
H	1.59005100	-1.93838000	-4.32509100
H	2.97944500	-0.90180000	-4.00794000
C	5.21193500	-0.79434400	1.45809200
C	5.78228500	-1.28723400	-0.92830500
H	6.55131300	-2.07740500	-0.86687400
H	6.30519500	-0.32245400	-0.94597700
C	3.07251600	2.19907300	-3.20211500
H	2.42116200	1.45137100	-2.74631100
H	4.07644900	1.77212500	-3.29059100
H	2.70274100	2.41404500	-4.20703300
C	-0.13579000	4.15004300	-4.71875200
H	-0.03110600	5.04654800	-4.10516600
H	-1.12583200	4.23411500	-5.19435700
C	-4.05573000	-3.96706600	-2.83207000
H	-4.90588100	-3.73683300	-2.18761600
H	-3.74040000	-4.99027600	-2.55737800
C	2.26550600	-3.95402000	1.39783900
H	1.43901700	-3.26948400	1.19601100
H	2.57483200	-3.77242700	2.44322300
C	-5.50138900	-2.01920900	-0.07925100
H	-6.22036200	-2.70290000	-0.56415700
H	-6.08412200	-1.25116700	0.44348900
C	-0.31961100	1.69742600	-4.40528100
H	-0.40585500	1.00178100	-3.56704700
H	0.56757700	1.37893800	-4.97887800
C	-2.73633600	3.63122700	-2.18657700
H	-2.67229700	3.94016900	-3.23248400
H	-3.78717900	3.64162300	-1.88302800
H	-2.37097500	2.60625500	-2.10562700
C	-2.66238700	-4.29390400	0.77393100
C	-1.00641200	-0.12819600	7.16569500
H	-2.02251600	0.16127800	6.88964300
H	-0.82746500	0.20012400	8.19577900
H	-0.94698400	-1.22127400	7.15517400
C	-1.94084000	4.57536400	-1.28918300
C	1.69301400	5.40589900	-1.69922300
H	1.73365900	6.16364300	-2.49976100
H	2.50396500	5.63276600	-0.99657200
C	2.38931800	1.86857200	3.74449700
H	2.40567400	1.35215600	4.70711600
H	3.40341100	2.20600800	3.51288500
H	2.08235700	1.15360300	2.97894500
C	-1.96068200	-3.63865400	1.96815000
H	-1.44873800	-2.72819600	1.64891300
H	-1.22409400	-4.31936200	2.40751300
H	-2.66964500	-3.37209200	2.75731900
C	1.51449400	-1.82638800	5.11212500
H	1.52428600	-1.84985800	6.20717500
H	2.35271500	-1.21104000	4.77732700
H	1.68986500	-2.84897700	4.76407600
C	-1.74109100	-3.21035400	-3.22167500
H	-1.62557800	-4.27976700	-3.45970700
H	-0.93764300	-2.94682000	-2.53108300
C	4.77173000	-5.47166800	-0.38211700
H	3.96850600	-6.21141600	-0.33862900
H	5.72034700	-5.98967900	-0.19531200
H	4.80083900	-5.05754400	-1.39160600
C	3.84278400	-3.50638600	-4.05604900
H	4.53689500	-2.82057200	-4.55016000
H	3.17084700	-3.89443200	-4.82790000
H	4.41776100	-4.34358500	-3.64975700
C	-3.39298500	0.90897600	3.86697700
C	6.63796500	-1.21905500	1.83264800
H	6.72863500	-2.30866900	1.86603300
H	6.89470500	-0.82864600	2.82239800
H	7.38157400	-0.83652700	1.12708100
H	-5.00939000	3.90953900	1.85990800
H	-4.49059500	3.03885800	3.28702500
C	-3.81814100	-0.93235400	2.24606000
H	-3.12083200	-0.78546600	1.41887400
H	-4.70809300	-0.33107400	2.05523100
H	-4.11477500	-1.98411800	2.25314600
C	-6.19643200	2.17671100	2.32159300
H	-6.61946000	2.01171200	1.32670300
H	-6.91930500	2.77207500	2.88766500
H	-6.10239000	1.20656900	2.81439700
C	-1.95038900	-1.46774200	3.79637000
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H	-2.22637800	-2.52216200	3.70867400
H	-1.51696000	-1.33143400	4.79204100
P	1.77746600	2.37617400	-2.26440000
N	2.21659700	3.82165800	-1.51330500
N	3.09674800	1.95488300	-3.25379600
N	1.20269200	1.33921900	-1.25338700
N	0.85276500	2.83835200	-3.63964100
C	1.88505900	4.10561900	-0.12982100
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H	1.46551400	3.18721400	0.28554900
C	3.06811900	4.56754300	0.70955400
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C	4.43495000	1.50436000	-2.84101900
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H	5.40060400	3.33701400	-3.51289100
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H	5.45472900	2.03281600	-4.71152700
C	-0.58244300	3.18161700	-3.58829200
C	4.66956600	1.77957500	-1.35959800
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H	4.70281800	2.85110200	-1.15763000
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H	0.99795400	2.55508700	-5.72338400
C	4.57142900	0.00000000	-3.09011800
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H	5.57265400	-0.35161300	-2.82007600
H	3.83650200	-0.54041500	-2.49206400
C	2.81563800	2.05606100	-4.67042800
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H	3.23166200	1.20712600	-5.22385300
C	-0.87326100	4.20929300	-4.68751800
H	-0.70482300	3.80581000	-5.68976400
H	-1.91935700	4.52655400	-4.64049500
H	-0.23987900	5.09177300	-4.56597500
C	2.89892500	4.85775400	-2.26909100
H	3.90953900	5.00939000	-1.85990800
H	3.03885800	4.49059500	-3.28702500
C	-0.93235400	3.81814100	-2.24606000
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C	2.17671100	6.19643200	-2.32159300
H	2.01171200	6.61946000	-1.32670300
H	2.77207500	6.91930500	-2.88766500
H	1.20656900	6.10239000	-2.81439700
C	-1.46774200	1.95038900	-3.79637000
H	-1.25248000	1.17523300	-3.05573100
H	-2.52216200	2.22637800	-3.70867400
H	-1.33143400	1.51696000	-4.79204100
P	2.37617400	-1.77746600	2.26440000
N	3.82165800	-2.21659700	1.51330500
N	1.95488300	-3.09674800	3.25379600
N	1.33921900	-1.20269200	1.25338700
N	2.83835200	-0.85276500	3.63964100

C	1.45138200	3.07180300	3.78561700
C	-5.04362600	-0.30394700	-1.83818700
C	4.26714400	-1.28863200	2.55023300
H	3.22581700	-1.07707500	2.29773500
H	4.50312200	-0.78422800	3.49196200
H	4.37107600	-2.36515800	2.70693900
C	-2.24468400	3.11021800	4.00322300
H	-2.42060900	3.39850700	2.95524500
H	-3.04653000	3.54224100	4.61009300
C	0.35913400	5.47327100	-0.97536000
H	0.48459000	5.13010400	0.06287400
H	-0.00740600	6.50411200	-0.94628100
C	-4.04424900	0.02263600	-2.94345200
H	-3.05320600	0.22369900	-2.53146700
H	-4.38411000	0.91014900	-3.48518000
H	-3.95092400	-0.80359300	-3.64900100
C	4.08254000	4.45544500	-3.03022200
H	3.70107400	4.74767300	-4.01297600
H	5.06608300	3.99558900	-3.16871000
H	4.22751000	5.36506400	-2.44005700
C	-0.89509000	3.63849800	4.45606500
H	-0.69540200	4.60525100	3.97855800
H	-0.89783900	3.80571100	5.54692000
C	-3.45019900	-5.51942900	1.25163300
H	-4.17187900	-5.27213700	2.03542000
H	-2.76633000	-6.26572400	1.66819100
H	-3.99174200	-5.97321300	0.41644400
C	5.14457000	0.73429800	1.39641000
H	5.80228300	1.13084300	0.61691800
H	5.45356100	1.18189400	2.34742300
H	4.12615900	1.05439200	1.17439900
C	0.00821500	0.50932000	6.22383700
H	-0.11561800	1.59366800	6.23976000
H	1.02235300	0.31999500	6.60919500
C	0.93315900	4.13862900	-5.80484500
H	0.82633400	5.01546500	-6.45325300
H	0.86457900	3.25046400	-6.44094400
H	1.93294200	4.16196600	-5.36628200
C	-5.21210800	0.93949400	-0.95711900
H	-5.92664200	0.77276100	-0.14565100
H	-5.58022700	1.78498700	-1.54805500
H	-4.25496900	1.21783000	-0.51306000
C	-6.38834000	-0.64880300	-2.49127800
H	-6.29958200	-1.55169600	-3.10248200
H	-6.71657300	0.17099700	-3.13815800
H	-7.17540700	-0.81634700	-1.74948300
C	-1.60971800	-4.77861400	-0.21946200
H	-2.07745700	-5.22488300	-1.10075600
H	-0.98151400	-5.53741300	0.25339100
H	-0.96438700	-3.95875200	-0.54014400
C	-2.07041300	4.11185900	0.16625000
H	-1.59766500	3.13673500	0.30211900
H	-3.12512000	4.03331300	0.45052000
H	-1.59707200	4.81695500	0.85695500
C	-3.13318200	-0.58264300	4.06493500
H	-2.38887100	-0.94560700	3.35396500
H	-4.06086700	-1.13853300	3.89710200
H	-2.78405800	-0.79739900	5.07622900
C	1.50772600	3.80076200	2.43883500
H	1.16514300	3.14126900	1.63805200
H	2.52633200	4.13173600	2.20826100
H	0.86660800	4.68871600	2.44420000
C	-2.54973500	5.97504900	-1.43414600
H	-2.10480100	6.69830500	-0.74476200
H	-3.62165900	5.94002500	-1.21557100
H	-2.41714500	6.34563600	-2.45489100
C	3.67658500	3.09425100	-0.96523900
H	3.73844200	3.96861600	-0.30886200
H	4.68004200	2.66223000	-1.03563400
H	3.01464700	2.36171900	-0.50009300
C	4.10561900	-1.88505900	0.12982100
H	4.86188300	-1.08768800	0.07427000
H	3.18721400	-1.46551400	-0.28554900
C	4.56754300	-3.06811900	-0.70955400
H	4.72495000	-2.74996900	-1.74388100
H	3.82487800	-3.86865300	-0.71279900
H	5.51408100	-3.48775300	-0.35559400
C	1.50436000	-4.43495000	2.84101900
C	2.25588700	-5.50396700	3.64196600
H	3.33701400	-5.40060400	3.51289100
H	1.96744100	-6.50048200	3.29537900
H	2.03281600	-5.45472900	4.71152700
C	3.18161700	0.58244300	3.58829200
C	1.77957500	-4.66956600	1.35959800
H	1.33531400	-3.88664700	0.74239000
H	1.34705100	-5.62814100	1.05871200
H	2.85110200	-4.70281800	1.15763000
C	2.07658500	-1.30567500	4.78980000
H	1.04737300	-0.91498600	4.79041300
H	2.55508700	-0.99795400	5.72338400
C	0.00000000	-4.57142900	3.09011800
H	-0.25335100	-4.40645000	4.14161800
H	-0.35161300	-5.57265400	2.82007600
H	-0.54041500	-3.83650200	2.49206400
C	2.05606100	-2.81563800	4.67042800
H	2.97586000	-3.24207500	5.10201200
H	1.20712600	-3.23166200	5.22385300
C	4.20929300	0.87326100	4.68751800
H	3.80581000	0.70482300	5.68976400
H	4.52655400	1.91935700	4.64049500
H	5.09177300	0.23987900	4.56597500
C	4.85775400	-2.89892500	2.26909100
H	5.00939000	-3.90953900	1.85990800
H	4.49059500	-3.03885800	3.28702500
C	3.81814100	0.93235400	2.24606000
H	3.12083200	0.78546600	1.41887400
H	4.70809300	0.33107400	2.05523100
H	4.11477500	1.98411800	2.25314600
C	6.19643200	-2.17671100	2.32159300
H	6.61946000	-2.01171200	1.32670300
H	6.91930500	-2.77207500	2.88766500
H	6.10239000	-1.20656900	2.81439700
C	1.95038900	1.46774200	3.79637000
H	1.17523300	1.25248000	3.05573100
H	2.22637800	2.52216200	3.70867400
H	1.51696000	1.33143400	4.79204100
P	-1.77746600	-2.37617400	-2.26440000
N	-2.21659700	-3.82165800	-1.51330500
N	-3.09674800	-1.95488300	-3.25379600
N	-1.20269200	-1.33921900	-1.25338700
N	-0.85276500	-2.83835200	-3.63964100
C	-1.88505900	-4.10561900	-0.12982100
H	-1.08768800	-4.86188300	-0.07427000
H	-1.46551400	-3.18721400	0.28554900
C	-3.06811900	-4.56754300	0.70955400
H	-2.74996900	-4.72495000	1.74388100
H	-3.86865300	-3.82487800	0.71279900
H	-3.48775300	-5.51408100	0.35559400
C	-4.43495000	-1.50436000	-2.84101900
C	-5.50396700	-2.25588700	-3.64196600
H	-5.40060400	-3.33701400	-3.51289100
H	-6.50048200	-1.96744100	-3.29537900
H	-5.45472900	-2.03281600	-4.71152700
C	0.58244300	-3.18161700	-3.58829200
C	-4.66956600	-1.77957500	-1.35959800
H	-3.88664700	-1.33531400	-0.74239000
H	-5.62814100	-1.34705100	-1.05871200
H	-4.70281800	-2.85110200	-1.15763000
C	-1.30567500	-2.07658500	-4.78980000
H	-0.91498600	-1.04737300	-4.79041300

C	-4.64325000	-2.78854000	0.90514600	H	-0.99795400	-2.55508700	-5.72338400
H	-4.25541700	-2.10392700	1.67535100	C	-4.57142900	0.00000000	-3.09011800
H	-5.23496400	-3.56135400	1.40579300	H	-4.40645000	0.25335100	-4.14161800
C	1.93614000	4.00455600	4.90148500	H	-5.57265400	0.35161300	-2.82007600
H	1.35021600	4.92667100	4.95715900	H	-3.83650200	0.54041500	-2.49206400
H	2.97803000	4.28900200	4.72434800	C	-2.81563800	-2.05606100	-4.67042800
H	1.87916500	3.50500100	5.87345300	H	-3.24207500	-2.97586000	-5.10201200
C	1.80370100	-5.39877700	1.27542600	H	-3.23166200	-1.20712600	-5.22385300
H	0.96526900	-5.58311000	1.95511300	C	0.87326100	-4.20929300	-4.68751800
H	2.59541700	-6.10750600	1.53963800	H	0.70482300	-3.80581000	-5.68976400
H	1.47396200	-5.62172000	0.25759300	H	1.91935700	-4.52655400	-4.64049500
C	-1.57015600	-2.36858800	-4.47972700	H	0.23987900	-5.09177300	-4.56597500
H	-2.37826800	-2.51852400	-5.20026300	C	-2.89892500	-4.85775400	-2.26909100
H	-0.62523100	-2.61211800	-4.97834600	H	-3.90953900	-5.00939000	-1.85990800
H	-1.54461000	-1.30999700	-4.21446200	H	-3.03885800	-4.49059500	-3.28702500
C	-1.54713700	1.59737300	-5.30042700	C	0.93235400	-3.81814100	-2.24606000
H	-2.45188200	1.89072900	-4.76277100	H	0.78546600	-3.12083200	-1.41887400
H	-1.67760300	0.56646700	-5.64154300	H	0.33107400	-4.70809300	-2.05523100
H	-1.46589500	2.22554700	-6.19391200	H	1.98411800	-4.11477500	-2.25314600
C	-3.86778600	1.12880300	2.42759300	C	-2.17671100	-6.19643200	-2.32159300
H	-4.12795100	2.17455900	2.23735600	H	-2.01171200	-6.61946000	-1.32670300
H	-4.76075000	0.52935400	2.22332000	H	-2.77207500	-6.91930500	-2.88766500
H	-3.08405400	0.83150700	1.72784500	H	-1.20656900	-6.10239000	-2.81439700
C	-4.49718600	1.33044600	4.84270300	C	1.46774200	-1.95038900	-3.79637000
H	-4.15613700	1.22789100	5.87720200	H	1.25248000	-1.17523300	-3.05573100
H	-5.37972800	0.69762800	4.70535800	H	2.52216200	-2.22637800	-3.70867400
H	-4.81657600	2.36517200	4.68870800	H	1.33143400	-1.51696000	-4.79204100

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