Supporting Information for

Distinct Electronic Structure and Bonding Interactions in Inverse-sandwich Samarium and Ytterbium Biphenyl Complexes

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1. Synthetic Procedures

1.1. General Considerations: All experiments were performed under a dry argon atmosphere using standard Schlenk techniques or in a nitrogen filled glove box unless otherwise specified. Solvents, hexanes, tetrahydrofuran (THF), diethyl ether (Et_2O), and toluene were collected from a Vigor YJC-5 Solvent Purification System under argon or purified using a two-column solid-state purification system by the method of Grubbs,[1] transferred to the glove box without exposure to air, and stored over activated molecular sieves. *n*-pentane was distilled under argon over calcium hydride and stored over activated molecular sieves. Deuterated solvents, benzene-d_6 (C_6D_6) and tetrahydrofuran-d_8 (C_4D_8O), were obtained from Cambridge Isotope Laboratories, degassed three times or brought directly into the glovebox in a sealed ampule, and stored over activated molecular sieves for one week prior to use. Sm_2O_3 and Yb_2O_3 were purchased from 9dingchem or Stanford Materials Corporation and used as received. $(NN^{TBS})SmI(THF)_2$ and $(NN^{TBS})YbCl(THF)_2$ were prepared following published procedures.[2] Biphenyl was purchased from Sigma-Aldrich and used as received. 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) was purchased from Alfa Aesar, recrystallized from hexanes and dried under a reduced pressure prior to use. Potassium graphite (KC_8) was synthesized following published procedures.[3] ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 400 MHz and 500 MHz spectrometers at room temperature in C_6D_6 or C_4D_8O unless otherwise specified. Chemical shifts are reported with respect to internal solvent (C_6D_6 at 7.16 ppm or C_4D_8O at 1.73 ppm). CHN analyses were performed on a Vario EL elemental analyzer at the Analytical Center of Peking University. The diffraction data were collected at 180 K using a Rigaku Oxford diffractometer equipped with a CCD collector using Mo Kα radiation or at 100 K using a Bruker SMART 1000 single-crystal X-ray diffractometer equipped with a SMATR APEX CCD detector using Mo Kα radiation. UV/Vis/NIR spectra were obtained on a SHIMADZU UV3600Plus at the Analytical Center of Peking University. Sm L_3-edge (eV) and Yb L_3-edge (eV) X-ray absorption measurements were conducted on the bending magnet beamline of the Materials Research Collaborative Access Team (MRCAT, 10-BM) at the Advanced Photon Source (APS), Argonne National Laboratory.

1.2. Synthetic Details

Synthesis of Sm_2-biph-K_2: 0.400 g of $(NN^{TBS})SmI(THF)_2$ (0.463 mmol) and 0.036 g of biphenyl (0.233 mmol, 0.5 equiv) were weighed in a vial and dissolved in 8 mL of THF. The solution was placed in a dry ice/acetone bath for 15 min prior to the addition of 0.156 g KC_8 (1.154 mmol, 2.5 equiv). Immediately after the addition, the solution color changed from orange to black. The vial was taken out from the dry ice/acetone bath and the reaction mixture was stirred at room temperature for 10 min. The solution was then filtered through Celite and washed with 2 mL of THF. The volatiles were removed under a reduced pressure. The remaining solid was washed with Et_2O and the dark microcrystalline solid was collected on a medium frit. Yield: 0.200 g, 54.8%. Single crystals of **Sm_2-biph-K_2** suitable for X-ray crystallography were obtained from a dilute toluene solution layered with hexanes stored at -35 ºC. ^1H NMR (500 MHz, C_4D_8O, 25 ºC) δ, ppm: 28.12, 18.45, 17.85, 15.55, 12.20, 10.61, 9.79, 7.01, 6.45, 3.27, 1.25, 0.16, -0.29, -6.18, -6.46, and -9.88. Anal. (%): Calcd. for $C_{64}H_{106}Fe_2K_2N_4O_2Si_4Sm_2$, M_w = 1566.52, as in the formula of $[(NN^{TBS})Sm]_2(\mu$-biphenyl$)[K(Et_2O)]_2$: C, 49.07; H, 6.82; N, 3.58. Found: C, 49.37; H, 6.72; N, 3.69. μ_{eff} = 2.47

μ_B (C_4D_8O, 25 ºC).

Synthesis of Sm_2-biph-[K(18-crown-6)]$_2$: 0.200 g of **Sm_2-biph-K_2** (0.128 mmol) and 0.068 g of 18-crown-6 (0.257 mmol, 2.0 equiv) were weighed in a vial. 5 mL of cold THF (pre-cooled at -78 ºC) was added and the mixture was stirred in a dry ice/acetone bath for 30 min. The volatiles were removed under a reduced pressure. The resulting microcrystalline solid was recrystallized from THF layered with *n*-pentane and stored at -35 ºC. Dark crystals formed and were washed with *n*-pentane. Yield: 0.190 g, 66.4%. Single crystals of **Sm_2-biph-[K(18-crown-6)]$_2$** suitable for X-ray crystallography were obtained from a dilute THF solution layered with hexanes stored at -35 ºC. ^{1}H NMR (500 MHz, C_4D_8O, 25 ºC) δ, ppm: 23.52, 21.05, 15.70, 14.85, 8.77, 8.33, 6.02, 4.88, 3.57, 3.07, 1.34, 0.88, -0.01, -0.55, -2.56, -5.72, and -6.07. Anal. (%): Calcd. for $C_{96}H_{166}Fe_2K_2N_4O_{16}Si_4Sm_2$, M_w = 2235.34, as in the formula of $[(NN^{TBS})Sm]_2(\mu$-biphenyl)$[K(18\text{-crown-}6)(THF)_2]_2$: C, 51.58; H, 7.49; N, 2.51. Found: C, 51.54; H, 7.11; N, 2.87. μ_{eff} = 2.39 μ_B (C_4D_8O, 25 ºC).

Synthesis of Yb_2-biph-K_2: 0.029 g of biphenyl (0.188 mmol, 0.75 equiv) was weighed in a vial and dissolved in 2 mL of THF. The solution was placed in a dry ice/acetone bath for 15 min prior to the addition of 0.102 g KC_8 (0.755 mmol, 3.0 equiv). Immediately after the addition, the solution turned black and the mixture was stirred at dry ice/acetone bath for 3 min. 0.200 g of $(NN^{TBS})YbCl(THF)_2$ (0.251 mmol) was weighed in the other vial and dissolved in 3 mL of THF. The solution was placed in a dry ice/acetone bath for 15 min and then dropwise added into the vial containing a mixture of biphenyl and KC_8. After the addition, the solution was taken out from the dry ice/acetone bath and stirred at room temperature for 3 min. The solution was then filtered through Celite and washed with 2 mL of THF. The volatiles were removed under a reduced pressure. The remaining dark solid was dispersed in Et_2O, transferred to a vial, layered with *n*-pentane, and stored at -35 ºC for three days. Dark microcrystalline solid was collected on a medium frit. Yield: 0.100 g, 51.9%. Single crystals of **Yb_2-biph-K_2** suitable for X-ray crystallography were obtained from a saturated Et_2O solution stored at -35 ºC for three days. ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) δ, ppm: 5.51 (t, J = 7.5 Hz, 4H, C*H* on biphenyl), 4.32 (d, J = 9.0 Hz, 4H, C*H* on biphenyl), 4.21, 4.12, 3.85, and 3.14 (s, 16H, C*H* on Cp), 3.44 (t, J = 6.1 Hz, 2H, C*H* on biphenyl), 1.12 (s, 36H, C(CH_3)$_3$), and 0.42 and 0.34 (s, 24H, SiCH_3). ^{1}H NMR (400 MHz, C_4D_8O, 25 ºC) δ, ppm: 5.41, 4.10 and 3.11 (br, 12H, C*H* on biphenyl and C*H* on Cp, some peaks were missing due to broadening of the peaks), 3.54 (m, 8H, CH_2O), 1.69 (m, 8H, CH_2CH_2O), 0.76 (s, 36H, C(CH_3)$_3$), and -0.04 (s, 24H, SiCH_3). ^{13}C NMR (126 MHz, C_4D_8O, 25 ºC) δ, ppm: 127.88, 102.17, 101.85, 87.24 (*C* on biphenyl), 117.38, 61.87, 61.78, 61.74, 60.97 (*C* on Cp), 27.28 (C(*C*H$_3$)$_3$), 19.76 (*C*(CH$_3$)$_3$) and -3.04 (Si*C*H$_3$). Anal. (%): Calcd. for $C_{60}H_{94}Fe_2K_2N_4OSi_4Yb_2$, M_w = 1535.77, as in the formula of $[(NN^{TBS})Yb]_2(\mu$-biphenyl)$[K(THF)_{0.5}]_2$: C, 46.92; H, 6.17; N, 3.65. Found: C, 46.75; H, 6.56; N, 3.39.

Synthesis of $[(NN^{TBS})Yb(THF)]_2$ and $(NN^{TBS})Yb(THF)_3$: 0.100 g of $(NN^{TBS})YbCl(THF)_2$ (0.126 mmol) was weighed in a vial and dissolved in 5 mL of THF. The solution was placed in a dry ice/acetone bath for 15 min prior to the addition of 0.026 g KC_8 (0.189 mmol, 1.5 equiv). Then the mixture was stirred at room temperature for 1 h. The solution was then filtered through Celite and washed with 2 mL of THF. The volatiles were removed under a reduced pressure. The remaining brown solid was dispersed in hexanes for 5 min and then the volatiles were removed under a reduced pressure. After repeating this hexanes

dispersion for 3 times, the brown solid was collected on a medium frit. Yield: 0.050 g, 54%. Single crystals of **[(NN^{TBS})Yb(THF)]$_2$** suitable for X-ray crystallography were obtained from a saturated Et_2O solution layered with hexanes stored at -35 ºC. Due to the poor solubility, satisfactory ^{1}H and ^{13}C NMR spectra of **[(NN^{TBS})Yb(THF)]$_2$** could not be obtained in non-coordinating aliphatic or aromatic solvents. However, dissolving **[(NN^{TBS})Yb(THF)]$_2$** in THF resulted in formation of **(NN^{TBS})Yb(THF)$_3$** (see below). Anal. (%): Calcd. for $C_{58}H_{106}Fe_2N_4O_2Si_4Yb_2$, M_w = 1461.60, as in the formula of [(NN^{TBS})Yb(THF)]$_2$ plus one C_6H_{14} molecule: C, 47.66; H, 7.31; N, 3.83. Found: C, 47.84; H, 7.01; N, 3.35. By dissolving the brown solid of **[(NN^{TBS})Yb(THF)]$_2$** in THF and then layered with hexanes, orange single crystals of **(NN^{TBS})Yb(THF)$_3$** suitable for X-ray crystallography were obtained after stored at -35 ºC for three days. ^{1}H NMR (500 MHz, C_4D_8O, 25 ºC) δ, ppm: 3.61 and 3.07 (m, 8H, C*H* on Cp), 3.53 (m, 4H, C*H*$_2$O), 1.67 (m, 4H, C*H*$_2$CH$_2$O), 0.65 (s, 18H, C(C*H*$_3$)$_3$), and -0.17 (s, 12H, SiC*H*$_3$). ^{13}C NMR (126 MHz, C_4D_8O, 25 ºC) δ, ppm: 115.94 (*C*N), 68.25, 64.16, 62.57 (*C*H$_2$O and *C*H on Cp), 28.35 (C(*C*H$_3$)$_3$), 26.37 (*C*H$_2$CH$_2$O), 21.42 (*C*(CH$_3$)$_3$) and -1.78 (Si*C*H$_3$). Due to the readily loss of the coordinating THF molecules upon drying, satisfactory result for elemental analysis could not be obtained for **(NN^{TBS})Yb(THF)$_3$**.

Synthesis of (NN^{TBS})Yb(18-crown-6): 0.305 g of **[(NN^{TBS})Yb(THF)]$_2$** (0.222 mmol) and 0.117 g of 18-crown-6 (0.444 mmol, 2.0 equiv) were weighed in a vial. 5 mL of cold (pre-cooled at -78 ºC) THF was added to the vial and the mixture was stirred in a dry ice/acetone bath for 1 h. The solution was then filtered through Celite and washed with 2 mL of THF. The volatiles were removed under a reduced pressure. The remaining brownish red solid was dispersed in Et_2O and layered with hexanes. Red microcrystalline solid was collected on a medium frit. Yield: 0.190 g, 48.6%. Single crystals of the different coordination isomers **(NN^{TBS})Yb(κ^3-18-crown-6)** and **(NN^{TBS})Yb(κ^4-18-crown-6)** suitable for X-ray crystallography were obtained from the same saturated Et_2O solution layered with hexanes stored at -35 ºC for three days. ^{1}H NMR (500 MHz, C_6D_6, 25 ºC) δ, ppm: 3.96 and 3.69 (s, 8H, C*H* on Cp), 3.43 (s, 24H, C*H*$_2$ on 18-crown-6), 1.21 (s, 18H, C(C*H*$_3$)$_3$), and 0.43 (s, 12H, SiC*H*$_3$). ^{13}C NMR (126 MHz, C_4D_8O, 25 ºC) δ, ppm: 118.78 (*C*N), 70.59 (*C*H$_2$O on 18-crown-6), 62.38, 62.35 (*C*H on Cp), 28.49 (C(*C*H$_3$)$_3$), 21.32 (*C*(CH$_3$)$_3$) and -0.91 (Si*C*H$_3$). Anal. (%): Calcd. for $C_{37}H_{69}FeN_2O_6Si_2Yb$, M_w = 923.04, as in the formula of (NN^{TBS})Yb(18-crown-6) plus 0.5 C_6H_{14} molecule: C, 48.15; H, 7.54; N, 3.03. Found: C, 48.15; H, 7.28 N, 3.20.

Reaction of Yb$_2$-biph-K$_2$ with 18-crown-6: 0.050 g of **Yb$_2$-biph-K$_2$** (0.031 mmol) and 0.033 g 18-crown-6 (0.125 mmol, 4.0 equiv) were weighed in a vial. 5 mL of cold (pre-cooled at -78 ºC) THF was added to the vial and the mixture was stirred in a dry ice/acetone bath for 1 h. The solution was then layered with hexanes and stored at -35 ºC for three days. Dark single crystals of **K(18-crown-6)-biphenyl** suitable for X-ray crystallography were obtained and the unit cell was determined and found to match the previously reported data.[4] The ^{1}H NMR spectrum of the supernatant showed that **(NN^{TBS})Yb(18-crown-6)** was the major Yb product.

2. ^{1}H and ^{13}C NMR Spectra

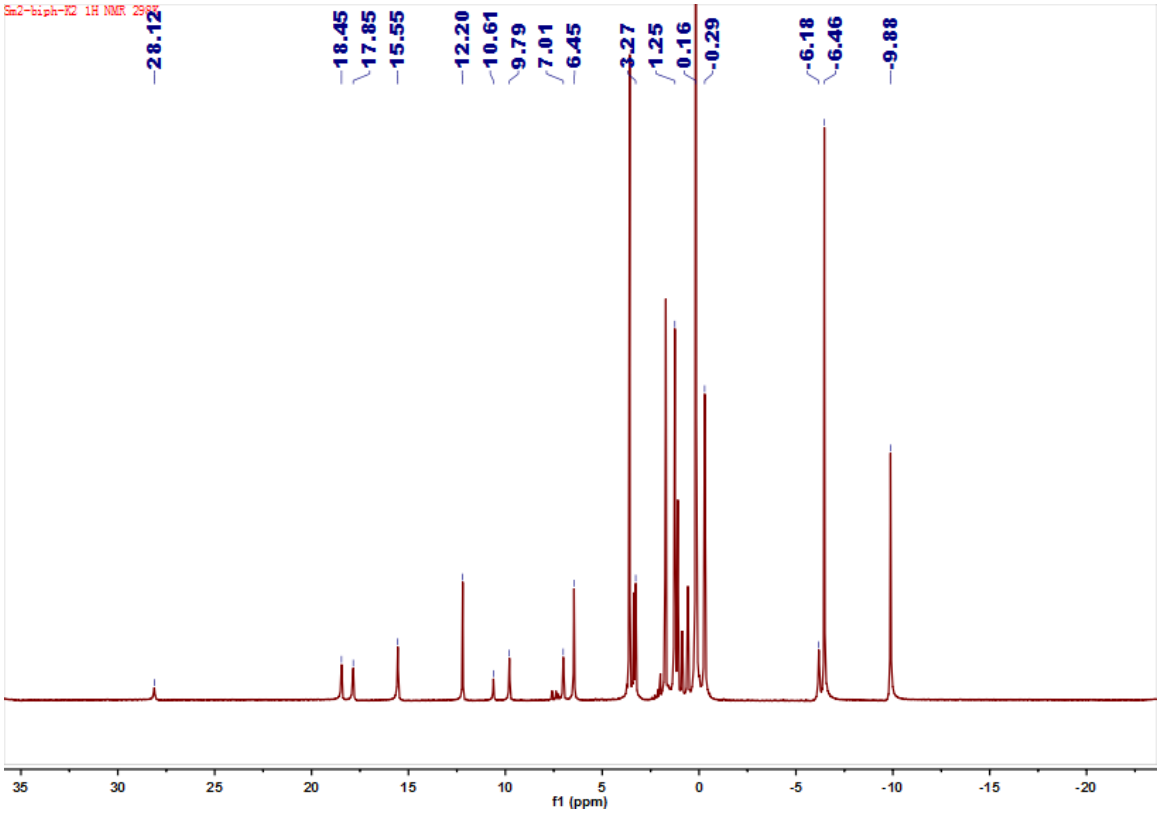


Figure S1. ^{1}H NMR (C_4D_8O, 500 MHz, 298 K) spectrum of **Sm_2-biph-K_2**.

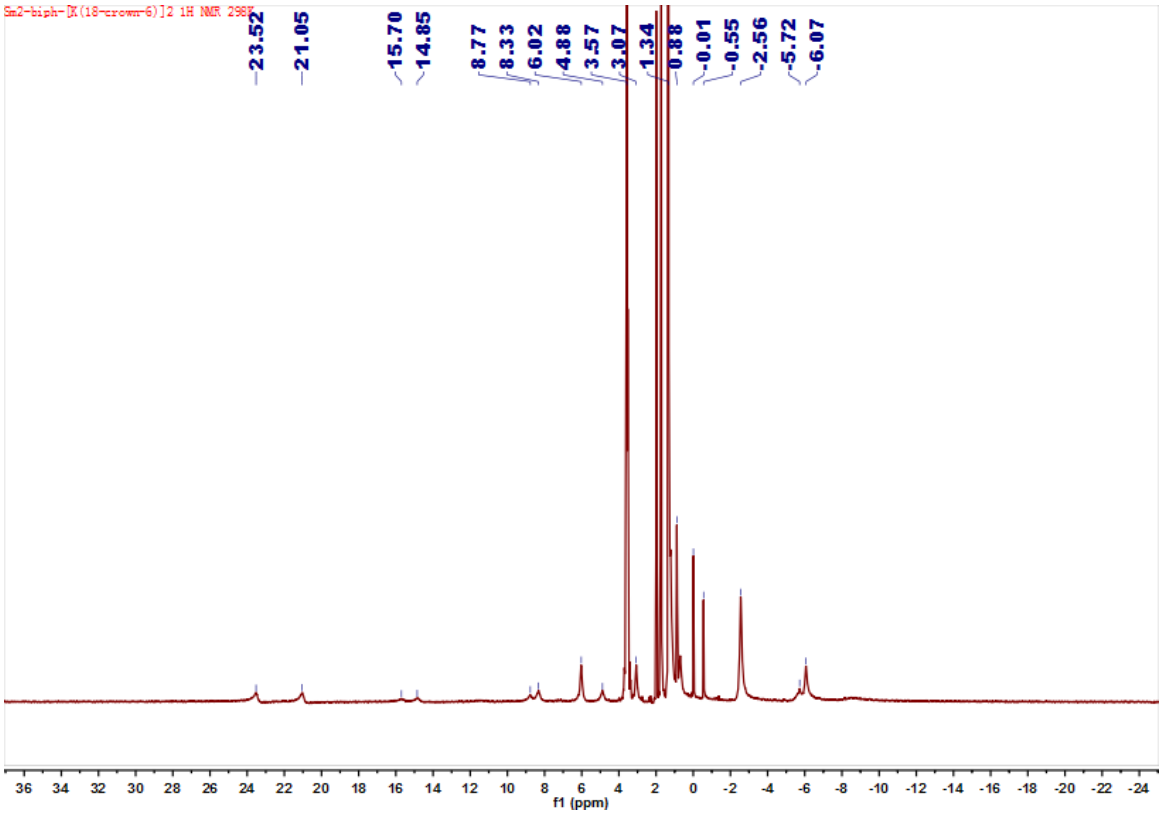


Figure S2. ^{1}H NMR (C_4D_8O, 500 MHz, 298 K) spectrum of **Sm_2-biph-[K(18-crown-6)]$_2$**.

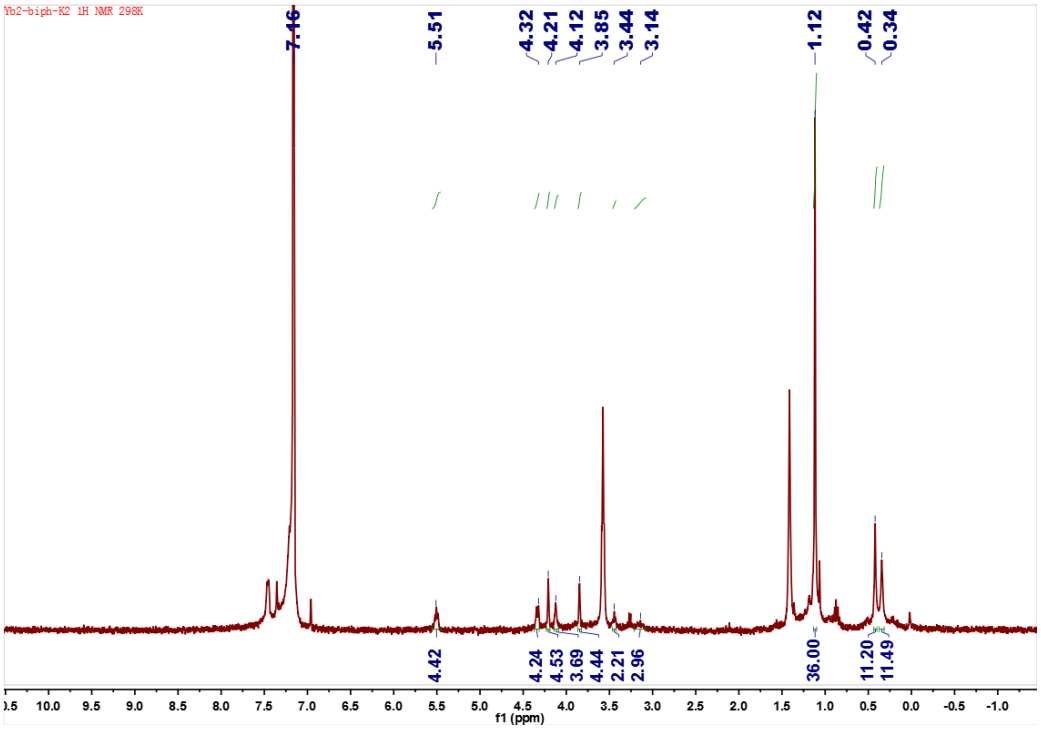


Figure S3. ^{1}H NMR (400 MHz, C_6D_6, 25 ºC) spectrum of **Yb$_2$-biph-K$_2$**. δ, ppm: 5.51 (t, J = 7.5 Hz, 4H, C*H* on biphenyl), 4.32 (d, J = 9.0 Hz, 4H, C*H* on biphenyl), 4.21, 4.12, 3.85, and 3.14 (s, 16H, C*H* on Cp), 3.44 (t, J = 6.1 Hz, 2H, C*H* on biphenyl), 1.12 (s, 36H, C(CH_3)$_3$), and 0.42 and 0.34 (s, 24H, SiCH_3).

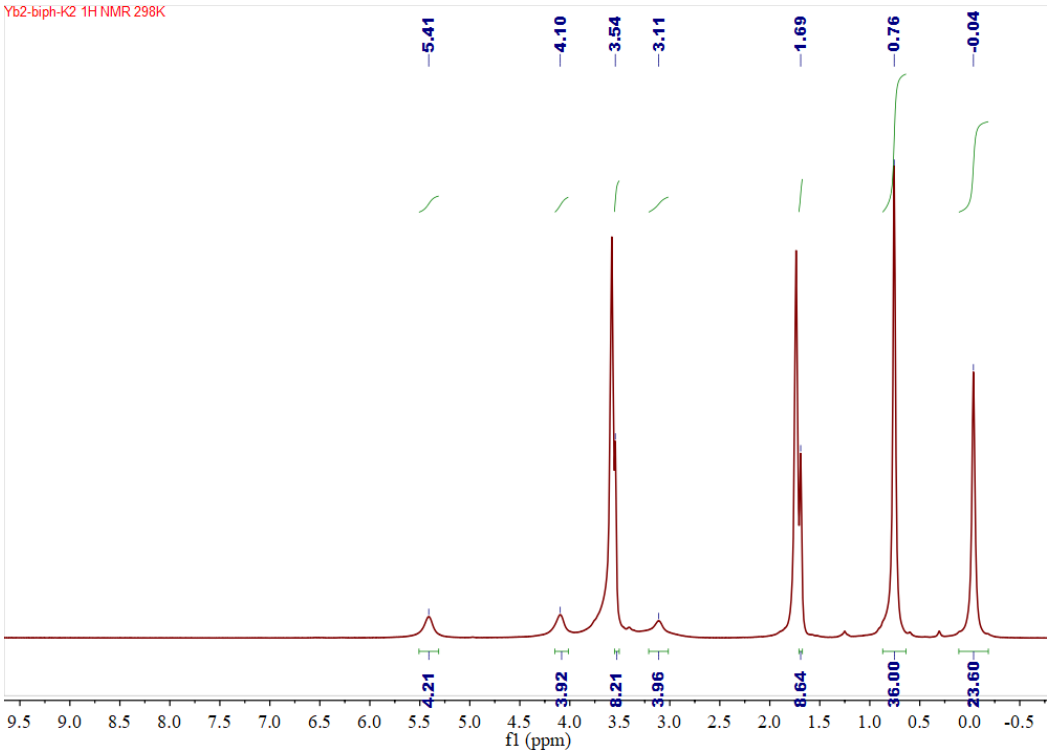


Figure S4. ^{1}H NMR (C_4D_8O, 400 MHz, 298 K) spectrum of **Yb$_2$-biph-K$_2$**. δ, ppm: 5.41, 4.10 and 3.11 (br, 12H, C*H* on biphenyl and C*H* on Cp, some peaks were missing due to broadening of the peaks), 3.54 (m, 8H, CH_2O), 1.69 (m, 8H, CH_2CH$_2$O), 0.76 (s, 36H, C(CH_3)$_3$), and -0.04 (s, 24H, SiCH_3).

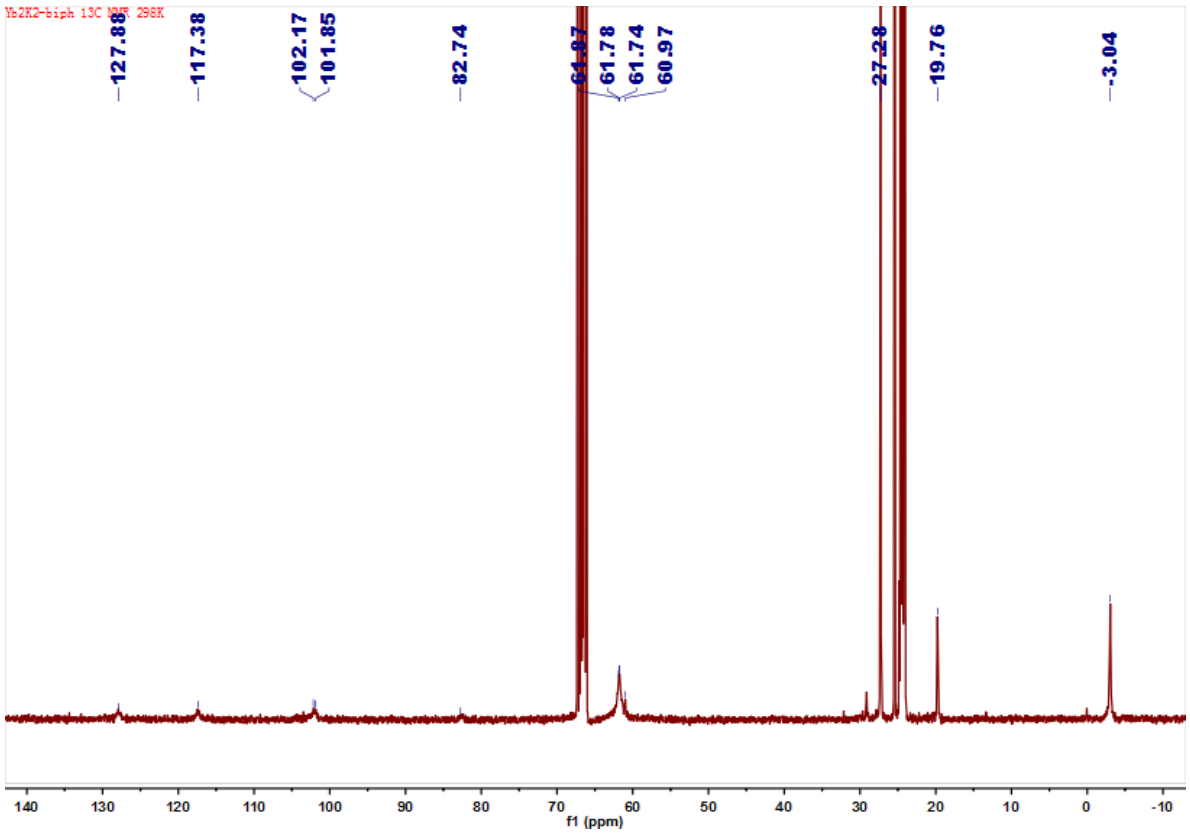


Figure S5. ^{13}C NMR (C_4D_8O, 126 MHz, 298 K) spectrum of **Yb_2-biph-K_2**.

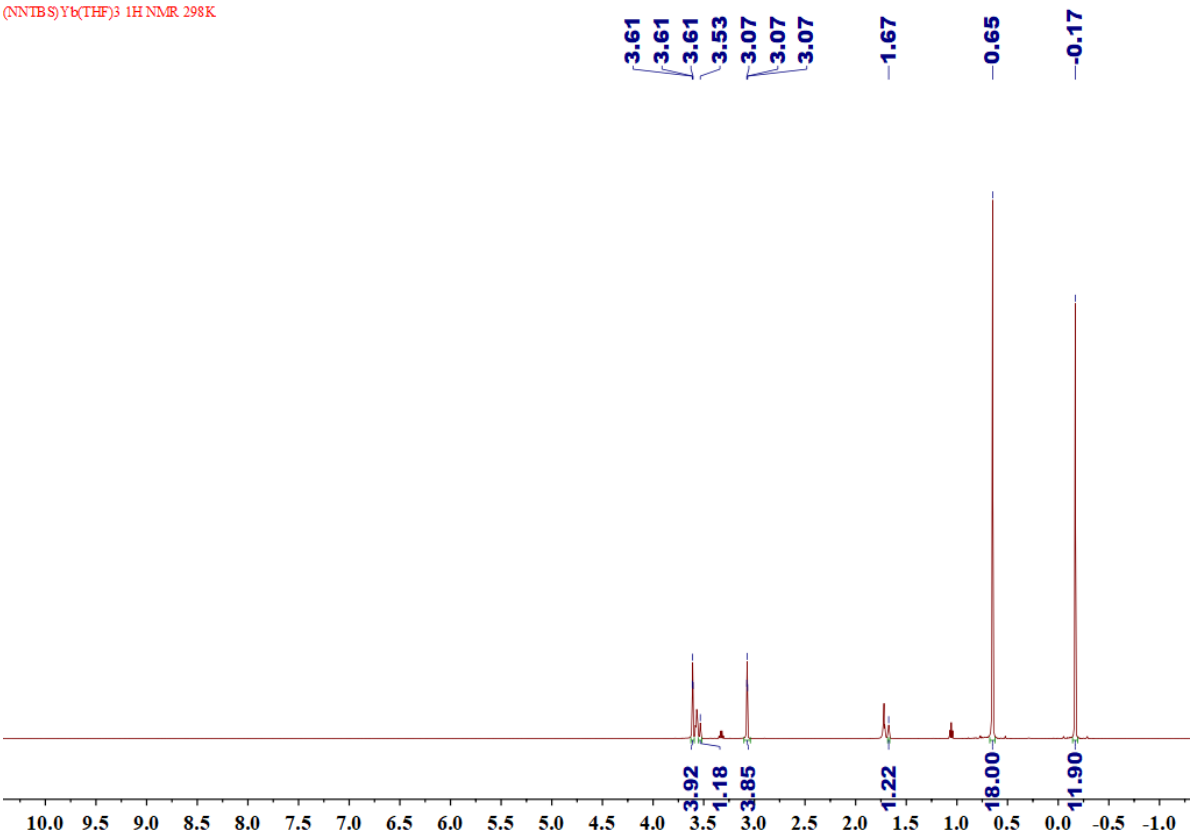


Figure S6. ^{1}H NMR (C_4D_8O, 500 MHz, 298 K) spectrum of **(NN^{TBS})Yb(THF)$_3$**. δ, ppm: 3.61 and 3.07 (m, 8H, C*H* on Cp), 3.53 (m, 4H, CH_2O), 1.67 (m, 4H, CH_2CH_2O), 0.65 (s, 18H, C(CH_3)$_3$), and -0.17 (s, 12H, SiCH_3).

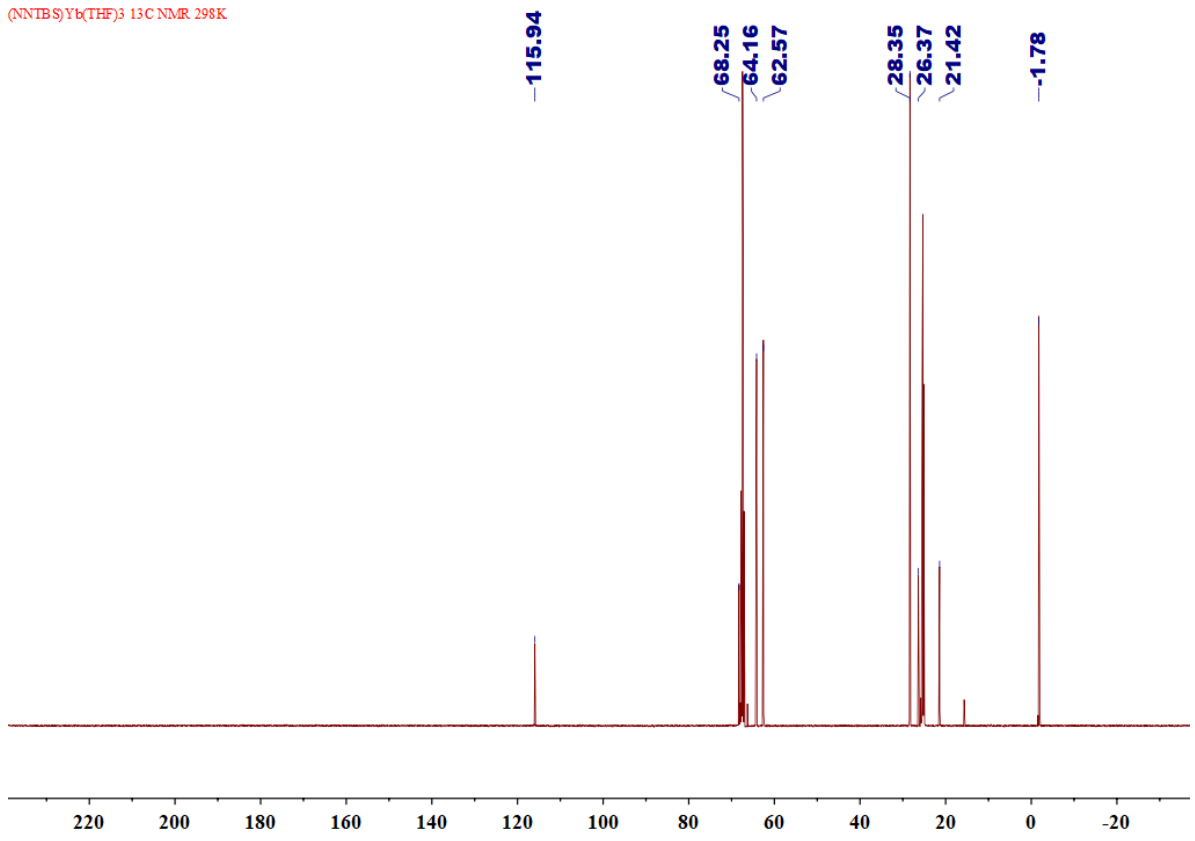


Figure S7. ^{13}C NMR (C_4D_8O, 126 MHz, 298 K) spectrum of **(NN^{TBS})Yb(THF)$_3$**.

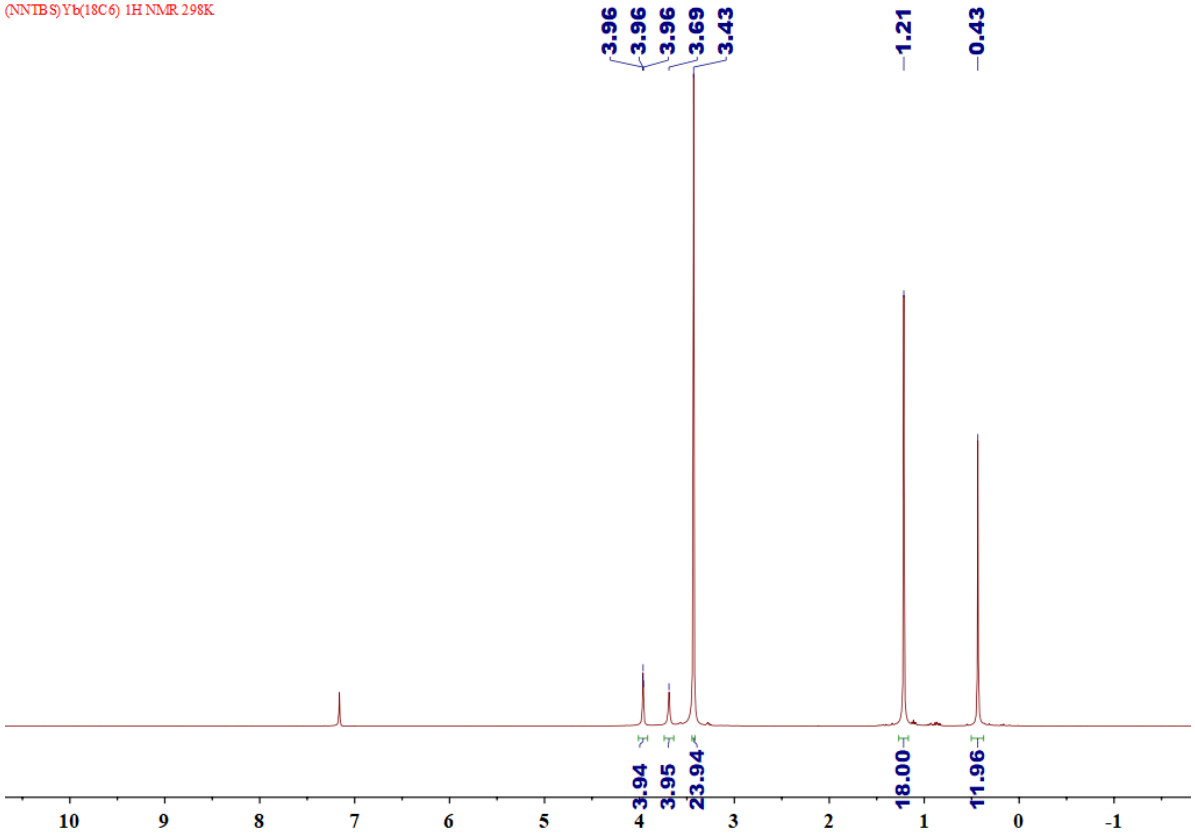


Figure S8. ^{1}H NMR (C_6D_6, 500 MHz, 298 K) spectrum of **(NN^{TBS})Yb(18-crown-6)**. δ, ppm: 3.96 and 3.69 (s, 8H, C*H* on Cp), 3.43 (s, 24H, CH_2 on 18-crown-6), 1.21 (s, 18H, C(CH_3)$_3$), and 0.43 (s, 12H, SiCH_3).

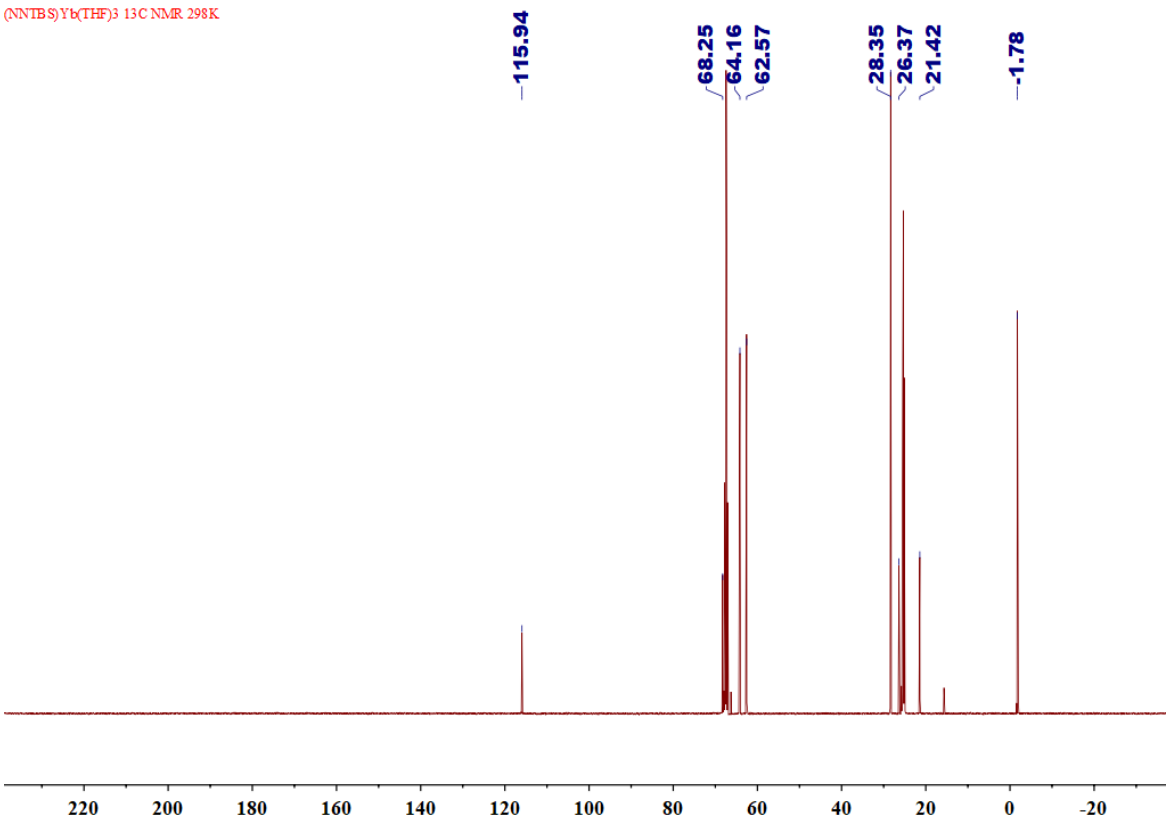


Figure S9. ^{13}C NMR (C_6D_6, 126 MHz, 298 K) spectrum of **(NN^{TBS})Yb(18-crown-6)**.

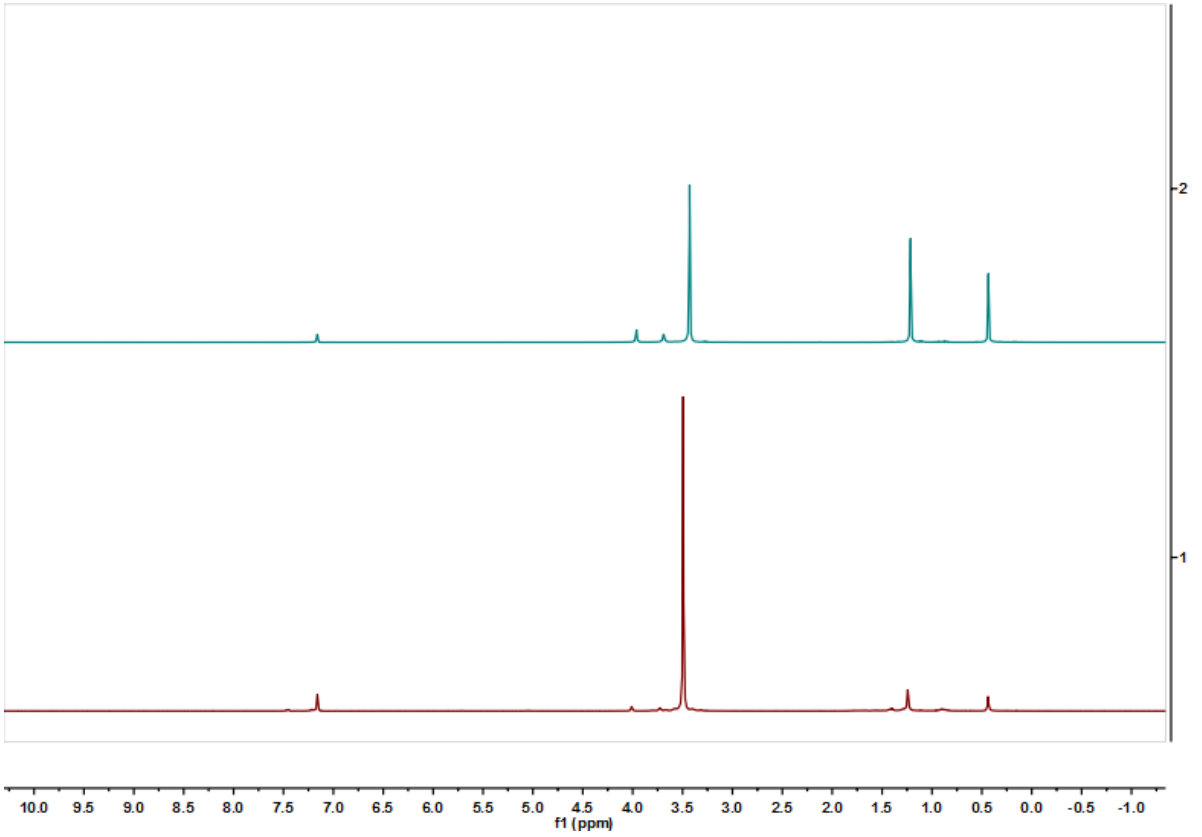


Figure S10. Comparison of ^{1}H NMR (C_6D_6, 500 MHz, 298 K) spectrum of pure **(NN^{TBS})Yb(18-crown-6)** (top) and ^{1}H NMR (C_6D_6, 400 MHz, 298 K) spectrum of supernatant from the reaction of **Yb$_2$-biph-K$_2$** with 18-crown-6 (bottom).

3. X-ray Crystallography

[(NN^{TBS})Sm]$_2$(μ-biphenyl)[K(toluene)]$_2$

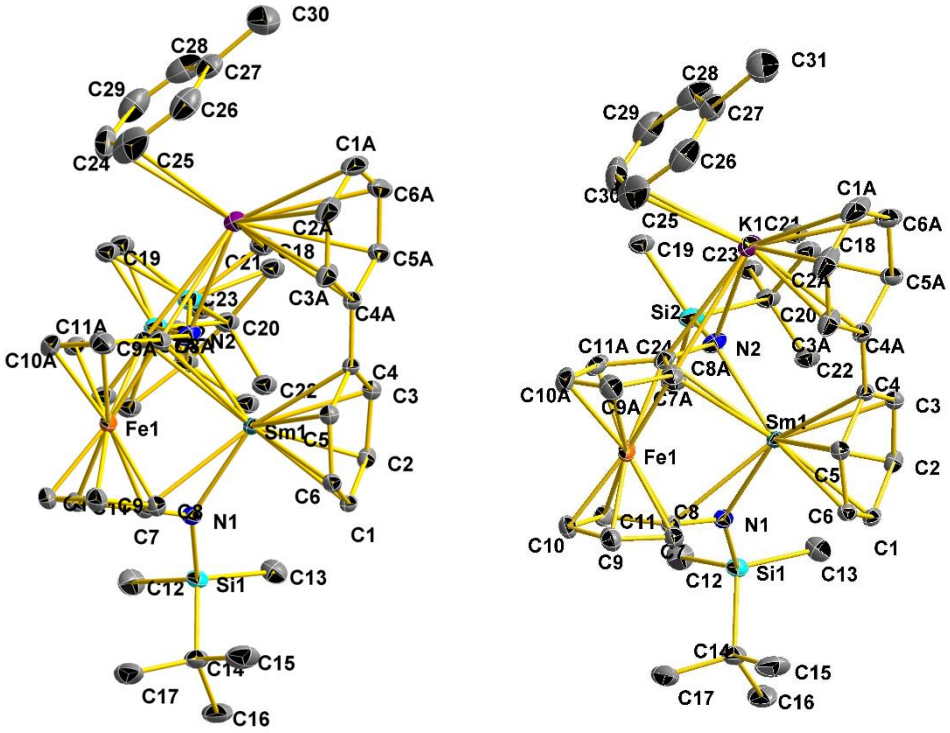


Figure S11. Representation of **Sm$_2$-biph-K$_2$** with thermal ellipsoids set at 50% probability. Left: Hydrogen and solvent atoms were omitted for clarity. Right: Disordered counterparts were also removed for clarity. Selected distances [Å] and angles [º]: Sm1-N1 2.341(6), Sm1-N2 2.452(7), Sm1-C1 2.614(2), Sm1-C2 2.574(3), Sm1-C3 2.639(4), Sm1-C4 2.623(1), Sm1-C5 2.569(7), Sm1-C6 2.639(3), Sm-C$_{centroid}$ 2.196(7), Sm1-Fe1 3.225(2), C1-C2 1.421(5), C2-C3 1.464(6), C3-C4 1.476(1), C4-C5 1.476(1), C5-C6 1.464(6), C6-C1 1.421(5), C4-C4A 1.412(7), C4A-C5A 1.442(2), C5A-C6A 1.389(7), C6A-C1A 1.389(1), C1A-C2A 1.389(1), C2A-C3A 1.389(7), C3A-C4A 1.442(2), K1-N2 2.817(7), K-C$_{centroid}$ 2.813(6); N1-Sm1-N2 103.5(7), C6-C1-C2 120.5(7), C1-C2-C3 120.5(2), C2-C3-C4 120.3(4), C3-C4-C5 117.0(9), C4-C5-C6 120.3(4), torsion angles between C2-C3 and C5-C6 6.3(9). Single crystals suitable for X-ray diffraction were grown from a concentrated toluene solution layered with hexanes. A total of 57096 reflections ($-20 \le h \le 20$, $-30 \le k \le 30$, $-37 \le l \le 37$) were collected at T = 100(2) K with $2\theta_{max}$ = 61.52º, of which 12196 were unique. The residual peak and hole electron density were 1.59 and -1.79 eA^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0347 and GOF = 1.032. Crystal and refinement data for **Sm$_2$-biph-K$_2$**: formula $C_{84}H_{116}N_4Si_4Fe_2Sm_2K_2$, space group $C2/_C$, a = 14.315(4), b = 21.977(6), c = 26.509(9), β = 95.580(3)º, V = 8300(4) Å^3, Z = 4, μ = 1.939 mm^{-1}, F(000) = 3672.0, R_1 = 0.0280 and wR_2 = 0.0611 (based on all data, I > 2σ(I)).

[(NN^{TBS})Sm]$_2$(μ-biphenyl)[K(18-crown-6)$_2$(THF)$_2$]$_2$

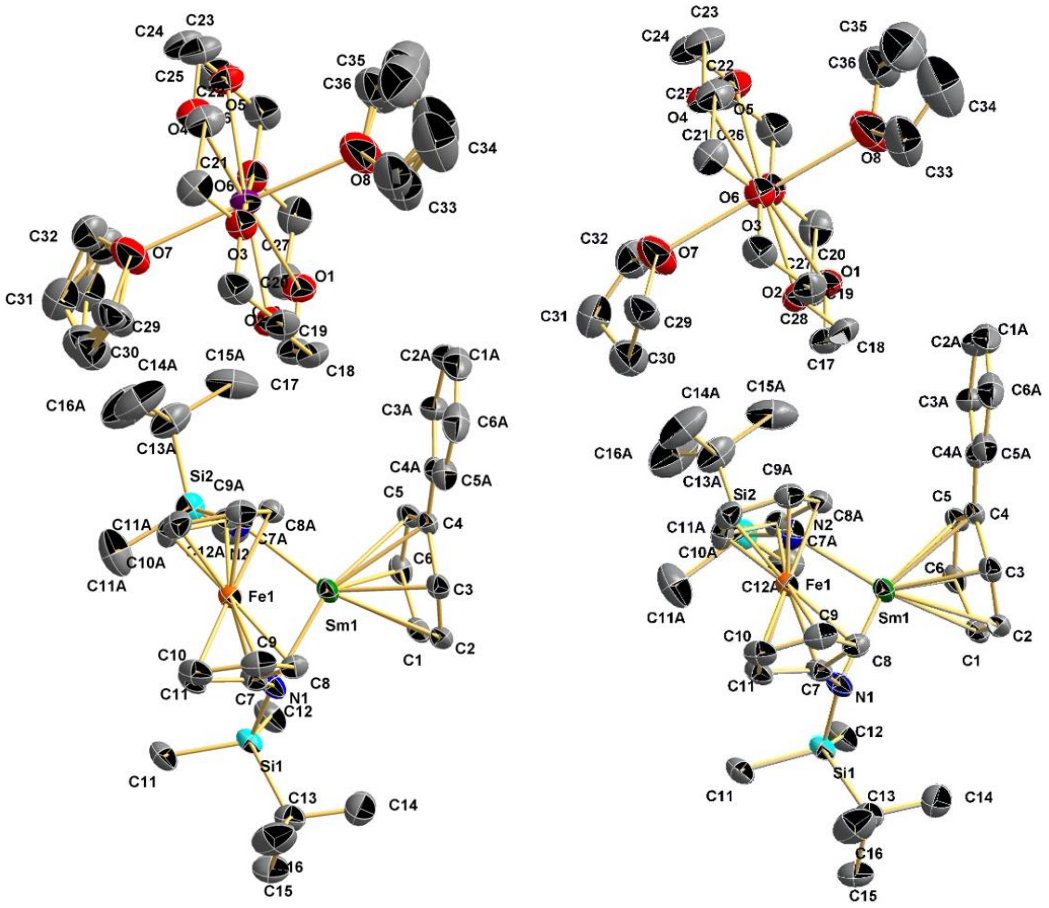


Figure S12. Representation of **Sm$_2$-biph-[K(18-crown-6)]$_2$** with thermal ellipsoids set at 50% probability. Left: Hydrogen and solvent atoms were omitted for clarity. Right: Disordered counterparts were also removed for clarity. Selected distances [Å] and angles [º]: Sm1-N1 2.380(5), Sm1-N2 2.409(2), Sm1-C1 2.603(2), Sm1-C2 2.652(1), Sm1-C3 2.512(3), Sm1-C4 2.615(6), Sm1-C5 2.625(6), Sm1-C6 2.549(4), Sm1-Fe1 3.352(1), Sm-$C_{centroid}$ 2.146(8), C1-C6 1.432(2), C1-C2 1.447(3), C2-C3 1.458(2), C3-C4 1.479(1), C4-C5 1.477(4), C5-C6 1.451(3), C4-C4A 1.439(8), C4A-C5A 1.407(9), C5A-C6A 1.392(1), C6A-C1A 1.374(3), C1A-C2A 1.379(9), C2A-C3A 1.384(2), C3A-C4A 1.4284; N1-Sm1-N2 98.1(3), C6-C1-C2 119.9(7), C1-C2-C3 120.3(1), C2-C3-C4 119.2(4), C3-C4-C5 117.6(1), C4-C5-C6 120.6(9), torsion angles between C2-C3 and C5-C6 10.7(9). Single crystals suitable for X-ray diffraction were grown from a concentrated THF solution layered with *n*-pentane. A total of 27609 reflections ($-19 \leq h \leq 19$, $-20 \leq k \leq 20$, $-36 \leq l \leq 36$) were collected at T = 180 K with $2\theta_{max}$ = 54.97º, of which 22792 were unique. The residual peak and hole electron density were 0.734 and -0.510 eA^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0426 and GOF = 1.032. Crystal and refinement data for **Sm$_2$-biph-[K(18-crown-6)]$_2$**: formula $C_{104}H_{182}Fe_2K_2N_4O_{16}Si_4Sm_2$, space group P-1, a = 15.015(8), b = 15.806(2), c = 28.221(4), α = 83.357(2), β = 79.591(2), γ = 66.665(2)º, V = 6041.8(3) Å^3, Z = 2, μ = 1.360 mm^{-1}, F(000) = 2496.0, R_1 = 0.0313 and wR_2 = 0.0748 (based on all data, I > 2σ(I)).

[(NN^{TBS})Yb]$_2$(μ-biphenyl)[K(Et$_2$O)]$_2$

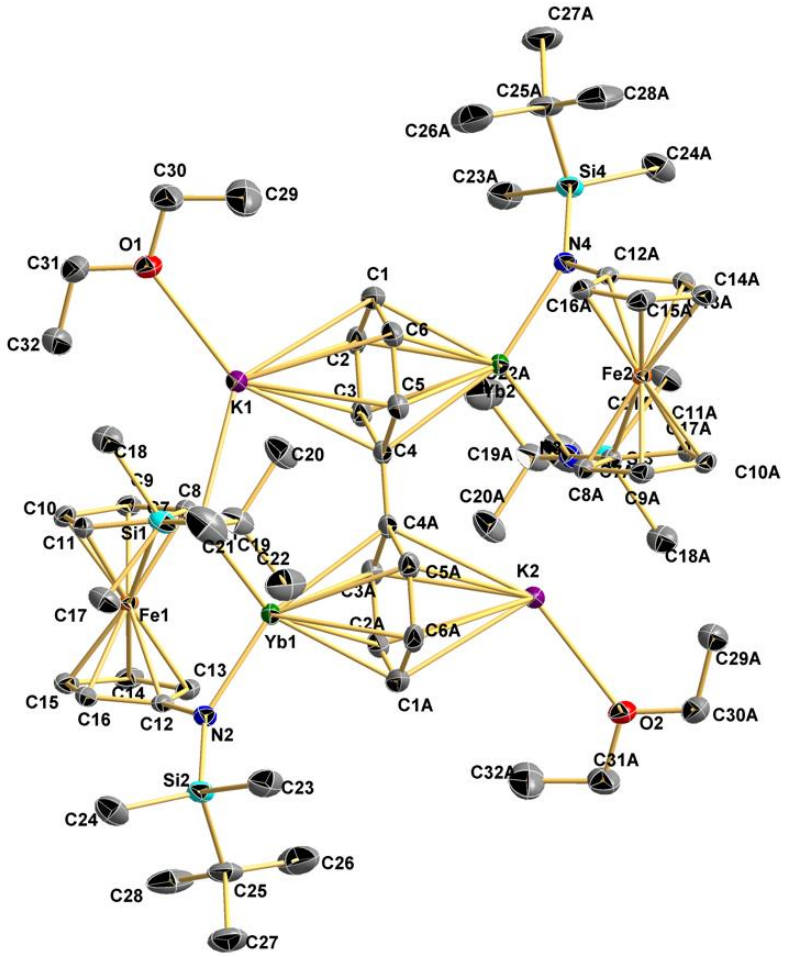


Figure S13. Representation of **Yb$_2$-biph-K$_2$** with thermal ellipsoids set at 50% probability. Hydrogen and solvent atoms were omitted for clarity. Selected distances [Å] and angles [º]: Yb1-N1 2.395 (9), Yb1-N2 2.312(2), Yb1-C1A 2.773(3), Yb1-C2A 2.791(7), Yb1-C3A 2.812(5), Yb1-C4A 2.860(3), Yb1-C5A 2.797(5), Yb1-C6A 2.775(9), Yb1-C$_{centroid}$ 2.415(6), Yb1-Fe1 3.097(7), C1A-C2A 1.413(7), C2A-C3A 1.376(7), C3A-C4A 1.469(8), C4A-C5A 1.471(9), C5A-C6A 1.378(8), C6A-C1A 1.412(1), K1-C$_{centroid}$ 2.829(8); N1-Yb1-N2 104.2(1), C6A-C1A-C2A 116.9(8), C1A-C2A-C3A 122.5(8), C2A-C3A-C4A 122.2(2), C3A-C4A-C5A 113.4(8), C4A-C5A-C6A 122.1(9). Single crystals suitable for X-ray diffraction were grown from a concentrated Et$_2$O solution layered with *n*-pentane. A total of 40803 reflections ($-18 \leq h \leq 18$, $-26 \leq k \leq 25$, $-20 \leq l \leq 20$) were collected at T = 100(2) K with $2\theta_{max} = 61.42$º, of which 10446 were unique. The residual peak and hole electron density were 2.77 and -1.13 eA^{-3}. The least-squares refinement converged normally with residuals of $R_1 = 0.0365$ and GOF = 1.104. Crystal and refinement data for **Yb$_2$-biph-K$_2$**: formula $C_{64}H_{106}Fe_2K_2N_4O_2Si_4Yb_2$, space group $P2_1/n$, a = 13.246(7), b = 18.780(2), c = 14.543(6), β = 100.579(0)º, V = 3556.6(7) Å^3, Z = 2, μ = 3.231 mm^{-1}, F(000) = 1640.0, $R_1 = 0.0297$ and $wR_2 = 0.0645$ (based on all data, $I > 2\sigma(I)$).

(NN^{TBS})Yb(THF)$_3$

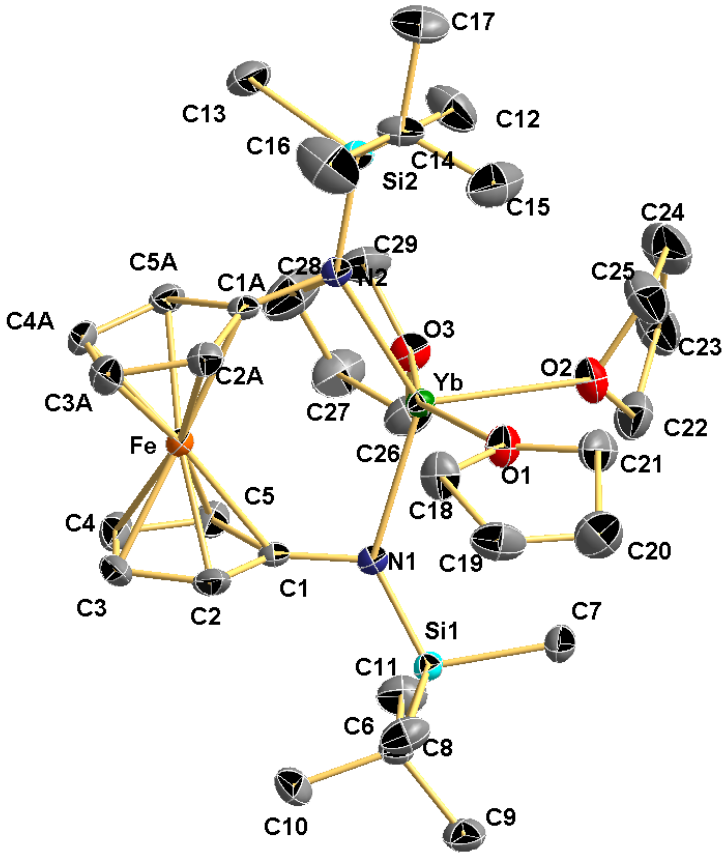


Figure S14. Representation of **(NN^{TBS})Yb(THF)$_3$** with thermal ellipsoids set at 50% probability. Hydrogen and solvent atoms were omitted for clarity. Selected distances [Å] and angles [º]: Yb-N1 2.324(5), Yb-N2 2.332(6), Yb-O1 2.454 (1), Yb-O2 2.487(1), Yb-O3 2.465(5), Yb-Fe 3.447(3); N1-Yb-N2 130.5(9), O1-Yb-O2 76.8(2), O2-Yb-O3 78.3(4), O1-Yb-N1 91.4(3). Single crystals suitable for X-ray diffraction were grown from a concentrated THF solution layered with hexanes. A total of 50496 reflections ($-18 \le h \le 18$, $-20 \le k \le 20$, $-22 \le l \le 22$) were collected at T = 180 K with $2\theta_{max} = 54.96$º, of which 8606 were unique. The residual peak and hole electron density were 0.59 and -0.40 eA^{-3}. The least-squares refinement converged normally with residuals of $R_1 = 0.0183$ and GOF = 1.033. Crystal and refinement data for **(NN^{TBS})Yb(THF)$_3$**: formula $C_{34}H_{62}FeN_2O_3Si_2Yb$, space group $P2_12_12_1$, a = 13.972(3), b = 15.853(9), c = 16.985(8), V = 3762.6 (3) Å^3, Z = 4, μ = 2.953 mm^{-1}, F(000) =1712.0, R_1 = 0.0175 and wR_2 = 0.0399 (based on all data, I > 2σ(I)).

[(NN^{TBS})Yb(THF)]$_2$

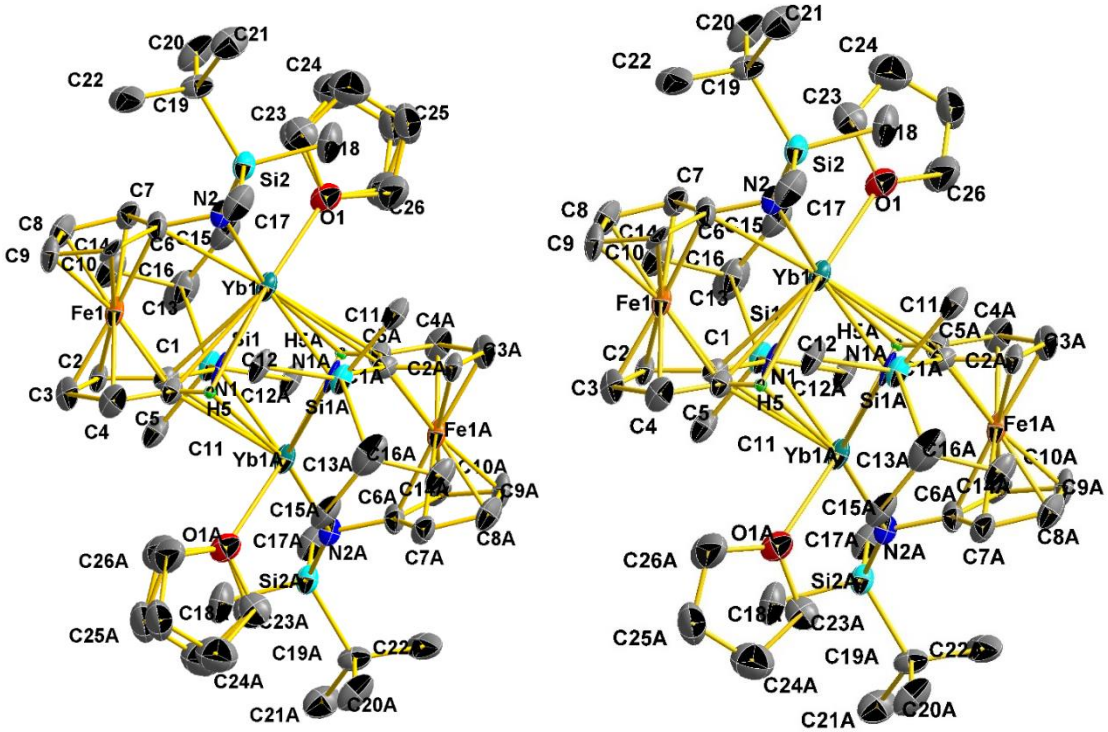


Figure S15. Representation of **[(NN^{TBS})Yb(THF)]$_2$** with thermal ellipsoids set at 50% probability. Left: Hydrogen and solvent atoms were omitted for clarity. Right: Disordered counterparts were also removed for clarity. Agostic H5 was located in the electron diffraction map. Selected distances [Å] and angles [º]: Yb1-N1 2.360(5), Yb1-N2 2.558(7), Yb1-N2A 2.514(8), Yb1-O1 2.443(1), Yb1-Fe1 3.251(4), Yb1-C5 3.019(6), Yb1-H5 2.747(8); N1-Yb1-N2 133.8(5), N2-Yb1-N3 87.2(9), Yb1-N2-Yb2 92.7(1). Single crystals suitable for X-ray diffraction were grown from a concentrated ether solution layered with hexanes. A total of 10641 reflections ($-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $-14 \leq l \leq 14$) were collected at T = 180 K with $2\theta_{max} = 50.05º$, of which 10641 were unique. The residual peak and hole electron density were 5.96 and -2.08 eA^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0845 and GOF = 1.064. Crystal and refinement data for **[(NN^{TBS})Yb(THF)]$_2$**: formula $C_{52}H_{92}Fe_2N_4O_2Si_4Yb_2$, space group P-1, a = 11.555(4), b = 12.381(3), c = 12.451(3), α = 112.215(5), β = 96.684(4), γ = 113.262(4)º, V = 1439.25(13) Å^3, Z = 1, μ = 3.837 mm^{-1}, F(000) = 696.0, R_1 = 0.0752 and wR_2 = 0.1838 (based on all data, $I > 2\sigma(I)$).

(NN^{TBS})Yb(κ^3-18-crown-6)

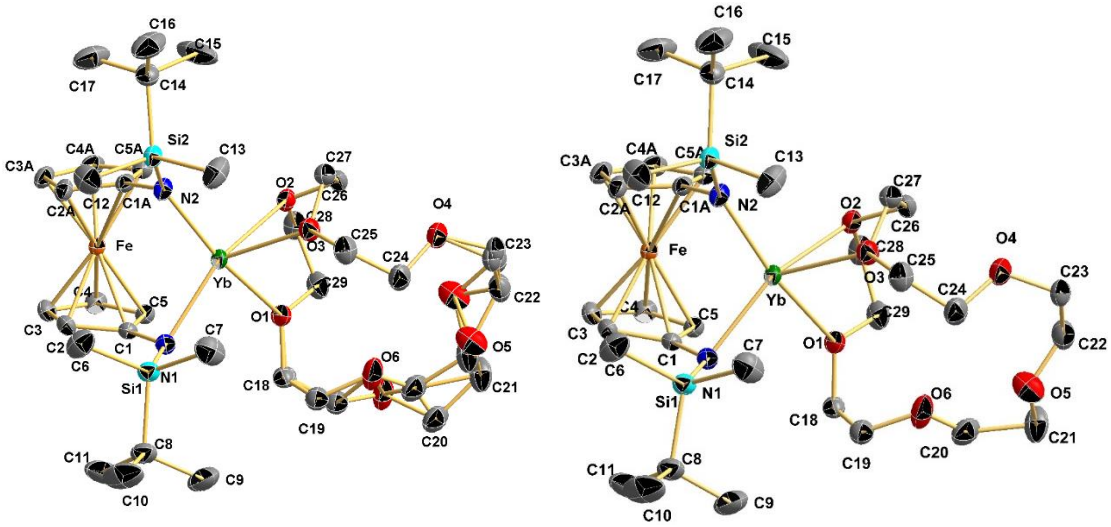


Figure S16. Representation of **(NN^{TBS})Yb(κ^3-18-crown-6)** with thermal ellipsoids set at 50% probability. Left: Hydrogen and solvent atoms were omitted for clarity. Right: Disordered counterparts were also removed for clarity. Selected distances [Å] and angles [º]: Yb-N1 2.351(7), Yb-N2 2.337(3), Yb-O1 2.568(4), Yb-O2 2.507(1), Yb-O3 2.526(9), Yb-Fe 3.203(8); N1-Yb-N2 104.9(5). Single crystals suitable for X-ray diffraction were grown from a concentrated ether solution layered with hexanes. A total of 26121 reflections ($-14 \leq h \leq 14$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$) were collected at T = 180 K with $2\theta_{max}$ = 54.97º, of which 9033 were unique. The residual peak and hole electron density were 0.78 and -0.44 eA^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0244 and GOF = 1.025. Crystal and refinement data for **(NN^{TBS})Yb(κ^3-18-crown-6)**: formula $C_{34}H_{62}FeN_2O_6Si_2Yb$, space group P-1, a = 11.314(5), b = 13.037(4), c = 14.243(2), α = 87.291(0), β = 81.628(0), γ = 71.282(2)º, V = 1968.71(6) Å^3, Z = 2, μ = 2.832 mm^{-1}, F(000) = 904.0, R_1 = 0.0214 and wR_2 = 0.0533 (based on all data, I > 2σ(I)).

(NN^{TBS})Yb(κ^4-18-crown-6)

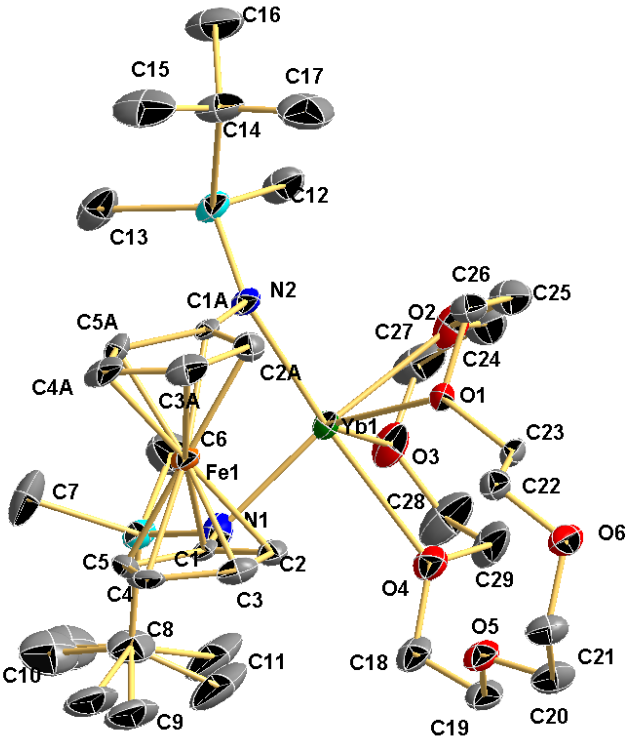


Figure S17. Representation of **(NN^{TBS})Yb(κ^4-18-crown-6)** with thermal ellipsoids set at 50% probability. Hydrogen and solvent atoms were omitted for clarity. Selected distances [Å] and angles [º]: Yb-N1 2.376(7), Yb-N2 2.370(7), Yb-O1 2.524(3), Yb-O2 2.568(4), Yb-O3 2.674(0), Yb-O4 2.693(4), Yb-Fe 3.438(3); N1-Yb-N2 103.2(9). Single crystals suitable for X-ray diffraction were grown from a concentrated ether solution layered with hexanes. A total of 29463 reflections ($-13 \leq h \leq 13$, $-42 \leq k \leq 42$, $-15 \leq l \leq 15$) were collected at T = 180 K with $2\theta_{max} = 54.97$º, of which 16431 were unique. The residual peak and hole electron density were 1.43 and -1.44 eA^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0524 and GOF = 1.017. Crystal and refinement data for **(NN^{TBS})Yb(κ^4-18-crown-6)**: formula $C_{34}H_{62}FeN_2O_6Si_2Yb$, space group $P2_1$, a = 10.201(0), b = 33.041(4), c = 12.173(9), β = 105.418(3)º, V = 3955.6(2) Å^3, Z = 4, μ = 2.819 mm^{-1}, F(000) = 1808.0, R_1 = 0.0439 and wR_2 = 0.0829 (based on all data, I > 2σ(I)).

4. X-ray Absorption Near-Edge Structure (XANES) Spectroscopy

X-ray absorption measurements were acquired on the bending magnet beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. The data was collected in transmission step scan mode. Photon energies were selected using a water-cooled, double-crystal Si(111) monochromator, which was detuned by approximately 50% to reduce harmonic reflections. The ionization chambers were optimized for the maximum current with linear response (~10^{10} photons detected/sec) with 10% absorption in the incident ion chamber and 70% absorption in the transmission and fluorescent X-ray detector. Mn foil (6.5390 KeV) and Cu foil (8.9789 KeV) were used to calibrate the energy for Sm and Yb measurements, respectively. Reference compounds were ordered from Sigma-Aldrich and used as received.

Air sensitive samples were prepared in a glove box diluted with boron nitride to give an adsorption edge of about 0.5-1.0. The samples were sealed in an environmental cell to exclude exposure to air and water. The edge energy was determined from the inflection point in the edge, i.e., the maximum in the first derivative of the XANES spectrum. Background and normalization procedures were carried out using the Athena software package using standard methods, i.e., a linear fit to the pre-edge and a 3rd order polynomial for the post edge region.

Note. The XANES study is inconclusive due to the presence of shoulders (additional peaks) in the spectra of **Sm_2-biph-K_2** and **Yb_2-biph-K_2**. These additional peaks (at the position of Sm(II) in the **Sm_2-biph-K_2** spectrum and at the position of Yb(III) in the **Yb_2-biph-K_2** spectrum) cannot be rationalized by the current data. A detailed analysis with appropriate control studies will be pursued in the future and reported in due course.

Table S1. Sm L_3-edge XANES data.

Compounds	L_3-Edge Peak Position (eV)	Oxidation State
Sm_2O_3	6723.0	III
$SmBr_3(THF)_4$	6722.5	III
$(\eta^5\text{-}C_5H_5)_3Sm$	6722.5	III
SmI_2	6714.5	II
Sm_2-biph-K_2	***6722.5***	***III***
$(NN^{TBS})SmI(THF)_2$	6722.5	III

Table S2. Yb L_3-edge XANES data.

Compounds	L_3-Edge Peak Position (eV)	Oxidation State
Yb_2O_3	8947.5	III
$(\eta^5\text{-}C_5H_5)_3Yb$	8947.0	III
YbI_2	8939.0	II
Yb_2-biph-K_2	***8939.5***	***II***
$(NN^{TBS})YbI(THF)_2$	8946.5	III

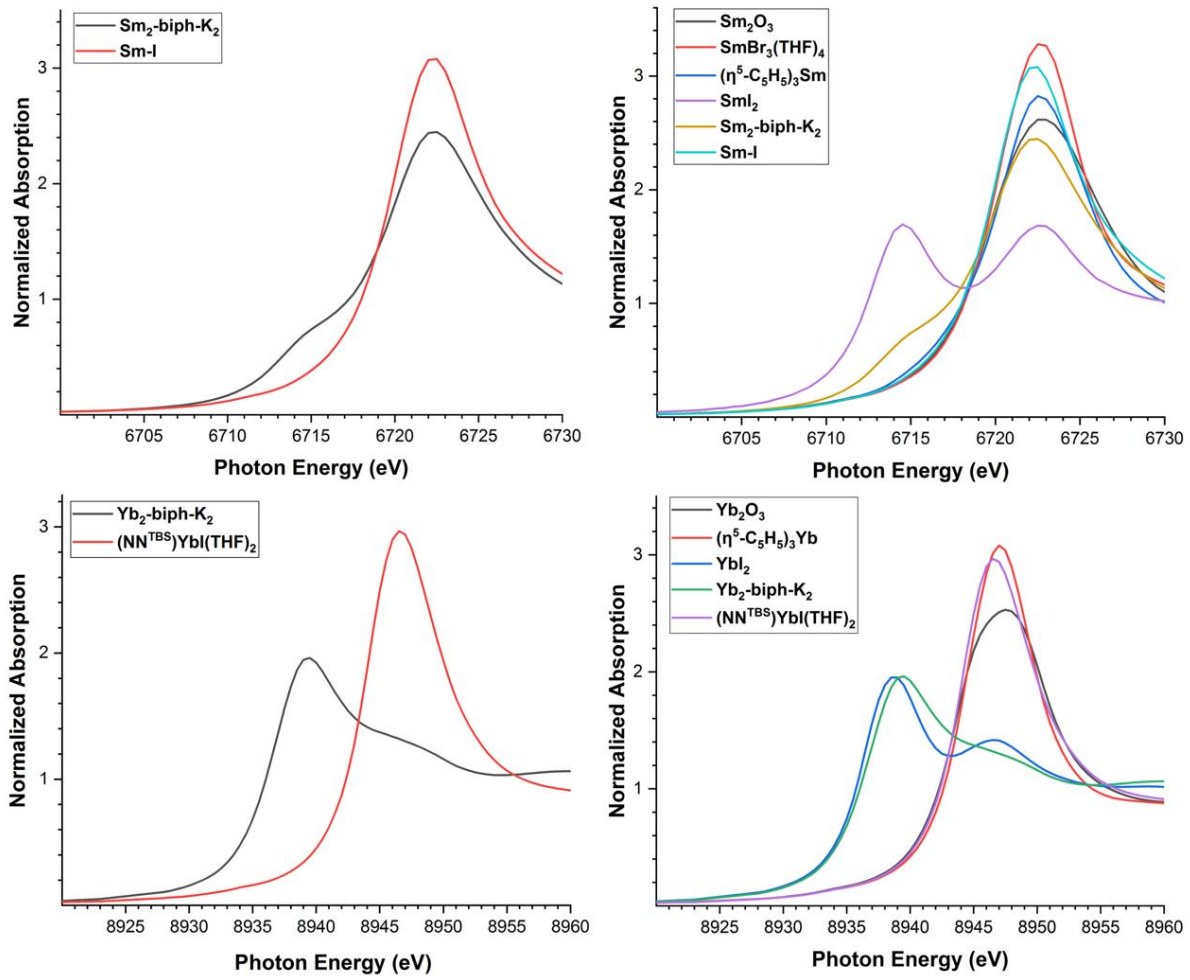


Figure S18. Normalized L_3-edge XANES spectra of Sm and Yb compounds.

5. DFT Calculations

The density functional theory (DFT) calculations were performed with ADF 2019 [ADF 2019.301 http://www.scm.com]; the scalar relativistic effects were taken into account at the zero-order regular approximation (ZORA).[5] The Slater-type-orbital (STO) basis sets with the quality of triple-ζ plus polarization functions (TZP) and double-ζ plus polarization functions (DZP) were used.[6] The frozen core approximations were applied to the [$1s^2$] shell of C, N and O, [$1s^2$-$2p^6$] shells of Si, K and Fe, [$1s^2$-$4d^{10}$] shells of Sm and Yb. The hybrid PBE0 functional[7] with the corresponding dispersion correction[8] was used to determine equilibrium geometries and vibrational frequencies of all the molecules in their ground states.

In the Gaussian 16 calculations [Gaussian 16, Revision C.01], the natural bond orbitals (NBO) analysis[9] was performed by using the PBE0 functional with 6-31+G* basis sets for the C, H, N, O, and Si, SDD basis set[10] for K and Fe. The Stuttgart energy-consistent relativistic pseudopotential ECP28MWB[11] with the corresponding ECP28MWB_SEG basis set[12] were used for Sm and Yb.

Principal interacting orbital (PIO) analysis, a novel approach to identifying the dominant interacting orbitals based on fragment orbital interactions, allows to understand the electronic structure of whole large molecules from the fragment point of view.

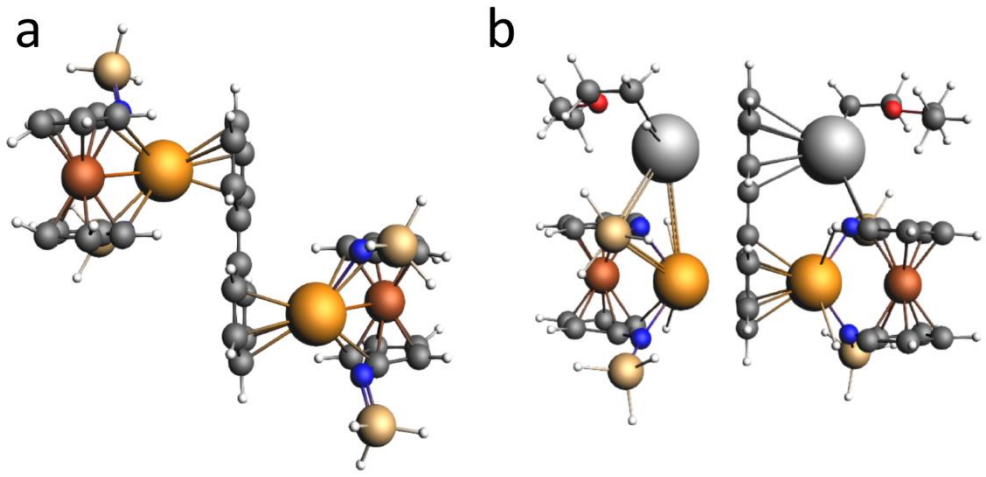


Figure S19. Two hypothetical compounds **$(Sm_2\text{-biph})_{iso}^{2-}$** (in **$(Sm_2\text{-biph})_{iso}^{2-}$**, the two Sm ions are bound to different phenyl rings, a) and **$[Yb_2\text{-biph-}K_2]_{iso}$** (in **$[Yb_2\text{-biph-}K_2]_{iso}$**, the two Yb ions are bound to the same phenyl ring while the two potassium ions are bonded to the other phenyl ring, b). All the alkyl substituents on the silicon atoms were replaced by hydrogen atoms for simplification.

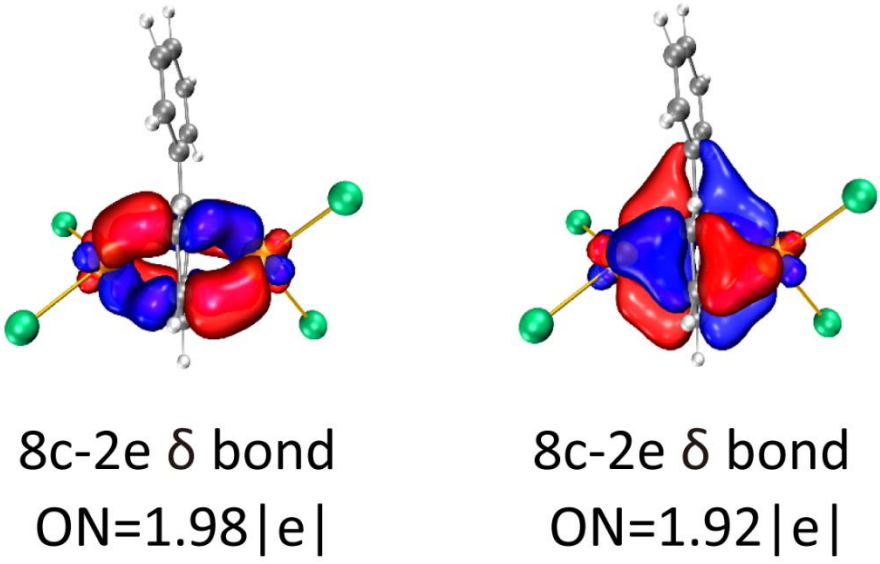


Figure S20. AdNDP bonding analyses for **$(Sm_2\text{-biph})^{2-}$** at the PBE0/6-31+G* level. Occupation numbers (ON) are shown. The NN^{TBS} ligands were replaced by chlorine atoms for balancing the charges and simplification.

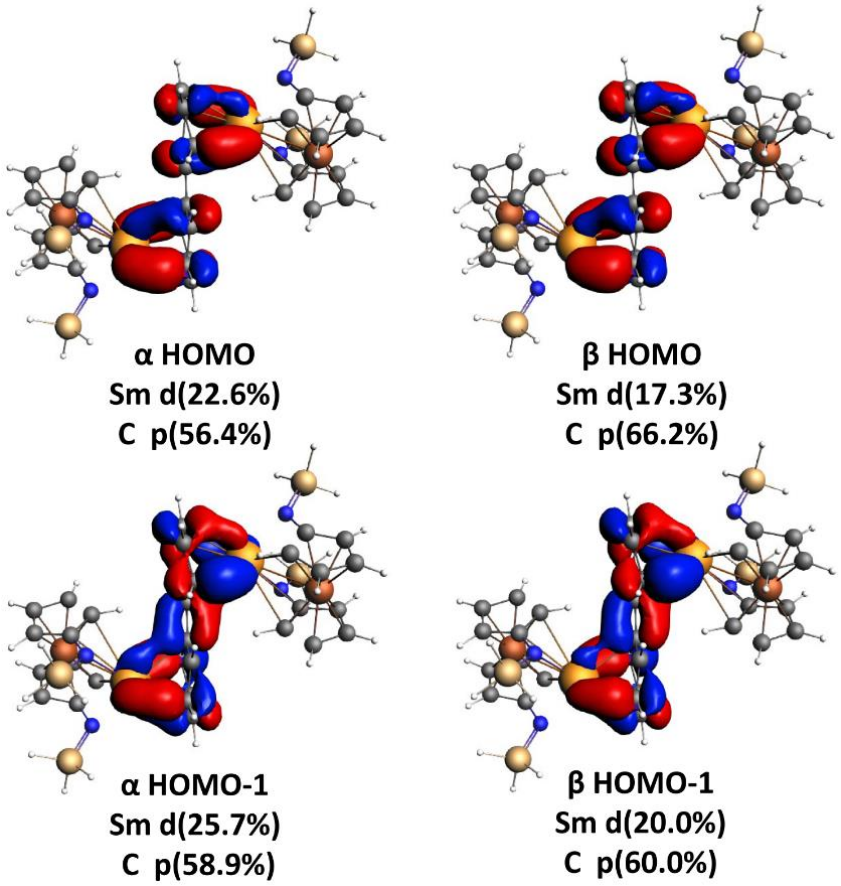


Figure S21. The contours of HOMO and HOMO-1 Kohn-Sham MOs and main AO contributions of $\mathbf{(Sm_2\text{-}biph)_{iso}^{2-}}$. All the alkyl substituents on the silicon atoms were replaced by hydrogen atoms for simplification (iso = 0.03).

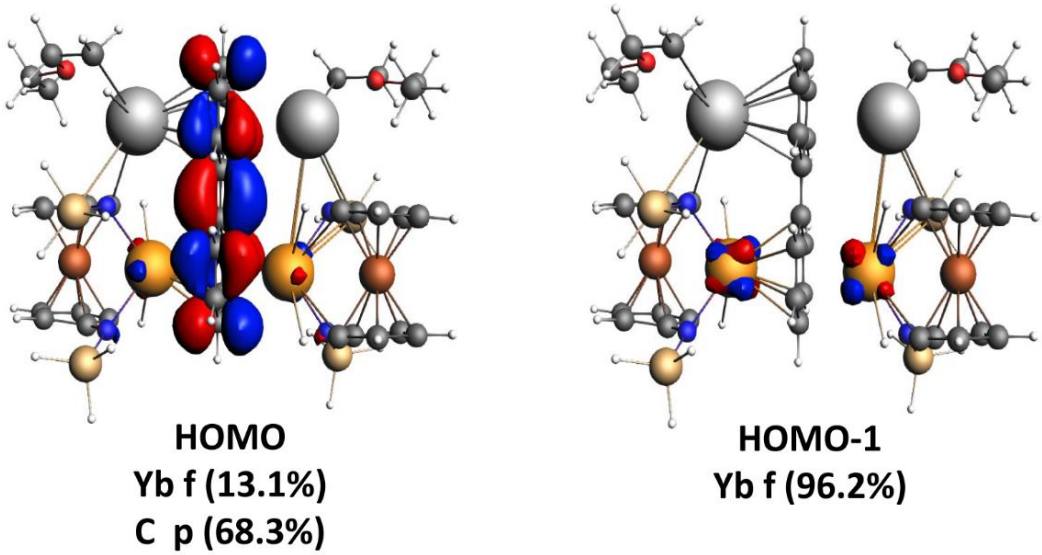


Figure S22. The contours of HOMO and HOMO-1 Kohn-Sham MOs and main AO contributions of $\mathbf{[Yb_2\text{-}biph\text{-}K_2]_{iso}}$. All the alkyl substituents on the silicon atoms were replaced by hydrogen atoms for simplification (iso = 0.03).

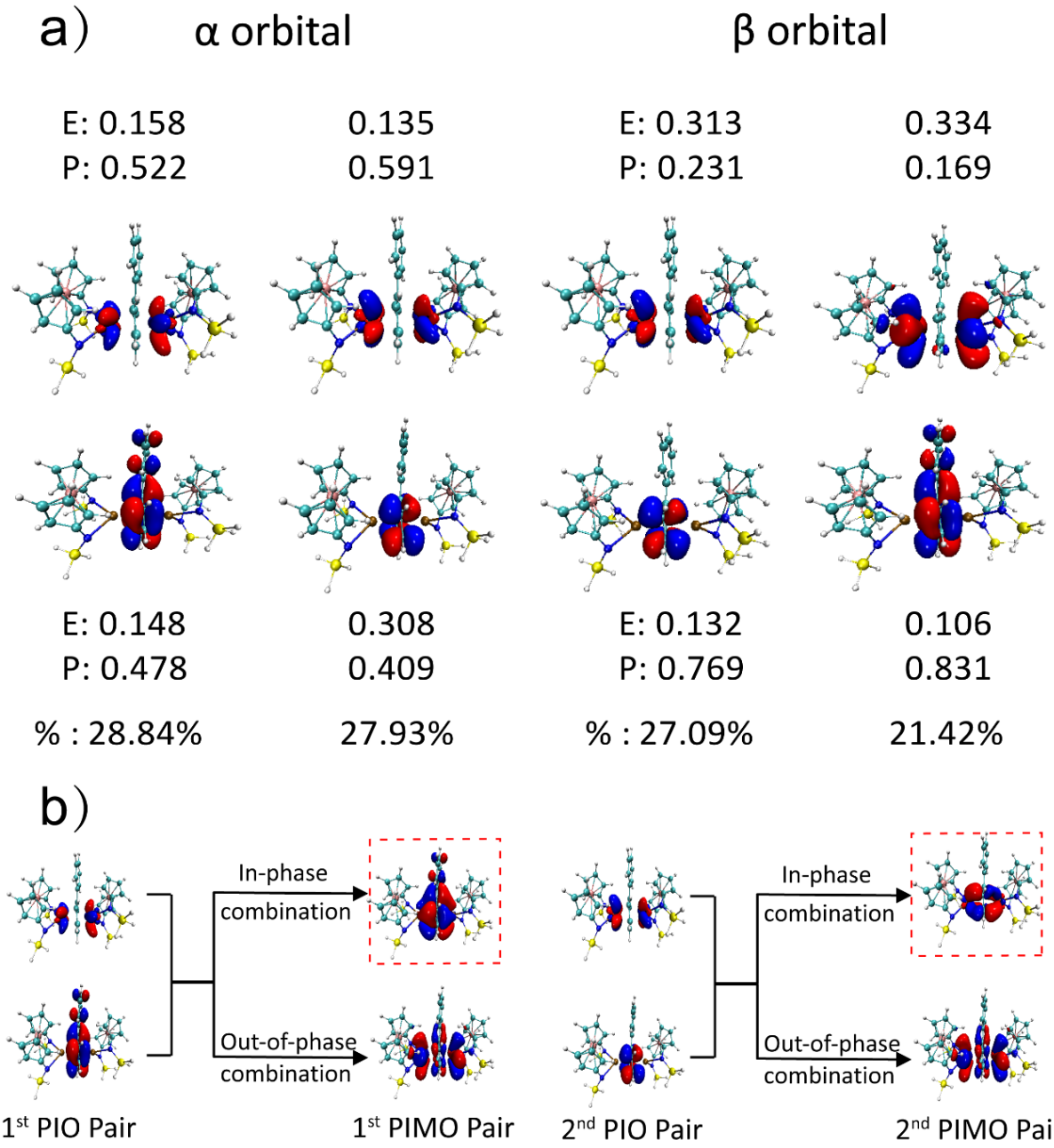


Figure S23. Results of principal interacting orbital (PIO) analysis for **(Sm$_2$-biph)$^{2-}$** at the PBE0/def2-pVTZ level. a) The top two PIOs for α and β, respectively, between two fragments. The orbital energies and populations (occupation numbers) are given as E and P respectively. Each pair's contribution (as %) to the total interactions between two fragments is also shown. b) The top two principal interacting molecular orbital (PIMO) pairs and their relationship with the corresponding PIO pair. Note that the phase of each PIO is naturally paired up with its counterpart. Isovalue: 0.03 for all orbitals.

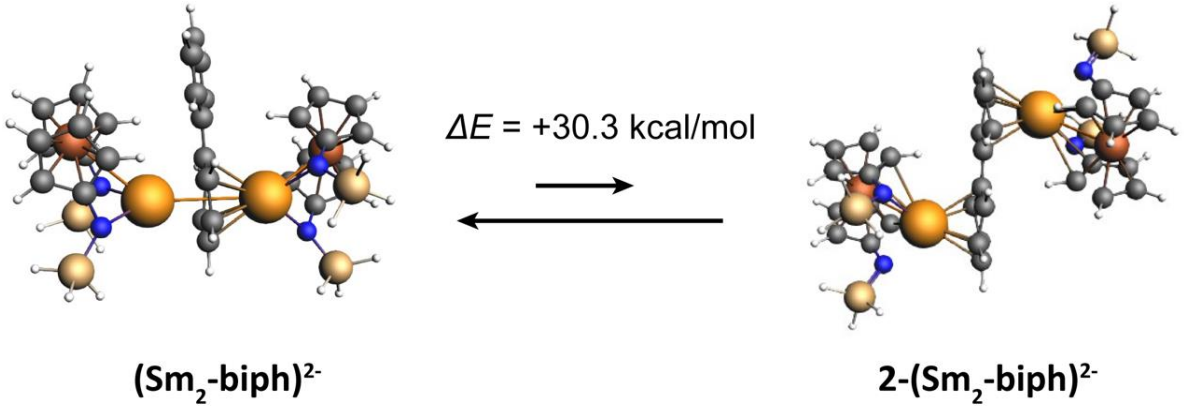
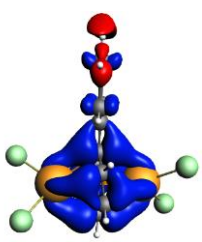
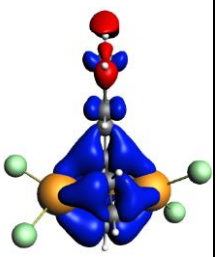
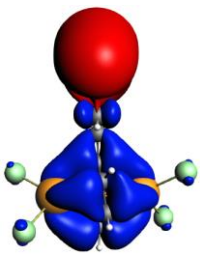
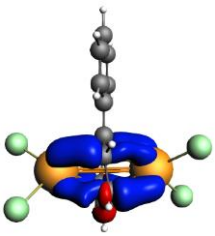
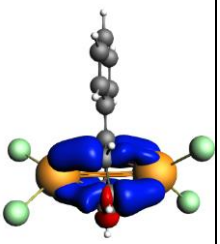
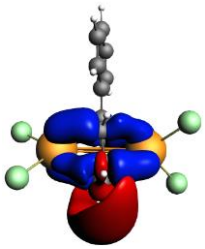
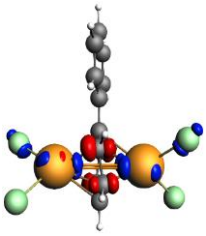
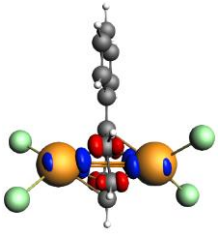
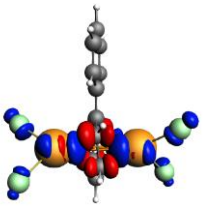


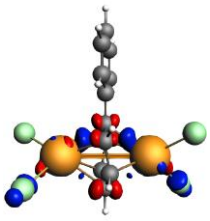
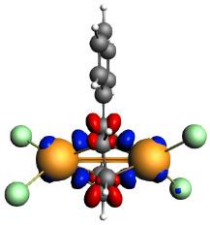
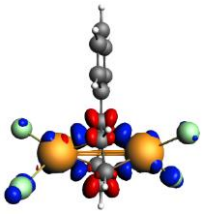
Figure S24. The calculated energy difference between the two isomers of the tetraanionic-substituted benzene complex **$(Sm_2\text{-biph})^{2-}$** and a hypothetical tetraanionic biphenyl complex, in which each ring coordinated to samarium is dianionic, **$(Sm_2\text{-biph})_{iso}^{2-}$**.

Table S3. Comparison of experimental and computationally optimized geometries. **Sm**, **Sm_{iso}**, **Yb**, and **Yb_{iso}** represent **$(Sm_2\text{-biph})^{2-}$**, **$(Sm_2\text{-biph})_{iso}^{2-}$**, **$Yb_2\text{-biph-}K_2$**, and **$[Yb_2\text{-biph-}K_2]_{iso}$**, respectively. For **Sm**, C1-C4 is in Sm-bound phenyl ring and C1A-C4A is in the non-bound phenyl ring; for **2-Sm**, each ring is coordinated by one Sm ion; for **Yb**, each ring is coordinated by one Yb ion; for **2-Yb**, C1-C4 is part of the Yb-bound phenyl ring and C1A-C4A is in the non-bound phenyl ring.

	Exp. Sm	**Sm**	**Sm_{iso}**	**Exp. Yb**	**Yb**	**Yb_{iso}**
C1A-C2A	1.374(3)	1.397	1.373	1.413(7)	1.422	1.416
C2A-C3A	1.392(1)	1.388	1.457	1.376(7)	1.384	1.383
C3A-C4A	1.407(9)	1.422	1.497	1.469(8)	1.472	1.459
Average C-C	1.391(4)	1.402	1.443	1.420(9)	1.426	1.419
C4-C4A	1.439(8)	1.443	1.459	1.396(0)	1.391	1.398
C3-C4	1.479(1)	1.487	1.390	1.471(9)	1.472	1.482
C2-C3	1.458(2)	1.470	1.446	1.378(8)	1.384	1.387
C1-C2	1.447(3)	1.451	1.461	1.412(1)	1.423	1.430
Average C-C	1.461(5)	1.469	1.432	1.420(9)	1.427	1.433
$M\text{-}C_{centroid}$	2.150(4)	2.102	2.188	2.415(6)	2.358	2.344
M-N1	2.380(5)	2.422	2.401	2.395(9)	2.383	2.386
M-N2	2.409(2)	2.393	2.405	2.312(2)	2.306	2.302
torsion angle	10.7(9)	10.2	20.5	0.0(8)	0.1	0.3
N1-M-N2	98.1(3)	92.4	94.9	104.2(1)	104.8	101.4

Table S4. Energy decomposition analysis of **$(Sm_2\text{-biph})^{2-}$** at the PBE0/TZP level and the associated deformation densities Δρ of the most important pairwise orbital interactions ΔE_{orb} (isosurfaces = 0.0015 au). The NN^{TBS} ligands were replaced by chlorine atoms for balancing the charges and simplification. The direction of the charge flow is red to blue. Energy values are given in kcal·mol^{-1}.

fragments	$(Sm_2Cl_4)^{2+}$: ^{11}B (f^{10})		$(biphenyl)^{4-}$: ^1A
ΔE_{int}	-1131.41		
ΔE_{Pauli}	598.85		
ΔE_{elstat}[a]	-1049.64 (60.66%)		
ΔE_{orb}[a]	-671.97 (38.84%)		
ΔE_{disp}[a]	-8.64 (0.50%)		
	α	β	$\alpha + \beta$
$\Delta E_{orb(\delta_2)}$[b]			
	-138.11	-140.64	-278.75 (41.48%)
$\Delta E_{orb(\delta_1)}$[b]			
	-97.85	-94.92	-192.77 (28.69%)
$\Delta E_{orb(\pi_2^*)}$[b]			
	-17.28	-17.20	-34.48 (5.13%)

$\Delta E_{orb(\pi_1^*)}$[b]			
	-12.41	-16.80	-29.21 (4.35%)

[a]The value in parentheses gives the percentage contribution to the total attractive interaction, $\Delta E_{elstat}+\Delta E_{orb}+\Delta E_{disp}$.

[b]The value in parentheses gives the percentage contribution to the total orbital interaction, ΔE_{orb}.

Table S5. Natural population analysis for **$(Sm_2\text{-biph})^{2-}$** (with the alkyl substituents on the silicon atoms being replaced by methyl groups).

Atom	No	Natural charge	Core	Valence	Rydberg	Total	Natural spin density
Sm	1	1.43180	53.99575	6.51060	0.06184	60.56820	5.40265
N	2	-1.18837	1.99997	6.17410	0.01430	8.18837	-0.01044
N	3	-1.19297	1.99997	6.17889	0.01411	8.19297	-0.00911
H	4	0.27775	0.00000	0.72018	0.00207	0.72225	0.00005
C	5	-0.50538	1.99996	4.47835	0.02707	6.50538	-0.05633
C	6	-0.52281	1.99996	4.49567	0.02718	6.52281	-0.11532
C	7	-0.55382	1.99996	4.52920	0.02466	6.55382	-0.13674
C	8	-0.29517	1.99996	4.27260	0.02260	6.29517	-0.07354
C	9	-0.54287	1.99996	4.51742	0.02549	6.54287	-0.14790
C	10	-0.50841	1.99996	4.48170	0.02675	6.50841	-0.10241
Si	11	1.07549	9.99993	2.87610	0.04848	12.92451	-0.00022
C	12	0.13838	1.99997	3.83172	0.02994	5.86162	0.00112
Si	13	1.07612	9.99993	2.87552	0.04843	12.92388	-0.00051
C	14	0.14336	1.99997	3.82666	0.03001	5.85664	-0.00189
Fe	15	0.31834	17.99959	7.60531	0.07675	25.68166	-0.00004
C	16	-0.33842	1.99996	4.31776	0.02069	6.33842	0.00007
Sm	17	1.46287	53.99573	6.47965	0.06175	60.53713	5.37728
H	18	0.27308	0.00000	0.72625	0.00067	0.72692	0.00298
H	19	0.27523	0.00000	0.72401	0.00076	0.72477	0.00395
H	20	0.26933	0.00000	0.72959	0.00108	0.73067	0.00391
H	21	0.27162	0.00000	0.72737	0.00101	0.72838	0.00416
H	22	0.27583	0.00000	0.72338	0.00080	0.72417	0.00375
C	23	-0.34919	1.99996	4.32926	0.01996	6.34919	-0.00363
C	24	-0.34633	1.99997	4.32810	0.01826	6.34633	-0.00038
C	25	-0.34536	1.99997	4.32707	0.01832	6.34536	0.00141
H	26	0.27261	0.00000	0.72592	0.00146	0.72739	0.00012
C	27	-0.31902	1.99997	4.29844	0.02061	6.31902	0.00145
H	28	0.25042	0.00000	0.74842	0.00116	0.74958	-0.00005
C	29	-0.31893	1.99997	4.29844	0.02052	6.31893	-0.00127
H	30	0.24427	0.00000	0.75444	0.00129	0.75573	-0.00014
H	31	0.25609	0.00000	0.74290	0.00101	0.74391	0.00002
C	32	-0.31021	1.99997	4.28940	0.02085	6.31021	-0.00030
H	33	0.25286	0.00000	0.74588	0.00125	0.74714	0.00000
C	34	-0.31881	1.99997	4.29840	0.02044	6.31881	-0.00078
H	35	0.24350	0.00000	0.75522	0.00128	0.75650	-0.00005
H	36	0.25552	0.00000	0.74348	0.00100	0.74448	-0.00003
N	37	-1.19749	1.99997	6.18353	0.01399	8.19749	-0.00819
N	38	-1.19939	1.99997	6.18535	0.01407	8.19939	-0.00495
Si	39	1.07813	9.99993	2.87354	0.04840	12.92187	-0.00002

C	40	0.13939	1.99997	3.83079	0.02985	5.86061	0.00184
Si	41	1.07834	9.99993	2.87327	0.04845	12.92166	-0.00017
C	42	0.13971	1.99997	3.83053	0.02980	5.86029	-0.00108
Fe	43	0.31588	17.99959	7.60641	0.07813	25.68412	-0.00286
C	44	-0.34495	1.99997	4.32669	0.01829	6.34495	-0.00160
C	45	-0.33614	1.99996	4.31564	0.02053	6.33614	-0.00148
C	46	-0.34553	1.99997	4.32731	0.01825	6.34553	0.00099
C	47	-0.34794	1.99996	4.32813	0.01985	6.34794	-0.00194
H	48	0.25539	0.00000	0.74363	0.00098	0.74461	0.00006
C	49	-0.31917	1.99997	4.29888	0.02032	6.31917	-0.00023
H	50	0.24330	0.00000	0.75543	0.00127	0.75670	-0.00013
C	51	-0.30800	1.99997	4.28715	0.02088	6.30800	0.00063
H	52	0.25778	0.00000	0.74094	0.00128	0.74222	-0.00001
H	53	0.27549	0.00000	0.72217	0.00235	0.72451	0.00000
H	54	0.25602	0.00000	0.74300	0.00099	0.74398	-0.00003
C	55	-0.31881	1.99997	4.29841	0.02043	6.31881	-0.00075
H	56	0.24418	0.00000	0.75452	0.00129	0.75582	-0.00013
C	57	-0.31661	1.99997	4.29607	0.02057	6.31661	-0.00034
H	58	0.25223	0.00000	0.74656	0.00120	0.74777	-0.00001
H	59	0.26900	0.00000	0.72956	0.00144	0.73100	0.00004
C	60	-0.05589	1.99997	4.03824	0.01768	6.05589	0.00718
C	61	-0.28104	1.99997	4.26671	0.01435	6.28104	-0.05261
C	62	-0.25632	1.99998	4.24224	0.01410	6.25632	-0.05102
C	63	-0.24451	1.99998	4.22983	0.01470	6.24451	0.02364
H	64	0.24212	0.00000	0.75671	0.00116	0.75788	0.00166
C	65	-0.24882	1.99998	4.23414	0.01470	6.24882	0.02202
H	66	0.23586	0.00000	0.76304	0.00111	0.76414	0.00163
C	67	-0.31627	1.99998	4.30127	0.01501	6.31627	-0.07208
H	68	0.22614	0.00000	0.77271	0.00116	0.77386	-0.00075
H	69	0.22605	0.00000	0.77279	0.00116	0.77395	-0.00069
H	70	0.22140	0.00000	0.77757	0.00103	0.77860	0.00249
H	71	-0.22606	0.00000	1.22511	0.00095	1.22606	-0.00023
H	72	-0.20348	0.00000	1.20314	0.00034	1.20348	0.00009
H	73	-0.22847	0.00000	1.22749	0.00098	1.22847	-0.00002
H	74	-0.20305	0.00000	1.20271	0.00034	1.20305	-0.00005
H	75	-0.22772	0.00000	1.22677	0.00095	1.22772	-0.00014
H	76	-0.22770	0.00000	1.22672	0.00097	1.22770	-0.00009
H	77	-0.20240	0.00000	1.20205	0.00034	1.20240	-0.00019
H	78	-0.22586	0.00000	1.22490	0.00096	1.22586	-0.00036
H	79	-0.22582	0.00000	1.22487	0.00095	1.22582	-0.00090
H	80	-0.22664	0.00000	1.22563	0.00101	1.22664	-0.00014
H	81	-0.20264	0.00000	1.20232	0.00032	1.20264	-0.00022
H	82	-0.22813	0.00000	1.22716	0.00096	1.22813	-0.00069

* Total *	-2.00000	255.9892	234.7590	1.25172	492.0000	10.0000

Sm spin density: 5.39
Sm charge: 1.45
Total charge of bound ring: -1.56
Total charge of non-bound ring: -0.25

Table S6. Natural population analysis for **$(Sm_2\text{-biph})_{iso}^{2-}$** (with alkyl substituents on the silicon atoms being replaced by methyl groups).

Atom	No	Natural charge	Core	Valence	Rydberg	Total	Natural spin density
Sm	1	1.34863	53.99564	6.60051	0.05522	60.65137	5.48373
Fe	2	0.31834	17.99959	7.60505	0.07702	25.68166	0.00057
Si	3	1.07024	9.99993	2.88160	0.04822	12.92976	-0.00047
Si	4	1.07578	9.99993	2.87611	0.04818	12.92422	-0.00037
N	5	-1.17542	1.99997	6.16079	0.01465	8.17542	-0.00691
N	6	-1.18299	1.99997	6.16883	0.01420	8.18299	-0.00959
C	7	0.14475	1.99997	3.82499	0.03030	5.85525	-0.00174
C	8	-0.34800	1.99996	4.32627	0.02177	6.34800	-0.00244
C	9	-0.30418	1.99997	4.28318	0.02103	6.30418	0.00052
C	10	-0.31598	1.99997	4.29529	0.02072	6.31598	-0.00063
C	11	-0.34654	1.99997	4.32816	0.01841	6.34654	0.00087
C	12	-0.35563	1.99996	4.33520	0.02046	6.35563	-0.00182
C	13	-0.31634	1.99997	4.29544	0.02094	6.31634	0.00078
C	14	-0.31829	1.99997	4.29762	0.02071	6.31829	-0.00158
C	15	-0.34516	1.99997	4.32684	0.01835	6.34516	0.00113
C	16	0.13534	1.99997	3.83454	0.03015	5.86466	-0.00093
C	17	-0.12286	1.99997	4.10072	0.02216	6.12286	-0.04208
C	18	-0.55166	1.99996	4.52820	0.02350	6.55166	-0.18007
C	19	-0.28361	1.99997	4.26310	0.02053	6.28361	-0.01647
C	20	-0.33057	1.99997	4.30932	0.02128	6.33057	-0.04314
C	21	-0.51876	1.99997	4.49372	0.02507	6.51876	-0.16648
C	22	-0.27885	1.99997	4.25963	0.01926	6.27885	-0.02029
Sm	23	1.34863	53.99564	6.60051	0.05522	60.65137	5.48373
Fe	24	0.31834	17.99959	7.60505	0.07702	25.68166	0.00057
Si	25	1.07024	9.99993	2.88160	0.04822	12.92976	-0.00047
Si	26	1.07578	9.99993	2.87611	0.04818	12.92422	-0.00037
N	27	-1.17542	1.99997	6.16079	0.01465	8.17542	-0.00691
N	28	-1.18299	1.99997	6.16883	0.01420	8.18299	-0.00959
C	29	-0.12286	1.99997	4.10072	0.02216	6.12286	-0.04208
C	30	-0.55166	1.99996	4.52820	0.02350	6.55166	-0.18007
C	31	-0.28361	1.99997	4.26310	0.02053	6.28361	-0.01647
C	32	-0.33057	1.99997	4.30932	0.02128	6.33057	-0.04314
C	33	-0.51876	1.99997	4.49372	0.02507	6.51876	-0.16648
C	34	-0.27885	1.99997	4.25963	0.01926	6.27885	-0.02029
C	35	0.14475	1.99997	3.82499	0.03030	5.85525	-0.00174
C	36	-0.34800	1.99996	4.32627	0.02177	6.34800	-0.00244
C	37	-0.30418	1.99997	4.28318	0.02103	6.30418	0.00052
C	38	-0.31598	1.99997	4.29529	0.02072	6.31598	-0.00063

C	39	-0.34654	1.99997	4.32816	0.01841	6.34654	0.00087
C	40	-0.35563	1.99996	4.33520	0.02046	6.35563	-0.00182
C	41	-0.31634	1.99997	4.29544	0.02094	6.31634	0.00078
C	42	-0.31829	1.99997	4.29762	0.02071	6.31829	-0.00158
C	43	-0.34516	1.99997	4.32684	0.01835	6.34516	0.00113
C	44	0.13534	1.99997	3.83454	0.03015	5.86466	-0.00093
H	45	0.25581	0.00000	0.74317	0.00102	0.74419	-0.00004
H	46	0.24494	0.00000	0.75375	0.00131	0.75506	-0.00008
H	47	0.25515	0.00000	0.74366	0.00119	0.74485	-0.00004
H	48	0.28575	0.00000	0.71228	0.00197	0.71425	-0.00021
H	49	0.24587	0.00000	0.75281	0.00132	0.75413	-0.00013
H	50	0.25779	0.00000	0.74116	0.00104	0.74221	-0.00002
H	51	0.25248	0.00000	0.74633	0.00119	0.74752	-0.00003
H	52	0.27289	0.00000	0.72542	0.00169	0.72711	0.00025
H	53	0.24153	0.00000	0.75751	0.00096	0.75847	0.00191
H	54	0.24126	0.00000	0.75772	0.00103	0.75874	0.00104
H	55	0.24861	0.00000	0.75051	0.00089	0.75139	0.00391
H	56	0.25218	0.00000	0.74684	0.00097	0.74782	0.00105
H	57	0.24767	0.00000	0.75098	0.00135	0.75233	0.00225
H	58	0.24767	0.00000	0.75098	0.00135	0.75233	0.00225
H	59	0.24126	0.00000	0.75772	0.00103	0.75874	0.00104
H	60	0.24153	0.00000	0.75751	0.00096	0.75847	0.00191
H	61	0.24861	0.00000	0.75051	0.00089	0.75139	0.00391
H	62	0.25218	0.00000	0.74684	0.00097	0.74782	0.00105
H	63	0.25779	0.00000	0.74116	0.00104	0.74221	-0.00002
H	64	0.24587	0.00000	0.75281	0.00132	0.75413	-0.00013
H	65	0.25248	0.00000	0.74633	0.00119	0.74752	-0.00003
H	66	0.27289	0.00000	0.72542	0.00169	0.72711	0.00025
H	67	0.24494	0.00000	0.75375	0.00131	0.75506	-0.00008
H	68	0.25581	0.00000	0.74317	0.00102	0.74419	-0.00004
H	69	0.25515	0.00000	0.74366	0.00119	0.74485	-0.00004
H	70	0.28575	0.00000	0.71228	0.00197	0.71425	-0.00021
H	71	-0.22304	0.00000	1.22204	0.00100	1.22304	-0.00016
H	72	-0.20073	0.00000	1.20044	0.00030	1.20073	-0.00018
H	73	-0.22898	0.00000	1.22804	0.00094	1.22898	-0.00093
H	74	-0.22246	0.00000	1.22157	0.00088	1.22246	-0.00103
H	75	-0.22574	0.00000	1.22465	0.00108	1.22574	-0.00012
H	76	-0.19923	0.00000	1.19894	0.00029	1.19923	-0.00002
H	77	-0.22574	0.00000	1.22465	0.00108	1.22574	-0.00012
H	78	-0.22246	0.00000	1.22157	0.00088	1.22246	-0.00103
H	79	-0.19923	0.00000	1.19894	0.00029	1.19923	-0.00002
H	80	-0.20073	0.00000	1.20044	0.00030	1.20073	-0.00018
H	81	-0.22898	0.00000	1.22804	0.00094	1.22898	-0.00093

H	82	-0.22304	0.00000	1.22204	0.00100	1.22304	-0.00016
* Total *		-2.00000	255.98901	234.74584	1.26515	492.00000	10.00000

Sm spin density: 5.48
Sm charge: 1.35
Total charge of each biphenyl ring: -0.86

Table S7. Natural population analysis for **Yb_2-biph-K_2** (with alkyl substituents on the silicon atoms being replaced by methyl groups).

Atom	No	Natural Charge	Core	Valence	Rydberg	Total
Yb	1	1.20651	53.99867	14.73503	0.05979	68.79349
N	2	-1.19273	1.99997	6.17911	0.01365	8.19273
N	3	-1.21889	1.99997	6.20427	0.01465	8.21889
C	4	0.16835	1.99997	3.80196	0.02972	5.83165
C	5	0.10247	1.99997	3.86808	0.02949	5.89753
C	6	-0.49821	1.99997	4.47232	0.02593	6.49821
C	7	-0.30539	1.99997	4.28397	0.02146	6.30539
C	8	-0.32195	1.99997	4.30088	0.02111	6.32195
C	9	-0.39190	1.99997	4.37081	0.02113	6.39190
C	10	-0.40226	1.99997	4.38076	0.02153	6.40226
C	11	-0.19789	1.99997	4.17722	0.02070	6.19789
C	12	-0.39112	1.99997	4.36976	0.02140	6.39112
C	13	-0.34269	1.99997	4.32127	0.02144	6.34269
Fe	14	0.09719	17.99948	7.85829	0.04505	25.90281
C	15	-0.28777	1.99997	4.26606	0.02174	6.28777
C	16	-0.29138	1.99997	4.26980	0.02162	6.29138
C	17	-0.27427	1.99997	4.25387	0.02043	6.27427
C	18	-0.27422	1.99997	4.25326	0.02100	6.27422
C	19	-0.31845	1.99997	4.29983	0.01866	6.31845
C	20	-0.29878	1.99997	4.28071	0.01810	6.29878
Si	21	1.04737	9.99991	2.90508	0.04764	12.95263
K	22	0.94220	17.99919	0.04869	0.00992	18.05780
Si	23	1.08023	9.99993	2.87350	0.04634	12.91977
O	24	-0.63240	1.99998	6.61876	0.01366	8.63240
C	25	-0.32195	1.99997	4.30088	0.02111	6.32195
C	26	-0.40226	1.99997	4.38076	0.02153	6.40226
C	27	-0.49821	1.99997	4.47232	0.02593	6.49821
C	28	-0.19789	1.99997	4.17722	0.02070	6.19789
C	29	-0.30539	1.99997	4.28397	0.02146	6.30539
C	30	-0.39190	1.99997	4.37081	0.02113	6.39190
C	31	-0.12106	1.99997	4.10555	0.01553	6.12106
C	32	-0.11931	1.99997	4.10350	0.01584	6.11931
K	33	0.94220	17.99919	0.04869	0.00992	18.05780
H	34	0.26549	0.00000	0.73361	0.00090	0.73451
H	35	0.27146	0.00000	0.72770	0.00084	0.72854
H	36	0.27744	0.00000	0.72185	0.00072	0.72256
H	37	0.27740	0.00000	0.72185	0.00075	0.72260
H	38	0.26587	0.00000	0.73329	0.00084	0.73413
H	39	0.26988	0.00000	0.72851	0.00161	0.73012
H	40	0.27291	0.00000	0.72646	0.00062	0.72709

H	41	0.27223	0.00000	0.72722	0.00055	0.72777
H	42	0.27697	0.00000	0.72241	0.00061	0.72303
H	43	0.26718	0.00000	0.73138	0.00144	0.73282
H	44	0.26830	0.00000	0.73104	0.00066	0.73170
H	45	0.26834	0.00000	0.73108	0.00059	0.73166
H	46	0.27590	0.00000	0.72348	0.00062	0.72410
C	47	-0.73694	1.99997	4.72691	0.01006	6.73694
H	48	0.25644	0.00000	0.74208	0.00148	0.74356
H	49	0.24070	0.00000	0.75775	0.00155	0.75930
H	50	0.25913	0.00000	0.74018	0.00069	0.74087
H	51	0.21333	0.00000	0.78435	0.00232	0.78667
H	52	0.21602	0.00000	0.78177	0.00221	0.78398
C	53	-0.73808	1.99997	4.72840	0.00971	6.73808
H	54	0.21604	0.00000	0.78176	0.00220	0.78396
H	55	0.21547	0.00000	0.78207	0.00246	0.78453
H	56	0.25884	0.00000	0.74045	0.00070	0.74116
H	57	0.23978	0.00000	0.75796	0.00226	0.76022
H	58	0.24671	0.00000	0.75171	0.00158	0.75329
Yb	59	1.20651	53.99867	14.73503	0.05979	68.79349
H	60	0.27146	0.00000	0.72770	0.00084	0.72854
N	61	-1.21889	1.99997	6.20427	0.01465	8.21889
N	62	-1.19273	1.99997	6.17911	0.01365	8.19273
C	63	0.10247	1.99997	3.86808	0.02949	5.89753
H	64	0.26988	0.00000	0.72851	0.00161	0.73012
H	65	0.26718	0.00000	0.73138	0.00144	0.73282
C	66	0.16835	1.99997	3.80196	0.02972	5.83165
Si	67	1.04737	9.99991	2.90508	0.04764	12.95263
Si	68	1.08023	9.99993	2.87350	0.04634	12.91977
H	69	0.26549	0.00000	0.73361	0.00090	0.73451
H	70	0.27744	0.00000	0.72185	0.00072	0.72256
H	71	0.27740	0.00000	0.72185	0.00075	0.72260
H	72	0.26587	0.00000	0.73329	0.00084	0.73413
Fe	73	0.09719	17.99948	7.85829	0.04505	25.90281
C	74	-0.39112	1.99997	4.36976	0.02140	6.39112
C	75	-0.31845	1.99997	4.29983	0.01866	6.31845
C	76	-0.34269	1.99997	4.32127	0.02144	6.34269
C	77	-0.29878	1.99997	4.28071	0.01810	6.29878
C	78	-0.29138	1.99997	4.26980	0.02162	6.29138
H	79	0.27291	0.00000	0.72646	0.00062	0.72709
C	80	-0.28777	1.99997	4.26606	0.02174	6.28777
H	81	0.27223	0.00000	0.72722	0.00055	0.72777
H	82	0.27697	0.00000	0.72241	0.00061	0.72303
C	83	-0.27422	1.99997	4.25326	0.02100	6.27422

H	84	0.26830	0.00000	0.73104	0.00066	0.73170
C	85	-0.27427	1.99997	4.25387	0.02043	6.27427
H	86	0.26834	0.00000	0.73108	0.00059	0.73166
H	87	0.27590	0.00000	0.72348	0.00062	0.72410
O	88	-0.63240	1.99998	6.61876	0.01366	8.63240
C	89	-0.12106	1.99997	4.10555	0.01553	6.12106
C	90	-0.11931	1.99997	4.10350	0.01584	6.11931
C	91	-0.73694	1.99997	4.72691	0.01006	6.73694
H	92	0.21333	0.00000	0.78435	0.00232	0.78667
H	93	0.21602	0.00000	0.78177	0.00221	0.78398
H	94	0.21604	0.00000	0.78176	0.00220	0.78396
H	95	0.21547	0.00000	0.78207	0.00246	0.78453
C	96	-0.73808	1.99997	4.72840	0.00971	6.73808
H	97	0.25644	0.00000	0.74208	0.00148	0.74356
H	98	0.24070	0.00000	0.75775	0.00155	0.75930
H	99	0.25913	0.00000	0.74018	0.00069	0.74087
H	100	0.25884	0.00000	0.74045	0.00070	0.74116
H	101	0.23978	0.00000	0.75796	0.00226	0.76022
H	102	0.24671	0.00000	0.75171	0.00158	0.75329
H	103	-0.20157	0.00000	1.20087	0.00069	1.20157
H	104	-0.19621	0.00000	1.19590	0.00031	1.19621
H	105	-0.20551	0.00000	1.20486	0.00065	1.20551
H	106	-0.18478	0.00000	1.18390	0.00088	1.18478
H	107	-0.21284	0.00000	1.21202	0.00082	1.21284
H	108	-0.17951	0.00000	1.17922	0.00029	1.17951
H	109	-0.20157	0.00000	1.20087	0.00069	1.20157
H	110	-0.19621	0.00000	1.19590	0.00031	1.19621
H	111	-0.20551	0.00000	1.20486	0.00065	1.20551
H	112	-0.18478	0.00000	1.18390	0.00088	1.18478
H	113	-0.21284	0.00000	1.21202	0.00082	1.21284
H	114	-0.17951	0.00000	1.17922	0.00029	1.17951
* Total *		0.00000	311.99298	314.62876	1.37826	628.00000

Yb charge: 1.20
Total charge of each biphenyl ring: -0.75

Table S8. Natural population analysis for **[Yb$_2$-biph-K$_2$]$_{iso}$** (with alkyl substituents on the silicon atoms being replaced by methyl groups).

Atom	No	Natural Charge	Core	Valence	Rydberg	Total
Yb	1	1.20750	53.99861	14.73129	0.06260	68.79250
Fe	2	0.09464	17.99948	7.86040	0.04549	25.90536
Si	3	1.05403	9.99991	2.89817	0.04788	12.94597
Si	4	1.08249	9.99993	2.87145	0.04614	12.91751
N	5	-1.21191	1.99997	6.19651	0.01543	8.21191
N	6	-1.19259	1.99997	6.17884	0.01378	8.19259
C	7	0.10006	1.99997	3.87005	0.02992	5.89994
C	8	-0.39683	1.99997	4.37503	0.02183	6.39683
C	9	-0.28966	1.99997	4.26827	0.02143	6.28966
C	10	-0.29057	1.99997	4.26935	0.02126	6.29057
C	11	-0.32333	1.99997	4.30469	0.01867	6.32333
C	12	-0.34212	1.99997	4.32014	0.02201	6.34212
C	13	-0.27127	1.99997	4.25036	0.02094	6.27127
C	14	-0.27380	1.99997	4.25347	0.02036	6.27380
C	15	-0.29668	1.99997	4.27848	0.01823	6.29668
C	16	0.17025	1.99997	3.79990	0.02988	5.82975
K	17	0.93853	17.99912	0.04806	0.01429	18.06147
O	18	-0.63409	1.99998	6.62043	0.01367	8.63409
C	19	-0.28027	1.99996	4.25758	0.02273	6.28027
C	20	-0.41914	1.99996	4.39515	0.02404	6.41914
C	21	-0.33508	1.99996	4.30967	0.02545	6.33508
C	22	-0.50036	1.99996	4.46905	0.03134	6.50036
C	23	-0.33508	1.99996	4.30967	0.02545	6.33508
C	24	-0.41914	1.99996	4.39515	0.02404	6.41914
C	25	-0.73673	1.99997	4.72675	0.01002	6.73673
C	26	-0.11971	1.99997	4.10414	0.01560	6.11971
C	27	-0.11874	1.99997	4.10299	0.01577	6.11874
C	28	-0.73706	1.99997	4.72748	0.00961	6.73706
C	29	-0.12869	1.99997	4.11177	0.01695	6.12869
C	30	-0.37626	1.99998	4.35924	0.01705	6.37626
C	31	-0.29823	1.99998	4.28129	0.01696	6.29823
C	32	-0.47537	1.99998	4.45376	0.02164	6.47537
C	33	-0.29823	1.99998	4.28129	0.01696	6.29823
C	34	-0.37626	1.99998	4.35924	0.01705	6.37626
H	35	0.25929	0.00000	0.74003	0.00068	0.74071
H	36	0.24316	0.00000	0.75505	0.00179	0.75684
H	37	0.24189	0.00000	0.75642	0.00170	0.75811
H	38	0.22440	0.00000	0.77338	0.00223	0.77560
H	39	0.21339	0.00000	0.78428	0.00233	0.78661
H	40	0.22378	0.00000	0.77397	0.00224	0.77622

H	41	0.21293	0.00000	0.78478	0.00229	0.78707
H	42	0.26081	0.00000	0.73852	0.00067	0.73919
H	43	0.23822	0.00000	0.76025	0.00153	0.76178
H	44	0.24764	0.00000	0.75038	0.00198	0.75236
H	45	0.27564	0.00000	0.72372	0.00064	0.72436
H	46	0.27271	0.00000	0.72674	0.00055	0.72729
H	47	0.27360	0.00000	0.72580	0.00061	0.72640
H	48	0.26793	0.00000	0.73013	0.00194	0.73207
H	49	0.26815	0.00000	0.73127	0.00059	0.73185
H	50	0.27579	0.00000	0.72360	0.00061	0.72421
H	51	0.26915	0.00000	0.73019	0.00066	0.73085
H	52	0.27033	0.00000	0.72813	0.00153	0.72967
H	53	0.25409	0.00000	0.74512	0.00079	0.74591
H	54	0.25484	0.00000	0.74419	0.00097	0.74516
H	55	0.25484	0.00000	0.74419	0.00097	0.74516
H	56	0.25093	0.00000	0.74805	0.00102	0.74907
H	57	0.25093	0.00000	0.74805	0.00102	0.74907
H	58	0.28205	0.00000	0.71713	0.00082	0.71795
H	59	0.29530	0.00000	0.70392	0.00078	0.70470
H	60	0.29988	0.00000	0.69936	0.00076	0.70012
H	61	0.29530	0.00000	0.70392	0.00078	0.70470
H	62	0.28205	0.00000	0.71713	0.00082	0.71795
Yb	63	1.20750	53.99861	14.73129	0.06260	68.79250
Fe	64	0.09464	17.99948	7.86040	0.04549	25.90536
Si	65	1.05403	9.99991	2.89817	0.04788	12.94597
Si	66	1.08249	9.99993	2.87145	0.04614	12.91751
N	67	-1.21191	1.99997	6.19651	0.01543	8.21191
N	68	-1.19259	1.99997	6.17884	0.01378	8.19259
C	69	0.10006	1.99997	3.87005	0.02992	5.89994
C	70	-0.39683	1.99997	4.37503	0.02183	6.39683
C	71	-0.28966	1.99997	4.26827	0.02143	6.28966
C	72	-0.29057	1.99997	4.26935	0.02126	6.29057
C	73	-0.32333	1.99997	4.30469	0.01867	6.32333
C	74	-0.34212	1.99997	4.32014	0.02201	6.34212
C	75	-0.27127	1.99997	4.25036	0.02094	6.27127
C	76	-0.27380	1.99997	4.25347	0.02036	6.27380
C	77	-0.29668	1.99997	4.27848	0.01823	6.29668
C	78	0.17025	1.99997	3.79990	0.02988	5.82975
K	79	0.93853	17.99912	0.04806	0.01429	18.06147
O	80	-0.63409	1.99998	6.62043	0.01367	8.63409
C	81	-0.73673	1.99997	4.72675	0.01002	6.73673
C	82	-0.11971	1.99997	4.10414	0.01560	6.11971
C	83	-0.11874	1.99997	4.10299	0.01577	6.11874

C	84	-0.73706	1.99997	4.72748	0.00961	6.73706
H	85	0.25929	0.00000	0.74003	0.00068	0.74071
H	86	0.24316	0.00000	0.75505	0.00179	0.75684
H	87	0.24189	0.00000	0.75642	0.00170	0.75811
H	88	0.22440	0.00000	0.77338	0.00223	0.77560
H	89	0.21339	0.00000	0.78428	0.00233	0.78661
H	90	0.22378	0.00000	0.77397	0.00224	0.77622
H	91	0.21293	0.00000	0.78478	0.00229	0.78707
H	92	0.26081	0.00000	0.73852	0.00067	0.73919
H	93	0.23822	0.00000	0.76025	0.00153	0.76178
H	94	0.24764	0.00000	0.75038	0.00198	0.75236
H	95	0.27564	0.00000	0.72372	0.00064	0.72436
H	96	0.27271	0.00000	0.72674	0.00055	0.72729
H	97	0.27360	0.00000	0.72580	0.00061	0.72640
H	98	0.26793	0.00000	0.73013	0.00194	0.73207
H	99	0.26815	0.00000	0.73127	0.00059	0.73185
H	100	0.27579	0.00000	0.72360	0.00061	0.72421
H	101	0.26915	0.00000	0.73019	0.00066	0.73085
H	102	0.27033	0.00000	0.72813	0.00153	0.72967
H	103	-0.20663	0.00000	1.20598	0.00065	1.20663
H	104	-0.19901	0.00000	1.19833	0.00069	1.19901
H	105	-0.19716	0.00000	1.19683	0.00032	1.19716
H	106	-0.19716	0.00000	1.19683	0.00032	1.19716
H	107	-0.19901	0.00000	1.19833	0.00069	1.19901
H	108	-0.20663	0.00000	1.20598	0.00065	1.20663
H	109	-0.22558	0.00000	1.22463	0.00096	1.22558
H	110	-0.18159	0.00000	1.18066	0.00093	1.18159
H	111	-0.18025	0.00000	1.17990	0.00035	1.18025
H	112	-0.18025	0.00000	1.17990	0.00035	1.18025
H	113	-0.22558	0.00000	1.22463	0.00096	1.22558
H	114	-0.18159	0.00000	1.18066	0.00093	1.18159
* Total *		0.00000	311.99272	314.61236	1.39492	628.00000

Yb charge: 1.20
Total charge of Yb-bound ring: -0.83
Total charge of non-bound biphenyl ring: -0.68

Table S9. Optimized structure for **$(Sm_2\text{-biph})^{2-}$** (with alkyl substituents on the silicon atoms being replaced by methyl groups).

Sm	0.011893	-0.061674	-2.151134
N	-1.392222	-1.159682	-3.792291
N	1.567900	0.666483	-3.817823
H	0.314356	2.869706	-2.486965
C	-0.267395	-1.504063	-0.032110
C	-1.367541	-0.558203	0.012914
C	-1.113284	0.879200	-0.161828
C	0.276816	1.391470	-0.032484
C	1.378090	0.404594	0.005675
C	1.097987	-1.026068	-0.084106
Si	-1.104539	-2.577893	-4.705436
C	-2.050933	-0.065687	-4.309961
Si	2.683477	-0.297329	-4.686625
C	0.894086	1.739753	-4.352155
Fe	-1.212218	1.857031	-4.719315
C	0.251401	2.767169	-3.567290
Sm	-0.020044	-0.013063	2.053827
H	-0.470659	-2.571903	-0.036649
H	-2.387293	-0.924233	-0.079896
H	-1.935485	1.558505	0.052187
H	2.395671	0.739693	-0.175668
H	1.920377	-1.730885	0.008035
C	-2.648933	0.983474	-3.514987
C	-2.205078	0.353145	-5.681905
C	0.557774	2.026748	-5.724853
H	-2.682743	0.992246	-2.428270
C	-3.207937	1.976648	-4.376377
H	-3.724771	2.874632	-4.058187
C	-2.941508	1.580800	-5.723755
H	-3.218980	2.126970	-6.618684
H	-1.800589	-0.176085	-6.537886
C	-0.394388	3.694617	-4.438749
H	-0.936487	4.578270	-4.123303
C	-0.197531	3.242578	-5.779735
H	-0.576797	3.716595	-6.678347
H	0.824458	1.402016	-6.570209
N	-1.526370	0.870507	3.707107
N	1.336601	-1.102537	3.709774
Si	-2.711762	0.020456	4.600149
C	-0.790319	1.917236	4.216651
Si	0.963094	-2.506957	4.611197
C	2.053605	-0.037917	4.211240
Fe	1.312537	1.929504	4.586460
C	-0.444353	2.221718	5.583487
C	-0.092113	2.890204	3.410563
C	2.226952	0.393701	5.576153

C	2.701552	0.967395	3.399894
H	-0.747065	1.635000	6.443765
C	0.376453	3.396120	5.610092
H	0.779481	3.869739	6.498592
C	0.600443	3.803752	4.259009
H	1.196580	4.641041	3.915297
H	-0.129104	2.961697	2.327789
H	1.796884	-0.101419	6.439871
C	3.023922	1.583999	5.598510
H	3.325419	2.130607	6.485419
C	3.309613	1.945165	4.245065
H	3.862961	2.815170	3.910629
H	2.735816	0.950198	2.314275
C	0.545938	2.809000	0.006107
C	-0.476734	3.776013	-0.198849
C	1.841442	3.326662	0.281275
C	-0.223380	5.137901	-0.110058
H	-1.478368	3.440325	-0.450476
C	2.081556	4.688734	0.366933
H	2.658468	2.636363	0.466857
C	1.055468	5.622771	0.177745
H	-1.043820	5.836404	-0.271440
H	3.090712	5.030532	0.594987
H	1.248280	6.690313	0.249310
H	0.417800	-2.285953	6.018216
H	-0.102763	-3.269598	3.849992
H	2.127781	-3.472465	4.817097
H	-3.054926	-1.237926	3.828941
H	-2.310379	-0.426804	6.002783
H	-4.021579	0.772034	4.820583
H	2.941112	-1.546754	-3.869460
H	2.241818	-0.763636	-6.070086
H	4.040164	0.354623	-4.934468
H	-0.463275	-2.384685	-6.076122
H	-0.163874	-3.462407	-3.913869
H	-2.349660	-3.411503	-5.001834

Table S10. Optimized structure for **$(Sm_2\text{-biph})_{iso}^{2-}$** (with alkyl substituents on the silicon atoms being replaced by methyl groups).

Sm	0.405807	-3.106411	-0.193103
Fe	-2.444180	-4.522633	0.478160
Si	1.038662	-4.592656	3.196737
Si	1.230800	-6.758117	-0.589227
N	0.109859	-3.616245	2.135158
N	0.253241	-5.391819	-0.926917
C	-1.259707	-3.684353	2.079726
C	-2.089317	-2.700815	1.419477
C	-3.457664	-3.098778	1.509012
C	-3.503036	-4.355726	2.185816
C	-2.156941	-4.737892	2.490812
C	-1.969440	-4.432692	-1.533853
C	-3.341177	-4.773252	-1.323570
C	-3.373427	-5.982434	-0.562609
C	-2.021611	-6.370031	-0.293602
C	-1.122208	-5.444425	-0.938443
C	0.426004	-0.448932	-0.386698
C	-0.123298	-1.160772	-1.584667
C	0.892404	-1.749935	-2.448366
C	2.130822	-2.107904	-1.975020
C	2.516509	-1.787333	-0.602239
C	1.709702	-0.772458	0.038552
Sm	-0.405807	3.106411	0.193103
Fe	2.444180	4.522633	-0.478160
Si	-1.038662	4.592656	-3.196737
Si	-1.230800	6.758117	0.589227
N	-0.109859	3.616245	-2.135158
N	-0.253241	5.391819	0.926917
C	-0.426004	0.448932	0.386698
C	0.123298	1.160772	1.584667
C	-0.892404	1.749935	2.448366
C	-2.130822	2.107904	1.975020
C	-2.516509	1.787333	0.602239
C	-1.709702	0.772458	-0.038552
C	1.259707	3.684353	-2.079726
C	2.089317	2.700815	-1.419477
C	3.457664	3.098778	-1.509012
C	3.503036	4.355726	-2.185816
C	2.156941	4.737892	-2.490812
C	1.969440	4.432692	1.533853
C	3.341177	4.773252	1.323570
C	3.373427	5.982434	0.562609
C	2.021611	6.370031	0.293602
C	1.122208	5.444425	0.938443
H	-1.847176	-5.669344	2.952398
H	-4.394323	-4.934043	2.402645

H	-4.301077	-2.533179	1.131289
H	-1.746452	-1.746745	1.016490
H	-4.263569	-6.498405	-0.220150
H	-1.708674	-7.212368	0.313455
H	-4.196834	-4.204549	-1.668364
H	-1.617363	-3.557890	-2.078760
H	-2.811561	2.674621	2.607979
H	-0.611035	2.039336	3.460937
H	-3.549702	1.916407	0.291226
H	-2.082576	0.334222	-0.959632
H	0.977012	0.713835	2.086543
H	-0.977012	-0.713835	-2.086543
H	0.611035	-2.039336	-3.460937
H	2.811561	-2.674621	-2.607979
H	3.549702	-1.916407	-0.291226
H	2.082576	-0.334222	0.959632
H	1.708674	7.212368	-0.313455
H	4.263569	6.498405	0.220150
H	4.196834	4.204549	1.668364
H	1.617363	3.557890	2.078760
H	4.394323	4.934043	-2.402645
H	1.847176	5.669344	-2.952398
H	4.301077	2.533179	-1.131289
H	1.746452	1.746745	-1.016490
H	-0.847775	7.577084	-0.636968
H	-2.651312	6.282573	0.373276
H	-1.277661	7.786992	1.716198
H	-0.822397	4.286012	-4.674574
H	-0.806424	6.096825	-3.096408
H	-2.503632	4.363270	-2.899103
H	0.806424	-6.096825	3.096408
H	0.822397	-4.286012	4.674574
H	2.503632	-4.363270	2.899103
H	2.651312	-6.282573	-0.373276
H	1.277661	-7.786992	-1.716198
H	0.847775	-7.577084	0.636968

Table S11. Optimized structure for **Yb_2-biph-K_2** (with alkyl substituents on the silicon atoms being replaced by methyl groups).

Yb	1.485101	-2.158599	-2.08192
N	2.655282	-3.864948	-3.100361
N	-0.659866	-2.183042	-3.121194
C	2.983205	-3.099354	-4.188958
C	-0.154994	-1.489462	-4.208801
C	3.014885	-2.008176	0.197207
C	1.748707	-2.524619	0.594109
C	3.024408	-0.705691	-0.374319
C	0.578724	-1.793991	0.47275
C	1.874993	0.054974	-0.508481
C	0.568832	-0.400975	-0.004569
C	0.540856	-0.218628	-4.097778
C	3.589693	-1.788568	-4.100378
Fe	1.791491	-1.52072	-5.084902
C	0.42331	-0.715338	-6.340132
C	0.872448	0.25854	-5.404664
C	3.231049	-2.193567	-6.333034
C	3.766545	-1.250524	-5.411128
C	-0.165318	-1.7954	-5.613693
C	2.704802	-3.290148	-5.588387
Si	-1.573021	-3.615877	-3.355103
K	-2.193672	0.084866	-2.567808
Si	2.424595	-5.554727	-3.142173
O	-4.329003	-0.879539	-3.958634
C	-3.024408	0.705691	0.374319
C	-1.874993	-0.054974	0.508481
C	-3.014885	2.008176	-0.197207
C	-0.568832	0.400975	0.004569
C	-1.748707	2.524619	-0.594109
C	-0.578724	1.793991	-0.47275
C	-4.346467	-0.901995	-5.375793
C	-5.253914	-1.792388	-3.394276
K	2.193672	-0.084866	2.567808
H	1.958663	1.03219	-0.973753
H	3.960013	-0.301662	-0.758203
H	3.909326	-2.617608	0.232922
H	1.685419	-3.551552	0.950498
H	-0.356611	-2.273164	0.743891
H	0.742063	0.314766	-3.168205
H	1.386243	1.183293	-5.634348
H	0.546635	-0.668254	-7.414946
H	-0.553313	-2.70977	-6.046568
H	3.963165	-1.341082	-3.182546
H	4.226352	-0.301306	-5.656131
H	3.188978	-2.077572	-7.409228
H	2.1818	-4.144672	-5.999634

C	-3.358066	0.114303	-5.903622
H	-2.329405	-0.152482	-5.636089
H	-3.59206	1.11689	-5.5255
H	-3.406189	0.151307	-6.996631
H	-5.363836	-0.673011	-5.731319
H	-4.084496	-1.911006	-5.729371
C	-5.132707	-1.754215	-1.886752
H	-5.046075	-2.805988	-3.768809
H	-6.274395	-1.519354	-3.70719
H	-5.879872	-2.412415	-1.43211
H	-5.298924	-0.739702	-1.506347
H	-4.14555	-2.101824	-1.560614
Yb	-1.485101	2.158599	2.08192
H	-3.960013	0.301662	0.758203
N	0.659866	2.183042	3.121194
N	-2.655282	3.864948	3.100361
C	0.154994	1.489462	4.208801
H	-0.742063	-0.314766	3.168205
H	-3.963165	1.341082	3.182546
C	-2.983205	3.099354	4.188958
Si	1.573021	3.615877	3.355103
Si	-2.424595	5.554727	3.142173
H	-1.958663	-1.03219	0.973753
H	-3.909326	2.617608	-0.232922
H	-1.685419	3.551552	-0.950498
H	0.356611	2.273164	-0.743891
Fe	-1.791491	1.52072	5.084902
C	-0.540856	0.218628	4.097778
C	0.165318	1.7954	5.613693
C	-3.589693	1.788568	4.100378
C	-2.704802	3.290148	5.588387
C	-0.872448	-0.25854	5.404664
H	-1.386243	-1.183293	5.634348
C	-0.42331	0.715338	6.340132
H	-0.546635	0.668254	7.414946
H	0.553313	2.70977	6.046568
C	-3.766545	1.250524	5.411128
H	-4.226352	0.301306	5.656131
C	-3.231049	2.193567	6.333034
H	-3.188978	2.077572	7.409228
H	-2.1818	4.144672	5.999634
O	4.329003	0.879539	3.958634
C	4.346467	0.901995	5.375793
C	5.253914	1.792388	3.394276
C	3.358066	-0.114303	5.903622
H	5.363836	0.673011	5.731319
H	4.084496	1.911006	5.729371
H	5.046075	2.805988	3.768809

H	6.274395	1.519354	3.70719
C	5.132707	1.754215	1.886752
H	2.329405	0.152482	5.636089
H	3.59206	-1.11689	5.5255
H	3.406189	-0.151307	6.996631
H	5.879872	2.412415	1.43211
H	5.298924	0.739702	1.506347
H	4.14555	2.101824	1.560614
H	3.694268	-6.350622	-3.242181
H	1.769908	-5.940879	-1.851949
H	1.550233	-6.07836	-4.24816
H	-0.832637	-4.812453	-3.868845
H	-2.722115	-3.432087	-4.312016
H	-2.164086	-3.98796	-2.032618
H	-3.694268	6.350622	3.242181
H	-1.769908	5.940879	1.851949
H	-1.550233	6.07836	4.24816
H	0.832637	4.812453	3.868845
H	2.722115	3.432087	4.312016
H	2.164086	3.98796	2.032618

Table S12. Optimized structure for **[Yb_2-biph-K_2]$_{iso}$** (with alkyl substituents on the silicon atoms being replaced by methyl groups).

Yb	1.282239	1.962305	-1.350783
Fe	4.184178	2.970158	-1.054887
Si	0.772870	5.130216	0.261060
Si	1.092172	4.575196	-3.976575
N	1.421218	3.550420	0.425130
N	1.826959	3.264102	-3.169889
C	2.792546	3.366605	0.507200
C	3.420145	2.061993	0.627713
C	4.839851	2.221190	0.709898
C	5.117498	3.614593	0.618388
C	3.878420	4.308390	0.463095
C	3.847055	1.866972	-2.769953
C	5.237684	2.089678	-2.537500
C	5.449065	3.497372	-2.540752
C	4.189287	4.133213	-2.746765
C	3.176341	3.134420	-2.966040
K	1.273696	2.484264	2.983796
O	2.244861	4.661807	4.337463
C	0.000000	0.000000	0.197773
C	1.036754	-0.681260	-0.613098
C	1.016578	-0.673087	-1.999952
C	0.000000	0.000000	-2.747379
C	-1.016578	0.673087	-1.999952
C	-1.036754	0.681260	-0.613098
C	4.405375	3.656306	4.153878
C	3.631915	4.950272	4.271679
C	1.463547	5.825251	4.543143
C	0.000000	5.444477	4.564915
C	0.000000	0.000000	1.596369
C	-1.070759	0.589089	2.394554
C	-1.059204	0.574072	3.778071
C	0.000000	0.000000	4.522214
C	1.059204	-0.574072	3.778071
C	1.070759	-0.589089	2.394554
H	-0.614249	6.319698	4.798475
H	-0.323889	5.072163	3.586139
H	-0.192819	4.680935	5.327518
H	1.656233	6.550028	3.737581
H	1.753543	6.295044	5.496696
H	3.834413	5.597843	3.404738
H	3.931593	5.497343	5.179870
H	5.480642	3.859212	4.179634
H	4.166244	2.985695	4.987628
H	4.201762	3.154726	3.201908
H	3.767975	5.374844	0.305709
H	6.100811	4.068398	0.623047
H	5.565469	1.424657	0.814017

H	2.893078	1.110844	0.705710
H	6.394178	3.998761	-2.371038
H	4.007085	5.200737	-2.744888
H	5.991289	1.326205	-2.390478
H	3.381339	0.893434	-2.902251
H	0.000000	0.000000	5.606913
H	-1.899631	1.024214	4.306137
H	1.899631	-1.024214	4.306137
H	1.918020	-1.050747	1.896085
H	-1.918020	1.050747	1.896085
H	1.827842	-1.232469	-0.116855
H	1.796450	-1.209762	-2.535718
H	0.000000	0.000000	-3.828355
H	-1.796450	1.209762	-2.535718
H	-1.827842	1.232469	-0.116855
Yb	-1.282239	-1.962305	-1.350783
Fe	-4.184178	-2.970158	-1.054887
Si	-0.772870	-5.130216	0.261060
Si	-1.092172	-4.575196	-3.976575
N	-1.421218	-3.550420	0.425130
N	-1.826959	-3.264102	-3.169889
C	-2.792546	-3.366605	0.507200
C	-3.420145	-2.061993	0.627713
C	-4.839851	-2.221190	0.709898
C	-5.117498	-3.614593	0.618388
C	-3.878420	-4.308390	0.463095
C	-3.847055	-1.866972	-2.769953
C	-5.237684	-2.089678	-2.537500
C	-5.449065	-3.497372	-2.540752
C	-4.189287	-4.133213	-2.746765
C	-3.176341	-3.134420	-2.966040
K	-1.273696	-2.484264	2.983796
O	-2.244861	-4.661807	4.337463
C	-4.405375	-3.656306	4.153878
C	-3.631915	-4.950272	4.271679
C	-1.463547	-5.825251	4.543143
C	0.000000	-5.444477	4.564915
H	0.614249	-6.319698	4.798475
H	0.323889	-5.072163	3.586139
H	0.192819	-4.680935	5.327518
H	-1.656233	-6.550028	3.737581
H	-1.753543	-6.295044	5.496696
H	-3.834413	-5.597843	3.404738
H	-3.931593	-5.497343	5.179870
H	-5.480642	-3.859212	4.179634
H	-4.166244	-2.985695	4.987628
H	-4.201762	-3.154726	3.201908
H	-3.767975	-5.374844	0.305709
H	-6.100811	-4.068398	0.623047

H	-5.565469	-1.424657	0.814017
H	-2.893078	-1.110844	0.705710
H	-6.394178	-3.998761	-2.371038
H	-4.007085	-5.200737	-2.744888
H	-5.991289	-1.326205	-2.390478
H	-3.381339	-0.893434	-2.902251
H	1.533567	5.947292	-3.546803
H	1.268635	4.561804	-5.467592
H	-0.378359	4.488931	-3.710076
H	0.378359	-4.488931	-3.710076
H	-1.268635	-4.561804	-5.467592
H	-1.533567	-5.947292	-3.546803
H	0.934308	5.965964	1.508377
H	1.345296	5.972603	-0.836110
H	-0.696916	4.990901	0.036059
H	0.696916	-4.990901	0.036059
H	-0.934308	-5.965964	1.508377
H	-1.345296	-5.972603	-0.836110

Table S13. Optimized structure for **$(Sm_2\text{-biph})_{iso}^{2-}$** (with the bulky ligands linked to the samarium atoms were replaced by chlorine atoms for balancing the charges and simplification).

C	0.000000	0.000000	-2.224873
H	0.000000	0.000000	-3.306035
C	1.246006	-0.135421	-1.503435
H	2.137904	-0.420459	-2.045467
C	1.222059	-0.344849	-0.052658
H	2.173515	-0.288551	0.459577
C	0.000000	0.000000	0.709571
C	0.000000	0.000000	2.146408
C	-1.104066	0.464124	2.900344
H	-1.970340	0.853068	2.381424
C	-1.098100	0.461338	4.280302
H	-1.971251	0.833919	4.807861
C	0.000000	0.000000	4.999337
C	-1.246006	0.135421	-1.503435
H	-2.137904	0.420459	-2.045467
C	-1.222059	0.344849	-0.052658
H	-2.173515	0.288551	0.459577
C	1.104066	-0.464124	2.900344
H	1.970340	-0.853068	2.381424
C	1.098100	-0.461338	4.280302
H	1.971251	-0.833919	4.807861
H	0.000000	0.000000	6.083072
Cl	2.315072	3.430581	0.279307
Cl	-0.750310	3.911651	-2.165964
Cl	0.750310	-3.911651	-2.165964
Cl	-2.315072	-3.430581	0.279307
Sm	0.378396	2.023751	-0.760989
Sm	-0.378396	-2.023751	-0.760989

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