Reduced Arene Complexes of Scandium
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Reduced Scandium Arene Complexes

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1. General considerations

All manipulations were performed under argon atmosphere using standard Schlenk or glovebox techniques. Prior to use, glassware were dried overnight at 150 °C. Solvents were dried, distilled and degassed using standard methods. If not otherwise stated, the reactions were performed at room temperature (21–24 °C) in Schlenk flasks or tubes of suitable size equipped with a PTFE magnetic stir bar. NMR measurements were performed on a Bruker Avance II or Avance III spectrometer operating at 400.3 MHz at 23 °C for 1H nuclei. The frequencies for the heteroatoms were as follows: 7Li (155.57 MHz), 13C (100.67 MHz) and 45Sc (97.27 MHz). The chemical shifts (δ in ppm) of the 1H and 13C{1H} NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane. The 45Sc NMR spectra were calibrated against an external aqueous solution of ScCl₃. If not otherwise stated, the signals in 13C{1H} NMR spectra are sharp singlets. Standard abbreviations indicating multiplicities were used as follows: s (singlet), d (doublet), t (triplet), m (multiplet). UV-Vis spectra were measured using a Cary 60 spectrophotometer from Agilent Technologies together with a fiber-optic quartz glass immersion probe (Hellma, 1 mm) in a specially designed Schlenk measurement cell. Elemental analyses were carried out using a CHN-O-Rapid VarioEL Element Analyzer. Elemental analyses of the reduced arene complexes were not performed due to the thermal instability.

The starting materials LiN(tBu)(Xy) (Xy = 3,5-Me₂C₆H₃) and [NEt₃H][BPh₄] were prepared according to the reported procedures. ¹² ScCl₃, naphthalene, Li granular, Na and K were purchased from Sigma Aldrich. Anthracene was purchased from ABCR. 4-Methoxybenzonitrile and tert-butyl nitrile were purchased from Alfa Aesar and ABCR, respectively, and dried with CaH₂ before use. Naphthalene was sublimed before use. To remove mineral oil, potassium was washed several times with n-pentane before use.

2. Syntheses, spectroscopic data, and NMR spectra

2.1. [Sc{N(tBu)(Xy)}₃]·THF (1)

THF (10 mL) was added to ScCl₃ (300 mg, 1.98 mmol) and the colorless suspension was stirred overnight at room temperature. A colorless solution of LiN(tBu)(Xy) (1.09 g, 5.95 mmol) in THF (7 mL) was added dropwise to the colorless suspension. Immediately, a light grey suspension formed which was stirred for 1 h at room temperature. The solvent was then removed in vacuo and the residue was extracted with n-pentane (15 mL). The solution was concentrated to ca. 5 mL and stored at –30 °C for 3 d. The product was isolated as colorless crystals, which were pulverized and dried for several hours in vacuo (929 mg, 82 %). Anal. calcd. for C₄₀H₄₀ClN₉OSc (644.90 g/mol): C, 74.38; H, 9.69; N, 6.51%. Found: C, 72.69; H, 9.53; N, 6.63%.
$^1$H NMR (400.3 MHz, benzene-$d_6$, 296 K): $\delta$ (ppm) = 0.76 (br s, $\Delta^{1/2} = 20$ Hz, 4H, THF), 1.60 (s, 27H, tBu), 2.25 (s, 18H, C$_6$H$_3$(CH$_3$)$_2$), 2.73 (br s, $\Delta^{1/2} = 27$ Hz, 4H, THF), 6.53 (s, 3H, p-C$_6$H$_3$), 7.05 (s, 6H, o-C$_6$H$_3$).

$^{13}$C($^1$H) NMR (100.67 MHz, benzene-$d_6$, 296 K): $\delta$ (ppm) = 21.6 (s, 6C, C$_6$H$_3$(CH$_3$)$_2$), 24.7 (s, 2C, THF), 32.1 (s, 9C, C(CH$_3$)$_3$), 56.1 (s, 3C, C(CH$_3$)$_3$), 70.6 (s, 2C, THF), 123.1 (s, 3C, p-C$_6$H$_3$), 125.6 (s, 6C, o-C$_6$H$_3$), 138.0 (s, 6C, m-C$_6$H$_3$), 152.4 (s, 2C, ipso-C$_6$H$_3$).

$^{45}$Sc NMR (97.27 MHz, benzene-$d_6$, 296 K): $\delta$ (ppm) = 359 (br s, $\Delta^{1/2} = \sim15000$ Hz).

**Figure S1.** $^1$H NMR spectrum of 1 in benzene-$d_6$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent.
Figure S2. $^{13}$C(NMR) NMR spectrum of 1 in benzene-$d_6$ at 296 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent.

Figure S3. $^{45}$Sc NMR spectrum of 1 in benzene-$d_6$ at 296 K; the line broadening (lb) value is set to 20 Hz.
2.2.  [Sc{N(tBu)(Xy)}2Cl]·THF (2)

After stirring a mixture of ScCl₃ (1.00 g, 6.61 mmol) in THF (30 mL) overnight, a solution of the LiN(tBu)(Xy) (3.02 g, 13.2 mmol) in THF (15 mL) was added dropwise at room temperature. The suspension turned light grey and was stirred for 2 h at room temperature. THF was removed in vacuo and the product was extracted with n-pentane (25 mL). After removing the volatiles in vacuo, the remaining yellow oil was dissolved in Et₂O (8 mL). The light-yellow solution was concentrated to ca. 3 mL and stored at -30 °C for 4 d. The desired product was isolated as colorless crystals, which were quickly washed with cold (-30 °C) n-pentane (1 mL). After washing, the crystals were pulverized and dried for 3 h (0.95 g). The supernatant solution was evaporated to dryness together with the n-pentane washing liquid and crystallized from 2 mL of Et₂O to obtain a further batch of compound 2 (0.76 g). Combined yield: 1.71 g (3.39 mmol, 51%).

Anal. calcd. for C₂₈H₄₄ClN₂OsC (504.07 g/mol): C 66.59; H 8.78; N 5.55%.

Found: C 65.32; H 8.11; N 5.70%.

¹H NMR (400.3 MHz, benzene-d₆, 296 K): δ (ppm) = 0.85 (br s, 6H, THF), 1.56 (s, 18H, tBu), 2.18 (s, 12H, C₆H₃(CH₃)₂), 3.19 (br s, 6H, THF), 6.52 (s, 2H, p-C₆H₃), 6.91 (s, 4H, o-C₆H₃).

¹³C{¹H} NMR (100.67 MHz, benzene-d₆, 296 K): δ (ppm) = 21.5 (s, 4C, C₆H₃(CH₃)₂), 24.9 (s, 2C, THF), 31.8 (s, 6C, C(CH₃)₃), 56.3 (s, 2C, C(CH₃)₃), 72.1 (s, 2C, THF), 124.3 (s, 2C, p-C₆H₃), 124.8 (s, 4C, o-C₆H₃), 139.0 (s, 4C, m-C₆H₃), 149.4 (s, 2C, ipso-C₆H₃).

⁴⁵Sc NMR (97.27 MHz, benzene-d₆, 296 K): δ (ppm) = 373 (br s, δν₁/₂ = ~12500 Hz).
Figure S4. $^1$H NMR spectrum of 2 in benzene-$d_6$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent.

Figure S5. $^{13}$C($^1$H) NMR spectrum of 2 in benzene-$d_6$ at 296 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent; the character • denotes the signal for traces of compound 1 formed in the solution during the NMR measurement due to the redistribution of anilide ligands.
Figure S6. $^{45}$Sc NMR spectrum of 2 in benzene-$d_6$ at 296 K; the line broadening (lb) value is set to 100 Hz.

2.3. [K(THF)$_2$][Sc{N((tBu)(Xy)}$_2$(Naph)] (3-Naph-K)

**Method A:** A colorless solution of 2 (500 mg, 0.78 mmol) in THF (25 mL) was treated with a dark green solution of potassium naphthalenide (10 mL, 0.16 mol/L, 1.6 mmol, 2.08 equiv.) in THF at −60 °C. While the reaction mixture was allowed to warm up to −25 °C, the color changed to purple. After the mixture was cooled to −60 °C again, $n$-pentane (50 mL) was added dropwise and the solution was stored at this temperature for 4 d. During this time, purple crystals were formed, that were isolated at −60 °C, washed with cold (−60 °C) $n$-pentane (10 mL) and stored at −30 °C. After powdering the crystals and drying shortly under reduced pressure, a dark purple solid was obtained. Yield: 145 mg (0.215 mmol, 26 %). Empirical formula for 3-Naph-K: C$_{42}$H$_{60}$KN$_2$O$_2$Sc (708.00 g/mol). Several attempts to obtain acceptable elemental analysis values of 3-Naph-K failed due to the thermal instability.

**Method B:** A colorless solution of 1 (500 mg, 0.99 mmol) in THF (4 mL) was treated with a dark green solution of potassium naphthalenide (8 mL, 0.26 mol/L, 2.1 mmol, 2.1 equiv.) in THF at −60 °C. Upon addition, the color of the solution changed directly to reddish purple. 25 mL of pre-cooled $n$-pentane was added dropwise at −60 °C and the solution was filtered and stored at −60 °C for 4 d. The supernatant solution was removed via filtration and the remaining
purple crystals were dried for 2 h under vacuum at 0 °C to obtain compound 3-Naph-K as a monosolvated solid. Yield: 401 mg (0.63 mmol, 64 %).

$^1$H NMR (400.3 MHz, THF-d$_8$, 296 K): $\delta$ (ppm) = 1.07 (s, 18H, tBu), 1.78 (m, 4H, THF),$^{[1]}$ 2.08 (s, 12H, C$_6$H$_3$(CH$_3$)$_2$), 3.40 (m, 2H, C$^{1,4}$-H, Naph), 3.62 (m, 4H, THF), 4.13 (m, 2H, C$^{2,3}$-H, Naph), 5.78, 6.18 (each m, 2H, C$^{5,8}$-H and C$^{6,7}$-H, Naph), 5.87 (s, 4H, o-C$_6$H$_3$), 6.03 (s, 2H, p-C$_6$H$_3$).

$^1$H NMR (400.3 MHz, THF-d$_8$, 253 K): $\delta$ (ppm) = 1.02 (s, 18H, tBu), 1.78 (m, 8H, THF), 2.08 (s, 12H, C$_6$H$_3$(CH$_3$)$_2$), 3.42 (m, 2H, C$^{1,4}$-H, Naph), 3.62 (m, 8H, THF), 4.15 (m, 2H, C$^{2,3}$-H, Naph), 5.71 (br s, 4H, o-C$_6$H$_3$), 5.75, 6.06 (each m, 2H, C$^{5,8}$-H and C$^{6,7}$-H, Naph), 5.97 (s, 2H, p-C$_6$H$_3$).

$^{13}$C{$^1$H} NMR (100.67 MHz, THF-d$_8$, 253 K): $\delta$ (ppm) = 22.1 (s, 4C, C$_6$H$_3$(CH$_3$)$_2$), 26.4 (s, 4C, THF), 31.2 (s, 6C, CH$_3$, tBu), 54.0 (s, 2C, C-N, tBu), 68.2 (s, 4C, THF), 73.4 (s, 2C, C$^{2,3}$-Naph), 116.1 (s, 2C, C$^{1,4}$-Naph), 116.4 (br s, 6C, o-C$_6$H$_3$ + p-C$_6$H$_3$, two signals overlap with each other), 117.1 (s, 2C, C$^{5,8}$-Naph), 121.8 (s, 2C, C$^{6,7}$-Naph), 139.6 (s, 4C, m-C$_6$H$_3$), 145.1 (s, 2C, C$^{9,10}$-Naph), 152.5 (s, 2C, ipso-C$_6$H$_3$).

$^{45}$Sc NMR (97.27 MHz, THF-d$_8$, 296 K): $\delta$ (ppm) = 364 (br s, $\delta\nu_{1/2} = \sim$20000 Hz).

Figure S7. $^1$H NMR spectrum of 3-Naph-K in THF-d$_8$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent and the character * denotes some unknown impurities formed due to decomposition at room temperature.

[1] Upon prolonged drying, one batch of complex 3-Naph-K was obtained as a monosolvated complex [K(THF)][Sc{N(tBu)(Xy)}$_2$(Naph)].
Figure S8. $^1$H NMR spectrum of 3-Naph-K in THF-$d_8$ at 253 K; the character S denotes the residual proton signal of the deuterated solvent and the character * denotes an unknown impurity.

Figure S9. $^{13}$C($^1$H) NMR spectrum of 3-Naph-K in THF-$d_8$ at 253 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent and the character * denotes some impurities formed due to the decomposition during sample preparation at room temperature.
Figure S10. $^{45}\text{Sc}$ NMR spectrum of 3-Naph-K in THF-$d_8$ at 296 K; the line broadening (lb) value is set to 50 Hz.

Figure S11. Variable temperature NMR spectroscopic investigation of the reaction between 1 and KNaph in THF-$d_8$ from −60 °C to +25 °C. The reaction was carried out by adding a pre-cooled (−60°C) THF-$d_8$ solution of KNaph to a frozen solution (−196°C) of 1 in THF-$d_8$ and slowly brought to r.t. in the NMR spectrometer. The signals of free naphthalene, which forms as a by-product, were not observed due to the broadening of the signals as commonly observed in a mixture with 3-Naph-K.
2.4. [Li(THF)$_3$][Sc(N(tBu)(Xy))$_2$(Anth)] (3-Anth-Li)

A colorless solution of 1 (500 mg, 0.99 mmol) in THF (5 mL) was treated with a dark blue solution of lithium anthracenide (10 mL, 0.203 mol/L, 2.03 mmol, 2.05 equiv.) in THF at −30 °C. The resulting dark blue solution was slowly brought to ambient temperature during 1 h and stirred for further 5 min at this temperature. During this process, the color of the solution changed to bright red. The solution was cooled again to −30 °C, treated with 5 mL of pre-cooled n-pentane (5 mL) and filtered into another Schlenk tube. 5 mL of pre-cooled n-pentane was added to the red filtrate and stored at −60 °C for 4 d. Upon storing, colorless crystals of anthracene together with a small amount of the desired compound precipitated. The solid was discarded by filtration, the red filtrate was treated with 10 mL of pre-cooled n-pentane and stored at −60 °C for 1 d. Dark red crystals formed upon cooling. These were isolated from the red solution by filtration and washed with 5 mL of pre-cooled n-pentane. The combined filtrate was again stored at −60 °C for 1 d to obtain another batch of dark red crystals. The isolated crystals were dried under reduced pressure for 1 h at 0 °C to obtain the desired compound as THF tetrasolvate. Combined yield: 395 mg (0.45 mmol, 46%). Upon prolong drying the compound was obtained as a THF trisolvate. Empirical formula for 3-Anth-Li: C$_{56}$H$_{70}$LiN$_2$O$_3$Sc (799.00 g/mol).

**Figure S12:** UV-Vis spectra of 3-Naph-K in THF at −40 °C (concentrations vary from ~6.0 – ~ 0.2 mmol).
$^1$H NMR (400.3 MHz, THF-$d_8$, 296 K): δ (ppm) = 0.87 (s, 18H, tBu), 1.78 (m, 16H, THF), 2.12 (s, 12H, C$_6$H$_3$(CH$_3$)$_2$), 3.62 (m, 16H, THF), 3.76 (s, 2H, C$_9$-H, Anth), 5.90 (s, 4H, o-C$_6$H$_3$), 5.99 (s, 2H, p-C$_6$H$_3$), 6.11 (m, 4H, C$_1$,$^4$,$^5$,$^8$-H, Anth), 6.17 (m, 4H, C$_2$,$^3$,$^6$,$^7$-H, Anth).

$^{13}$C($^1$H) NMR (100.67 MHz, THF-$d_8$, 296 K): δ (ppm) = 22.0 (s, 4C, C$_6$H$_3$(CH$_3$)$_2$), 26.4 (s, 4C, THF), 30.8 (s, 6C, CH$_3$, tBu), 54.3 (s, 2C, C-N, tBu), 68.2 (s, 4C, THF), 73.0 (s, 2C, C$_9$,$^{10}$-Anth), 117.2 (s, 4C, o-C$_6$H$_3$), 117.3 (s, 2C, p-C$_6$H$_3$), 119.8 (s, 4C, C$_1$,$^4$,$^5$,$^8$-Anth), 121.1 (s, 4C, C$_2$,$^3$,$^6$,$^7$-Anth), 138.9 (s, 4C, m-C$_6$H$_3$), 141.0 (s, 4C, C$_{4a}$,$^{8a}$,$^{9a}$,$^{10a}$-Anth), 151.2 (s, 2C, ipso-C$_6$H$_3$).

$^7$Li($^1$H) NMR (155.57 MHz, THF-$d_8$, 296 K): δ (ppm) = 0.25 (s).

Figure S13. $^1$H NMR spectrum of 3-Anth-Li in THF-$d_8$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent.
Figure S14. $^{13}\text{C}^\text{(H)}$ NMR spectrum of 3-Anth-Li in THF-$d_8$ at 296 K; the character S denotes the $^{13}\text{C}$ NMR signal of the deuterated solvent.

Figure S15. $^7\text{Li}^\text{(H)}$ NMR spectrum of 3-Anth-Li in THF-$d_8$ at 296 K.
2.5. \([\text{Na(THF)}_4] \{\text{Sc(N(tBu)(Xy))_2(Anth)}\}\) (3-Anth-Na)

A colorless solution of \(1\) (300 mg, 0.59 mmol) in THF (5 mL) was treated with a dark blue solution of sodium anthracenide (10 mL, 0.121 mol/L, 1.21 mmol, 2.05 equiv.) in THF at \(-30^\circ\text{C}\). After the addition, the dark blue solution was slowly brought to 0 °C within 30 min and stirred for further 30 min at this temperature. During this time, the color of the solution changed from dark blue to dark red. The resulting solution was concentrated to ~10 mL and then treated with 5 mL of pre-cooled \(n\)-pentane at \(-30^\circ\text{C}\). The red suspension was filtered into a Schlenk tube and treated again with 5 mL of pre-cooled \(n\)-pentane. The red suspension was stored at \(-60^\circ\text{C}\) for 18 h to obtain a microcrystalline bright red solid, which was isolated by filtration of the dark red supernatant and washed with 10 mL of pre-cooled \(n\)-pentane. Finally, the red solid was dried under reduced pressure for 1 h at 0 °C. Yield: 325 mg (0.37 mmol, 62%). Empirical formula for 3-Anth-Na: \(\text{C}_{54}\text{H}_{78}\text{N}_2\text{NaO}_4\text{Sc} (887.15 \text{ g/mol})\).

\(^1\text{H}\) NMR (400.3 MHz, THF-\(d_8\), 296 K): \(\delta\) (ppm) = 0.89 (s, 18H, tBu), 1.78 (m, 16H, THF), 2.13 (s, 12H, \(\text{C}_6\text{H}_3(\text{CH}_3)_2\)), 3.62 (m, 16H, THF), 3.80 (s, 2H, C\(^9,10\)-H, Anth), 5.91 (s, 4H, o-C\(_6\)H\(_3\)), 6.00 (s, 2H, \(p\)-C\(_6\)H\(_3\)), 6.14 (m, 4H, C\(^1,4,5,8\)-H, Anth), 6.19 (m, 4H, C\(^2,3,6,7\)-H, Anth).

\(^{13}\text{C}\{^1\text{H}\}\) NMR (100.67 MHz, THF-\(d_8\), 296 K): \(\delta\) (ppm) = 22.0 (s, 4C, \(\text{C}_6\text{H}_3(\text{CH}_3)_2\)), 26.4 (s, 4C, THF), 30.8 (s, 6C, CH\(_3\), tBu), 54.3 (s, 2C, C-N, tBu), 68.2 (s, 4C, THF), 73.1 (s, 2C, C\(^9,10\)-Anth), 117.0 (s, 4C, o-C\(_6\)H\(_3\)), 117.3 (s, 2C, p-C\(_6\)H\(_3\)), 119.8 (s, 4C, C\(^1,4,5,8\)-Anth), 121.1 (s, 4C, C\(^2,3,6,7\)-Anth), 139.1 (s, 4C, m-C\(_6\)H\(_3\)), 141.0 (s, 4C, C\(^4a,8a,9a,10a\)-Anth), 151.1 (s, 2C, ipso-C\(_6\)H\(_3\)).

\(^{23}\text{Na}\) NMR (105.89 MHz, THF-\(d_8\), 296 K): \(\delta\) (ppm) = 7.6.

*Figure S16.* \(^1\text{H}\) NMR spectrum of 3-Anth-Na in THF-\(d_8\) at 296 K; the character S denotes the residual proton signal of the deuterated solvent.
**Figure S17.** $^{13}$C($^1$H) NMR spectrum of 3-Anth-Na in THF-$d_8$ at 296 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent and the character * denotes an unknown impurity.

**Figure S18.** $^{23}$Na NMR spectrum of 3-Anth-Na in THF-$d_8$ at 296 K.
2.6. [K(THF)][Sc{N(tBu)(Xy)}₂(Anth)] (3-Anth-K)

A colorless solution of 1 (300 mg, 0.59 mmol) in THF (5 mL) was treated with a dark blue solution of potassium anthracenide (10 mL, 0.121 mol/L, 1.21 mmol, 2.05 equiv.) in THF at -30 °C. After addition, the dark blue solution was slowly brought to ambient temperature during 1 h and stirred for 5 min at this temperature. During this time, the color of the solution changed from dark blue to dark red. The red solution was cooled again to 0 °C and concentrated to ~10 mL. To this solution, 5 mL of pre-cooled n-pentane was added dropwise at -30 °C and the obtained solution was filtered. The filtrate was again treated with 5 mL of pre-cooled n-pentane and stored at -60 °C for 6 h to afford dark red microcrystals. The supernatant solution was removed via filtration and the remaining microcrystals were dried for 1 h under vacuum at 0 °C to obtain compound 3-Anth-K as a THF monosolvate. Yield: 301 mg (0.44 mmol, 74%).

Empirical formula for 3-Anth-K: C₄₂H₆₄KN₂OSc (686.96 g/mol).

¹H NMR (400.3 MHz, THF-d₆, 296 K): δ (ppm) = 0.89 (s, 18H, tBu), 1.78 (m, 4H, THF), 2.12 (s, 12H, C₆H₃(CH₃)₂), 3.62 (m, 4H, THF), 3.77 (s, 2H, C₅₋₁₀-H, Anth), 5.93 (s, 4H, ð-C₆H₃), 6.05 (s, 2H, ð-C₆H₃), 6.16 (m, 4H, C₁₋₄,₈-H, Anth), 6.25 (m, 4H, C₂₋₆,₇-H, Anth).

¹H NMR (400.3 MHz, THF-d₆, 253 K): δ (ppm) = 0.90 (s, 18H, tBu), 1.78 (m, 4H, THF), 2.13 (s, 12H, C₆H₃(CH₃)₂), 3.62 (m, 4H, THF), 3.78 (s, 2H, C₅₋₁₀-H, Anth), 5.94 (s, 4H, ð-C₆H₃), 6.06 (s, 2H, ð-C₆H₃), 6.16 (m, 4H, C₁₋₄,₈-H, Anth), 6.25 (m, 4H, C₂₋₆,₇-H, Anth).

¹³C(¹H) NMR (100.67 MHz, THF-d₆, 296 K): δ (ppm) = 21.9 (s, 4C, C₆H₃(CH₃)₂), 26.4 (s, 4C, THF), 30.9 (s, 6C, CH₃, tBu), 54.5 (s, 2C, C-N, tBu), 68.2 (s, 4C, THF), 72.4 (s, 2C, C₅₋₁₀-Anth), 117.7 (s, 4C, ð-C₆H₃), 118.2 (s, 2C, ð-C₆H₃), 119.7 (s, 4C, C₁₋₄,₈-Anth), 121.5 (s, 4C, C₂₋₆,₇-Anth), 139.2 (s, 4C, ð-C₆H₃), 141.2 (s, 4C, C₄₋₈,₉,₁₀-Anth), 151.7 (s, 2C, ipso-C₆H₃).

⁴⁵Sc NMR (97.27 MHz, THF-d₆, 296 K): δ (ppm) = 364 (br s, δν₁₂ = ~17500 Hz).
Figure S19. $^1$H NMR spectrum of 3-Anth-K in THF-$d_8$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent.

Figure S20. $^1$H NMR spectrum of 3-Anth-K in THF-$d_8$ at 253 K; the character S denotes the residual proton signal of the deuterated solvent.
**Figure S21.** $^{13}$C($^1$H) NMR spectrum of 3-Anth-K in THF-$d_8$ at 296 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent.

**Figure S22.** $^{13}$C($^1$H) NMR spectrum of 3-Anth-K in THF-$d_8$ at 253 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent.
Figure S23. $^{45}$Sc NMR spectrum of 3-Anth-K in THF-$d_8$ at 296 K; the line broadening (lb) value is set to 50 Hz.

Figure S24: UV-Vis spectra of 3-Anth-K in THF at -40 °C (concentrations vary from ~8.0 – ~ 0.5 mmol).
2.7. [Li][Sc{N(rBu)(Xy)}_2(Anth)(4-MeO-C_6H_4-C=N)] (4a)

To a red solution of 3-Anth-Li (100 mg, 0.11 mmol) in THF (2 mL), a colourless solution of 4-methoxynbenzonitrile (16 mg, 0.12 mmol, 1.05 equiv.) in THF (1 mL) was slowly added at −30 °C. Upon addition, the color of the solution immediately changed to reddish brown via an intermediate purple colour. A \(^1\)H NMR spectrum of an aliquot of the reddish brown solution after 5 min revealed a selective and complete conversion of the starting materials into product. All the volatiles were removed under reduced pressure and the residue was washed with n-pentane (2×3 mL) at ambient temperature to obtain a brick red solid, which was dried for 1 h at r.t. Yield: 62 mg (0.09 mmol, 75%). Anal. calcd. for C_{46}H_{53}LiN_3OSc (715.83 g/mol): C 77.18; H 7.46; N 5.87%. Found: C 71.47; H 7.28; N 5.46%. Multiple attempts to obtain acceptable EA (elemental analysis) values failed, probably due to the incomplete combustion.

\(^1\)H NMR (400 MHz, THF-\(d_8\), 296 K): \(\delta\) (ppm) = 0.96 (s, 18H, \(t\)Bu), 2.16 (s, 12H, C_6H_3(CH_3)_2), 3.49 (s, 1H, C^9-H, Anth), 3.79 (s, 3H, OCH_3), 5.68 (s, 1H, C^10-H, Anth), 6.07 (dd, 2H, \(^3\)J\(_{HH} = 7.8\) Hz, \(^4\)J\(_{HH} = 0.8\) Hz, C^1.8-H, Anth), 6.20 (s, 2H, \(p\)-C_6H_3), 6.29 (td, 2H, \(^3\)J\(_{HH} = 7.2\) Hz, \(^4\)J\(_{HH} = 1.2\) Hz, C^2.7-H, Anth), 6.36 (s, 4H, \(o\)-C_6H_3), 6.48 (td, 2H, \(^3\)J\(_{HH} = 7.4\) Hz, \(^4\)J\(_{HH} = 1.4\) Hz, C^3.6-H, Anth), 6.69 (dd, 2H, \(^3\)J\(_{HH} = 7.4\) Hz, \(^4\)J\(_{HH} = 1.2\) Hz, C^4.5-H, Anth), 6.85 (m, 2H, C^3.5-H, MeO-C_6H_4-CN), 8.14 (m, 2H, C^2.6-H, MeO-C_6H_4-CN).

\(^13\)C\{\(^1\)H\} NMR (101 MHz, THF-\(d_8\), 296 K): \(\delta\) (ppm) = 22.1 (s, 4C, C_6H_3(CH_3)_2), 31.8 (s, 6C, CH_3, \(t\)Bu), 54.3 (s, 2C, C-N, \(t\)Bu), 54.5 (s, 1C, C^10-H, Anth), 55.3 (s, 1C, OCH_3), 69.9 (s, 1C, Sc-C^9-H, Anth), 113.4 (s, 2C, C^3.5, C_6H_3), 117.6 (s, 4C, C^2.7-Aanth), 119.1 (s, 2C, \(p\)-C_6H_3), 124.2 (s, 4C, \(o\)-C_6H_3), 124.4 (s, 2C, C^1.8-Aanth), 124.9 (s, 4C, C^3.6-Aanth), 126.1 (s, 2C, C^4.5-Aanth), 129.7 (s, 2C, C^2.6, C_6H_4), 131.6 (s, 2C, C_6H_4-N-Aanth), 135.6 (s, 1C, C^1-CN, C_6H_4), 136.8 (s, 4C, m-C_6H_3), 144.6 (s, 2C, C^4a.10a-Aanth), 154.8 (s, 2C, ipso-C_6H_3), 161.0 (s, 1C, C^4, C_6H_4), 170.9 (s, 1C, C=N).

\(^7\)Li\{\(^1\)H\} NMR (155.57 MHz, THF-\(d_8\), 296 K): \(\delta\) (ppm) = −0.68 (s).

\(^45\)Sc NMR (97.27 MHz, THF-\(d_8\), 296 K): \(\delta\) (ppm) = 451 (br s, \(\Delta\nu_{1/2} \approx 16000\) Hz).
Figure S25. $^1$H NMR spectrum of 4a in THF-$d_8$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent.

Figure S26. $^{13}$C($^1$H) NMR spectrum of 4a in THF-$d_8$ at 296 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent.
**Figure S27.** $^{45}$Sc NMR spectrum of 4a in THF-$d_8$ at 296 K; the line broadening (lb) value is set to 20 Hz.

**Figure S28.** $^7$Li($^1$H) NMR spectrum of 4a in THF-$d_8$ at 296 K.
2.8. \([\text{Li(THF)}_2][\text{Sc\{N(tBu)(Xy)}\}_2(\text{Anth})(\text{tBu-C=N})](4b)\)

To a dark red solution of 3-\text{Anth-Li} (200 mg, 0.25 mmol) in THF (5 mL), a colourless solution of tBuCN (21 mg, 0.25 mmol, 1 equiv.) in THF (1 mL) was slowly added at \(-30\) °C and the resulting greenish yellow solution was slowly brought to room temperature. A \(^1\text{H}\) NMR spectrum of an aliquot of the greenish yellow solution after 10 min revealed a selective and complete conversion of the starting materials into product. All the volatiles were removed under reduced pressure and the residue was washed with \(n\)-pentane (2×2 mL) at ambient temperature to obtain a yellow solid. The yellow solid was dissolved into a mixture of diethyl ether and \(n\)-hexane (1:2, 6 mL) and stored at \(-40\) °C. Bright yellow microcrystals formed upon cooling, which were separated from the light yellow supernatant solution by filtration and dried under reduced pressure for 6 h to obtain a yellow solid. The supernatant solution and the \(n\)-pentane washing liquids were collected, concentrated to \(\sim 5\) mL and stored at \(-40\) °C to obtain another batch of the product. Combined yield: 182 mg (0.22 mmol, 90%).

**Anal. calcd. for C\(_{46}\)H\(_{53}\)LiN\(_3\)OSc (715.83 g/mol):** C 75.62; H 8.84; N 5.19%. Found: C 65.01; H 7.13, N 4.51%.

Multiple attempts to obtain acceptable EA values failed, probably due to the incomplete combustion.

\(^1\text{H}\) NMR (400 MHz, THF-\(d_8\), 296 K): \(\delta\) (ppm) = 0.95 (s, 18H, tBu), 1.26 (s, 9H, tBu-CN), 2.15 (s, 12H, C\(_6\)H\(_3\)(CH\(_3\))\(_2\)), 3.37 (s, 1H, Sc-C\(^9\)-H, Anth), 5.11 (s, 1H, C\(^10\)-H, Anth), 5.99 (dd, 2H, \(^3J_{H,H} = 7.8\) Hz, \(^4J_{H,H} = 1.2\) Hz, C\(^1,8\)-H, Anth), 6.18 (s, 2H, p-C\(_6\)H\(_3\)), 6.30 (td, 2H, \(^3J_{H,H} = 7.2\) Hz, \(^4J_{H,H} = 1.4\) Hz, C\(^2,7\)-H, Anth), 6.32 (s, 4H, o-C\(_6\)H\(_3\)), 6.44 (td, 2H, \(^3J_{H,H} = 7.2\) Hz, \(^4J_{H,H} = 1.4\) Hz, C\(^3,6\)-H, Anth), 6.72 (dd, 2H, \(^3J_{H,H} = 7.4\) Hz, \(^4J_{H,H} = 1.2\) Hz, C\(^4,5\)-H, Anth).

\(^{13}\text{C}\{^1\text{H}\}\) NMR (101 MHz, THF-\(d_8\), 296 K): \(\delta\) (ppm) = 22.1 (s, 4C, C\(_6\)H\(_3\)(CH\(_3\))\(_2\)), 29.4 (s, 3C, CH\(_3\), tBu-C=N), 31.8 (s, 6C, CH\(_3\), N-tBu), 41.9 (s, 1C, C-CN, tBu-C=N), 54.0 (s, 2C, C-N, N-tBu), 54.4 (s, 1C, C\(^10\)-Anth), 70.2 (s, 1C, Sc-C\(^9\)-Anth), 117.4 (s, 4C, C\(^2,7\)-Anth), 118.8 (s, 2C, p-C\(_6\)H\(_3\)), 124.0 (s, 4C, o-C\(_6\)H\(_3\)), 124.3 (s, 4C, C\(^3,6\)-Anth), 124.4 (s, 2C, C\(^1,8\)-Anth), 126.2 (s, 2C, C\(^4,5\)-Anth), 131.8 (s, 2C, C\(^8,9a\)-Anth), 136.8 (s, 4C, m-C\(_6\)H\(_3\)), 145.0 (s, 2C, C\(^4,10a\)-Anth), 154.9 (s, 2C, ipso-C\(_6\)H\(_3\)), 178.8 (s, 1C, tBu-C=N).

\(^7\text{Li}\{^1\text{H}\}\) NMR (155.57 MHz, THF-\(d_8\), 296 K): \(\delta\) (ppm) = -0.71 (s).

\(^{45}\text{Sc}\) NMR (97.27 MHz, THF-\(d_8\), 296 K): \(\delta\) (ppm) = 443 (br s, \(\ddot{\alpha}_{1/2} = \sim 8000\) Hz).
**Figure S29.** $^1$H NMR spectrum of 4b in THF-$d_8$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent.

**Figure S30.** $^{13}$C($^1$H) NMR spectrum of 4b in THF-$d_8$ at 296 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent.
Figure S31. $^{45}\text{Sc}$ NMR spectrum of 4b in THF-$d_8$ at 296 K; the line broadening (lb) value is set to 100 Hz.

Figure S32. $^7\text{Li}[^1\text{H}]$ NMR spectrum of 4b in THF-$d_8$ at 296 K.
2.9. [Sc(C_{14}H_{11})\{N(tBu)(Xy)\}_2]·THF (5)

A colorless solution of [NEt$_3$H][BPh$_4$] in THF (5 mL) was slowly added to a pre-cooled (−40°C), red solution of 3-Anth-Li in THF (5 mL). Upon addition, the color of the solution immediately changed to light orange. The solution was slowly brought to room temperature while stirring. An aliquot $^1$H NMR spectrum after 15 min confirmed the complete and selective conversion of the starting materials into the monoprotonated product [Sc(C_{14}H_{11})\{N(tBu)(Xy)\}_2]$^+$·THF (5) along with [LiBPh$_4$] as a by-product. All the volatiles were removed under reduced pressure and the residue was extracted with $n$-pentane (10 mL). The light orange extract was concentrated to ~6 mL and stored at −40 °C for 48 h for crystallization. Resulting light orange crystals were isolated by decantation of the light yellow supernatant, and washed with pre-cooled (−40°C) $n$-pentane (1 mL). After grinding and drying for 3 h at ambient temperature, compound 5 was obtained as an analytically pure, off white solid. Yield: 57 mg (0.09 mmol, 70%). Anal. calcd. for C$_{42}$H$_{55}$N$_2$Sc (648.87 g/mol): C 77.74; H 8.54; N 4.32%. Found: C 75.62; H 8.49; N 4.21%.

$^1$H NMR (400.3 MHz, benzene-$d_6$, 296 K): δ (ppm) = 0.81 (br s, $\delta$\textsubscript{1/2} = 12 Hz, 4H, THF), 1.37 (s, 18H, tBu), 2.25 (s, 12H, C$_6$H$_3$(CH$_3$)$_2$), 2.88 (br s, $\delta$\textsubscript{1/2} = 15 Hz, 4H, THF), 3.52 (s, 1H, C$_9$-H, Anth), 3.75, 3.93 (each d, $^2$\textsubscript{H,H} = 16.2 Hz, 1H each, C$_{10}$-H, Anth), 6.66 (s, 2H, p-C$_6$H$_3$), 6.82 (s, 4H, o-C$_6$H$_3$), 6.91 (d, 2H, $^2$\textsubscript{H,H} = 7.6 Hz, C$_{16}$-H, Anth), 7.12 (d, $^2$\textsubscript{H,H} = 7.4 Hz, 2H, C$_4$-H, Anth) 7.13 (t, 2H, C$_3$-H, Anth; this signal overlaps with the signal at 6.91 ppm), 7.14 (d, $^2$\textsubscript{H,H} = 7.4 Hz, 2H, C$_4$-H, Anth).

$^{13}$C\{$^1$H} NMR (100.67 MHz, benzene-$d_6$, 296 K): δ (ppm) = 21.5 (s, 4C, C$_6$H$_3$(CH$_3$)$_2$), 24.6 (s, 2C, THF), 31.1 (s, 6C, C(CH$_3$)$_3$), 38.5 (s, 1C, C$_{10}$-Anth), 56.8 (s, 2C, C(CH$_3$)$_3$), 72.1 (s, 1C, C$_9$-Anth), 72.4 (s, 2C, THF), 120.5 (s, 4C, C$_{27}$-Anth), 123.5 (s, 4C, C$_{16}$-Anth), 125.9 (s, 2C, C$_{36}$-Anth), 126.2 (s, 2C, p-C$_6$H$_3$), 127.1 (s, 2C, C$_{45}$-Anth), 128.3 (s, 2C, C$_{26,9a}$-Anth), 129.9 (s, 4C, o-C$_6$H$_3$), 137.9 (s, 4C, m-C$_6$H$_3$), 147.2 (s, 2C, C$_{4a,10a}$-Anth), 149.4 (s, 2C, ipso-C$_6$H$_3$).

$^{45}$Sc NMR (97.27 MHz, benzene-$d_6$, 296 K): δ (ppm) = 461 (br s, $\delta$\textsubscript{1/2} = ~13000 Hz).
Figure S33. $^1$H NMR spectrum of 5 in benzene-$d_6$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent.

Figure S34. $^{13}$C($^1$H) NMR spectrum of 5 in benzene-$d_6$ at 296 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent.
Figure S35. $^{45}$Sc NMR spectrum of 5 in benzene-$d_6$ at 296 K; the line broadening (lb) value is set to 50 Hz.

3. Crystal structure determination of 1, 2, 3-Naph-K, 3-Anth-Li, 3-Anth-Na, 3-Anth-K, 4a, 4b and 5

X-ray diffraction data were collected on an Eulerian 4-circle diffractometer STOE STADIVARI in ω-scan mode at 100 K with Mo-Kα radiation (1, 2, 3-Anth-Li, 3-Anth-K) or with Cu-Kα radiation (3-Naph-K and 3-Anth-Na, 4a). Data of 4b and 5 were collected on a Bruker AXS diffractometer at 100 K with Mo-Kα radiation. Using the program system Olex2, the structures were solved by direct methods with the program SHELXT. The crystal structures of 3-Naph-K and of 3-Anth-K contain two crystallographically independent molecules. Five of the THF molecules coordinated to the potassium atoms in 3-Anth-K are disordered. The disorder could be resolved by introducing splitting positions. All refinements were carried out against $F^2$ using SHELXL with anisotropic displacement parameters for the non hydrogen atoms. All hydrogen atoms of 2 and most hydrogen atoms in 3-Naph-K, 3-Anth-Li and 3-Anth-K were included in calculated positions and treated as riding throughout the refinement. Only the hydrogen atoms of the naphthalene ligand in 3-Naph-K (H1 – H8 as well as H47 – H54), the hydrogen atoms of the anthracene ligand in 3-Anth-Li (H1 – H10), the hydrogen atoms H9 and H10 as well as H59 and H60 of the anthracene ligand in 3-Anth-K, the hydrogen atoms H9 and H10 of the anthracene ligand in 4a, the hydrogen atoms H9 and H10 and H17 and H27 in 4b, as well as the hydrogen atoms H9, H10a and H10b of the anthracenyl ligand in 5 were refined in their
position. In the structures of 1 and 3-Anth-Na, all hydrogen atoms could be located in a Fourier difference map and are refined in their position.

Refinement results are given in Tables S1-S3. Graphical representations were performed with the program DIAMOND. CCDC-1968754-1968759, 1972178-1972179 and 1983913 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S1**: Crystallographic data of 1, 2 and 3-Naph-K.

|        | 1         | 2         | 3-Naph-K |
|--------|-----------|-----------|----------|
| formula| C₄₀H₆₂N₃OSc| C₂₈H₄₄ClN₂OSc| C₄₆H₆₈KN₂O₃Sc, |
| Fw /g mol⁻¹ | 645.88 | 505.06 | 781.08 |
| cryst. color, habit | colourless block | colourless plate | dark brown block |
| crystal size / mm | 0.09 × 0.17 × 0.21 | 0.08 × 0.18 × 0.26 | 0.09 × 0.13 × 0.18 |
| space group | Pbca | P1 | P2₁/c |
| a / Å | 14.6301(6) | 9.0028(8) | 33.3778(8) |
| b / Å | 19.3462(8) | 9.1975(9) | 10.7006(2) |
| c / Å | 26.9499(13) | 18.2896(2) | 24.4589(6) |
| Z | 8 | 2 | 8 |
| &dcalc/Mg m⁻³ | 1.125 | 1.202 | 1.188 |
| &µ(MoKα)/mm⁻¹ | 0.225 | 0.381 | |
| &µ(CuKα)/mm⁻¹ | | | 2.595 |
| F(000) | 2816 | 544 | 3376 |
| θ range / ° | 1.90, 26.37 | 2.26, 29.44 | 3.61, 71.78 |
| index ranges | -18≤h≤18; -20≤k≤24; -33≤l≤16 | -12≤h≤12; -12≤k≤12; -24≤l≤24 | -41≤h≤32; -9≤k≤13; -28≤l≤29 |
| refln. | 22019 | 11766 | 53103 |
| indep. refns (Rint) | 7725 (0.0460) | 6553 (0.0481) | 15776 (0.0592) |
| observed refns | 4734 | 3901 | 10016 |
| data/ restr./ param. | 7725 / 0 / 421 | 6553 / 0 / 474 | 15776 / 141 / 1161 |
| R₁, wR₂ [l> 2σ(l)] | 0.0444, 0.0954 | 0.0512, 0.1071 | 0.0680, 0.1701 |
| R₁, wR₂ (all data) | 0.0915, 0.1094 | 0.0921, 0.1163 | 0.1014, 0.1857 |
| Goof on F² | 0.938 | 0.895 | 0.945 |
| largest diff. peak, hole/e Å³ | 0.272, -0.311 | 0.466, -0.851 | 1.218, -0.906 |
| CCDC number | 1968755 | 1968754 | 1968756 |
Table S2: Crystallographic data of 3-Anth-Li, 3-Anth-Na and 3-Anth-K.

|                | 3-Anth-Li | 3-Anth-Na | 3-Anth-K |
|----------------|-----------|-----------|----------|
| formula        | C₃₈H₄₆N₂Sc, C₁₆H₃₂LiO₄ | C₃₈H₄₆N₂Sc, C₂₃H₂₈NaO₈ | C₅₄H₇₆KN₂O₄Sc |
| Fw /g mol⁻¹    | 871.08    | 1031.34   | 903.24   |
| cryst. color, habit | orange block | red rod | red block |
| crystal size / mm | 0.5 × 0.5 × 0.5 | 0.07 × 0.16 × 0.33 | 0.11 × 0.16 × 0.20 |
| crystal system  | monoclinic | monoclinic | Orthorhombic |
| space group    | P2₁/c     | P2₁/n     | Pca₂₁    |
| a / Å          | 11.7535(7) | 17.741(4) | 19.2284(7) |
| b / Å          | 16.1884(7) | 17.502(4) | 14.4460(2) |
| c / Å          | 26.1894(14)| 19.092(4) | 36.7470(6) |
| β / °          | 92.406(5)  | 99.77(3)  | 95.519(9)  |
| V / Å³         | 4978.7(4)  | 5842(2)   | 10207.3(3) |
| Z              | 4         | 4         | 8         |
| dcalc / Mg m⁻³ | 1.162     | 1.173     | 1.176     |
| μ(MoKα)/mm⁻¹   | 0.193     | 0.270     |           |
| μ(CuKα)/mm⁻¹   |           |           | 1.537     |
| F(000)         | 1888      | 2240      | 3904      |
| θ range / °    | 2.14, 30.91| 3.45, 70.44| 1.41, 25.78 |
| index ranges   | -13s≤h≤16; -22s≤k≤21; -28s≤l≤37 | -21s≤h≤21; -21s≤k≤19; -22s≤l≤18 | -21s≤h≤23; -17s≤k≤10; -40s≤l≤44 |
| refln.         | 45919     | 36454     | 64906     |
| independent refns (Rint) | 14050 (0.0973) | 10834 (0.0279) | 18121 (0.0653) |
| observed reflns | 5675      | 8559      | 12446     |
| data/restr./param. | 14050 / 0/ 593 | 10834 / 0/ 1025 | 18121 /511 / 1338 |
| R₁, wR₂ (l> 2σ(l)) | 0.0704, 0.1626 | 0.0365, 0.0915 | 0.0439, 0.0914 |
| R₁, wR₂ (all data) | 0.1760 | 0.2033 | 0.0652, 0.0965 |
| GoOF on F²     | 0.877     | 0.979     | 0.848     |
| largest diff. peak, hole/ e Å³ | 0.427, -0.590 | 0.283, -0.283 | 0.384, -0.365 |
| CCDC number    | 196875 7  | 196875 8  | 196875 9  |

Table S3: Crystallographic data of 4a, 4b and 5.

|    | 4a          | 4b          | 5           |
|----|-------------|-------------|-------------|
| formula | C₄₆H₅₃N₃OSc, C₁₆H₃₂LiO₄ | C₄₇H₆₃N₃LiOSc | C₄₂H₅₅N₂OSc |
| Fw /g mol⁻¹ | 1004.22 | 737.90 | 648.84 |
| cryst. color, habit | red plate | orange plate | yellow block |
| crystal size / mm | 0.05 × 0.16 × 0.21 | 0.07 × 0.35 × 0.36 | 0.13 × 0.20 × 0.25 |
| crystal system  | orthorhombic | orthorhombic | monoclinic |
| space group    | Pbca      | Pbca       | Pca₂₁      |
| a / Å          | 21.5267(15) | 19.883(5)  | 10.595(5)  |
| b / Å          | 21.6957(5)  | 19.598(5)  | 15.807(7)  |
| c / Å          | 25.8963(5)  | 21.622(6)  | 22.067(10) |
| β / °          |           |           | 95.519(9)  |
| V / Å³         | 12094.5(5) | 8425(4)    | 3679(3)    |
| Z              | 8         | 8         | 4          |
| dcalc / Mg m⁻³ | 1.103     | 1.163     | 1.172      |
| μ(MoKα)/mm⁻¹   | 0.212     | 0.234     |           |
| μ(CuKα)/mm⁻¹   | 1.401     |           |           |
| F(000)         | 4336      | 3184      | 1400       |
| θ range / °    | 4.87, 70.06 | 1.74, 26.65 | 1.85, 25.37 |
| index ranges          | -15 ≤ h ≤ 26; -24 ≤ k ≤ 26; -30 ≤ l ≤ 31 | -25 ≤ h ≤ 24; -24 ≤ k ≤ 24; -27 ≤ l ≤ 27 | -12 ≤ h ≤ 12; -18 ≤ k ≤ 17; -26 ≤ l ≤ 26 |
|----------------------|------------------------------------------|------------------------------------------|------------------------------------------|
| refln.               | 49965                                    | 146732                                   | 30072                                    |
| indep. refns (R_int)| 11124 (0.0803)                           | 8764 (0.1695)                            | 6679 (0.1309)                            |
| observed refns       | 5103                                     | 6006                                     | 4056                                     |
| data/ restr./ param. | 11124 / 64 / 785                         | 8764 / 0 / 505                           | 6679 / 0 / 434                           |
| R₁, wR₂ [I > 2σ(I)]  | 0.0811, 0.2034                           | 0.0691, 0.1859                           | 0.0559, 0.1246                           |
| R₁, wR₂ (all data)  | 0.1299, 0.2461                           | 0.1027, 0.2025                           | 0.1106, 0.1490                           |
| Goof on F²           | 0.887                                    | 1.038                                    | 1.009                                    |
| largest diff. peak, hole/ e Å³ | 0.247, -0.704            | 0.808, -0.532                           | 0.322, -0.415                           |
| CCDC number          | 1972178                                  | 1972179                                  | 1983913                                  |

**Figure S36.** Molecular structure of 1 in the solid state with displacement parameters at 30% probability level. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.0692(18), Sc1-N2 2.0622(17), Sc1-N3 2.0591(17), Sc1-O1 2.1759(14); O1-Sc1-N1 100.06(6), O1-Sc1-N2 100.23(6), O1-Sc1-N3 110.19(6), N1-Sc-N2 115.86(7), N1-Sc-N3 116.75(7), N2-Sc-N3 111.19(7).
**Figure S37.** Molecular structure of 2 in the solid state with displacement parameters at 30% probability level. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.0694(19), Sc1-N2 2.005(2), Sc1-Cl1 2.3858(7), Sc1-O1 2.1705(17); O1-Sc1-N1 112.38(7), O1-Sc1-N2 119.69(7), O1-Sc1-Cl1 92.73(5), Cl1-Sc1-N1 102.92(6), Cl1-Sc1-N2 104.46(6), N1-Sc-N2 118.76(8).

**Figure S38.** Molecular structure of one of the two crystallographically independent molecules of 3-Naph-K in the solid state with displacement parameters at 30% probability level. H atoms except for H22c are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.181(3), Sc1-N2 2.135(3), Sc1-C1 2.355(4), Sc1-C2 2.488(4), Sc1-C3 2.475(3), Sc1-C4 2.322(3), K1-N1 3.065(3), K1-O1 2.669(2), K1-O2 2.737(3), K1-O3 2.695(3), K1-C5 3.426(4), K1-C6 3.126(4), K1-C7 3.017(5), K1-C8 3.222(5); N1-Sc1-N2 107.93(10), C1-Sc1-C4 72.51(14), N1-K1-O2 153.68(8), Sc2-N3 2.183(3), Sc2-N4 2.147(3), Sc2-C47 2.309(4), Sc2-C48 2.471(4), Sc2-C49 2.505(4), Sc2-C50 2.348(4), K1-N3 3.115(3).
Figure S39. Molecular structure of 3-Anth-Li in the solid state with displacement parameters at 30% probability level. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.120(2), Sc1-N2 2.133(2), Sc1-C9 2.358(3), Sc1-C10 2.358(3), Sc1-C4A 2.724(3), Sc1-C8A 2.731(3), Sc1-C9A 2.706(3), Sc1-C10A 2.735(3), C4A-C9A 1.413(4), C9-C9A 1.461(4), C9-C8A 1.463(4), C8A-C10A 1.425(4), C10-C10A 1.466(4), C4A-C10 1.463(4); N1-Sc1-N2 107.63(9), C9-Sc1-C10 70.85(11).
Figure S40. Molecular structure of 3-Anth-Na in the solid state with displacement parameters at 30% probability level. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.1070(14), Sc1-N2 2.1312(12), Sc1-C9 2.3308(16), Sc1-C10 2.3443(16), Sc1-C4A 2.7853(15), Sc1-C8A 2.6929(18), Sc1-C9A 2.7787(15), Sc1-C10A 2.6899(17), N1-Sc1-N2 106.78(5).
Figure S41. Molecular structure of one of the two crystallographically independent molecules of 3-Anth-K in the solid state with displacement parameters at 30% probability level. Only one of the two crystallographically independent molecules is shown. Disordered oxygen and carbon atoms of the coordinated THF ligands are shown with only one split position. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.099(4), Sc1-N2 2.101(4), Sc1-C9 2.355(4), Sc1-C10 2.344(5), Sc1-C4A 2.754(5), Sc1-C8A 2.760(5), Sc1-C9A 2.764(5), Sc1-C10A 2.736(5), K1-C8A 3.186(5), K1-C9 3.075(4), K1-C9A 3.136(5), N1-Sc1-N2 108.73(16), Sc2-N3 2.107(4), Sc2-N4 2.106(4).
Figure S42. Molecular structure of 4a in the solid state with displacement parameters at 30% probability level. Li(THF)$_4$ cation and H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.043(4), Sc1-N2 2.128(3), Sc1-N3 2.072(3), Sc1-C9 2.348(4), N1-C11 1.259(5), C10-C11 1.547(6); N1-Sc1-N2 104.91(15), N1-Sc1-N3 112.29(14), N2-Sc1-N3 115.24(14), C9-Sc1-N1 93.37(15), C9-Sc1-N2 117.46(15), C9-Sc1-N3 111.18(15).

Figure S43. Molecular structure of 4b in the solid state with displacement parameters at 30% probability level. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.062(2), Sc1-N2 2.090(3), Sc1-N3 2.155(2), Sc1-C9 2.323(3), N1-C11 1.264(4), C10-C11 1.553(4), Li1-N1 1.952(6), Li1-N3 2.140(6), Li1-O1 1.924(6); N1-Sc1-N2 110.80(10), N1-Sc1-N3 90.97(9), N2-Sc1-N3 112.11(10), C9-Sc1-N1 91.21(10), C9-Sc1-N2 115.22(10), C9-Sc1-N3 128.17(11).
Figure S44. Molecular structure of 5 in the solid state with displacement parameters at 30% probability level. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.017(3), Sc1-N2 2.027(3), Sc1-O1 2.141(2), Sc1-C9 2.333(3), N1-Sc1-N2 113.75(11), O1-Sc1-N1 118.28(9), O1-Sc1-N2 100.81(10), N1-Sc1-C9 108.57(11), N2-Sc1-C9 108.52(11), O1-Sc1-C9 106.26(11).

4. Density Functional Theory Calculations

Density functional theory (DFT) calculations were performed with Gaussian 16, Revision B01. The geometry optimizations were started from the geometry of the solid-state structures using the TPSSh functional and with the Ahlrichs type basis set def2-TZVP as implemented in Gaussian 16, Revision B.01. As empirical dispersion correction, we used the D3 dispersion with Becke–Johnson damping as implemented in Gaussian16, Revision B.01. NBO calculations were accomplished using the program suite NBO 6.0 delivering the NBO charges and the charge-transfer energies by second order perturbation theory.

Table S4: Calculated spin states and relative energies for 3-Naph-K and 3-Anth-Na The energy is stated relative to the lowest spin state of the corresponding scandium complex which is set to 0.00 kcal/mol.

| Spin State | 3-Naph-K | 3-Anth-Na |
|------------|----------|-----------|
| singlet    | 0.0      | 0.0       |
| triplet    | 20.8     | 27.6      |
**Table S5.** Key geometric parameters of the complex 3-Naph-K (Gaussian16; TPSSH/def2-TZVP and the empirical dispersion correction with Becke-Johnson damping).

| Bond length [Å] | X-ray     | DFT     |
|-----------------|-----------|---------|
| Sc-N            | 2.181(3)  | 2.213   |
|                 | 2.135(3)  | 2.119   |
| Sc-C1           | 2.355(4)  | 2.385   |
| Sc-C2           | 2.488(4)  | 2.472   |
| Sc-C3           | 2.475(3)  | 2.451   |
| Sc-C4           | 2.322(3)  | 2.332   |
| K1-N            | 3.065(3)  | 2.931   |
| K-O             | 2.669(2)  | 2.726   |
|                 | 2.737(3)  | 2.833   |
|                 | 2.695(3)  | 2.730   |
| K-C5            | 3.426(4)  | 3.474   |
| K-C6            | 3.126(4)  | 3.283   |
| K-C7            | 3.017(5)  | 3.248   |
| K-C8            | 3.222(5)  | 3.411   |

**Table S6.** Key geometric parameters of the complex 3-Anth-Na (Gaussian16; TPSSH/def2-TZVP and the empirical dispersion correction with Becke-Johnson damping).

| Bond length [Å] | X-ray     | DFT     |
|-----------------|-----------|---------|
| Sc-N            | 2.120(2)  | 2.132   |
|                 | 2.1312(12)| 2.133   |
| Sc-C9           | 2.3308(16)| 2.346   |
| Sc-C10          | 2.3443(16)| 2.356   |
| Sc-C4A          | 2.7853(15)| 2.711   |
| Sc-C8A          | 2.6928(18)| 2.677   |
| Sc-C9A          | 2.7787(15)| 2.706   |
| Sc-C10A         | 2.6899(17)| 2.686   |

**Table S7.** Wiberg bond indices of selected bonds of 3-Naph-K and 3-Anth-Na (Gaussian16; TPSSH/def2-TZVP and the empirical dispersion correction with Becke-Johnson damping).

|            | 3-Naph-K | 3-Anth-Na |
|-----------|----------|-----------|
| Sc-N      | 0.42     | 0.46      |
|           | 0.52     | 0.46      |
| Sc-C1     | 0.40     | 0.37      |
| Sc-C2     | 0.22     | 0.37      |
| Sc-C3     | 0.21     | 0.10      |
| Sc-C4     | 0.44     | 0.10      |
|           |          | 0.09      |
|           |          | 0.10      |

**Table S8.** Natural bond orbital (NBO) charges (in e− units) and charge transfer energies (in kcal/mol) for selected atoms (Gaussian16; TPSSH/def2-TZVP and the empirical dispersion correction with Becke-Johnson damping).

|            | 3-Naph-K | 3-Anth-K |
|-----------|----------|----------|
| Sc        | 1.4      | 1.59     |
| N         | -0.75/-0.76 | -0.75/-0.77 |
| C1        | -0.58    | -0.59    |
| C2        | -0.28    | -0.59    |
| C3        | -0.28    | -0.06    |
| C4        | -0.60    | -0.07    |

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| Occupancy [electrons] | Hybridization (%) | Polarization [%] | Localization [%] |
|-----------------------|-------------------|------------------|------------------|
| **3-Naph-K**           |                   |                  |                  |
| Sc–C1                 | 1.63              | Sc s(11.7%) d7.55(88.2%) | 0.37             | 13.9             |
|                       |                   | C s(9.0%) p10.15(90.9%) | 0.93             | 86.1             |
| Sc – C4               | 1.67              | Sc s(10.3%) d8.76(89.6%) | 0.39             | 15.3             |
|                       |                   | C s(10.11%) p18.88(89.8%) | 0.92             | 84.7             |
| N1 LP1                | 1.82              | s(31.7%) p2.15(68.2%) |                  |                  |
| LP2                   | 1.62              | s(0.6%) p99.99(99.4%) |                  |                  |
| N2 LP1                | 1.80              | s(30.9%) p2.24(69.1%) |                  |                  |
| LP2                   | 1.61              | s(1.3%) p76.25(98.7%) |                  |                  |
| **3-Anth**            |                   |                  |                  |
| Sc–C9                 | 1.64              | Sc s(15.0%) d5.67(84.9%) | 0.36             | 12.6             |
|                       |                   | C s(9.1%) p9.94(90.7%) | 0.93             | 87.4             |
| Sc–C10                | 1.64              | Sc s(14.3%) d5.58(85.6%) | 0.35             | 12.5             |
|                       |                   | C s(9.18%) p9.88(90.7%) | 0.93             | 87.6             |
| N1 LP1                | 1.82              | s(31.1%) p2.22(68.9%) |                  |                  |
| LP2                   | 1.62              | s(1.4%) p72.82(98.6%) |                  |                  |
| N2 LP1                | 1.80              | s(31.4%) p2.19(68.6%) |                  |                  |
| LP2                   | 1.61              | s(1.4%) p99.08(98.5%) |                  |                  |

Table S9. Form and occupancy of desired bonds (NBO analysis).
NTO2 (592 nm)

NTO5 (493 nm)

NTO7 (433 nm)

NTO18 (344 nm)
Figure S45: Highest occupied natural transition orbitals (HONTOs) and lowest unoccupied natural transition orbitals (LUNTOs) of selected transitions of compound 3-Naph-K (isosurface value = 0.045 e/bohr$^{3}$).
Figure S46: Highest occupied natural transition orbitals (HONTOs) and lowest unoccupied natural transition orbitals (LUNTOs) of selected transitions of compound 3-Anth⁻ (isosurface value = 0.045 e/bohr³).
Figure S47: TD-DFT predicted optical spectra of 3-Anth\(^{-}\) (left) and 3-Naph-K (right) with TPSSh/def2-TZVP and GD3BJ.

Figure S48: Natural Bond Orbitals of the lone pair 1 (sp\(^2\) character, left) and lone pair 2 (p character, right) of N1 in 3-Anth (NBO6 with TPSSh/def2-TZVP and GD3BJ)
Figure S49: Natural Bond Orbital of the Sc – C9 bond (left) and the Sc – C10 bond (right) in 3-Anth (NBO6 with TPSSh/def2-TZVP and GD3BJ)

Table S10. Cartesian coordinates of the optimized structure of 3-Naph-K.

| Sc  | -1.84663400 | 0.23855700 | -1.30188000 |
| K   | 2.15333700  | 0.47529300 | -0.13022800 |
| O   | 3.33820000  | -0.79054200 | 2.11054800  |
| O   | 4.24895000  | -0.99996900 | -1.05793000 |
| O   | 3.59717100  | 2.61588900 | 0.75410600  |
| N   | -0.68952000 | 0.38346700 | 0.57871500  |
| N   | -3.62764900 | -0.84013200 | -0.91092400 |
| C   | -1.30918600 | 2.33336800 | -2.30818900 |
| H   | -1.46759700 | 3.33499200 | -1.92444600 |
| C   | -2.33246300 | 1.77501000 | -3.17661700 |
| H   | -3.25965200 | 2.31078200 | -3.34588800 |
| C   | -2.14307900 | 0.53103200 | -3.71706700 |
| H   | -2.92079400 | 0.05210800 | -4.29908200 |
| C   | -0.91397000 | -0.17804000 | -3.39791200 |
| H   | -0.75407700 | -1.14200900 | -3.87022400 |
| C   | 1.57304000  | 0.27812100 | -3.54988400 |
| H   | 1.72184600  | -0.68904000 | -4.02160100 |
| C   | 2.67312100  | 1.11479200 | -3.30830800 |
| H   | 3.67187000  | 0.78723200 | -3.57405100 |
| C   | 2.47163700  | 2.37084200 | -2.74831800 |
| H   | 3.31410100  | 3.03027400 | -2.56835100 |
| C   | 1.17379700  | 2.79431200 | -2.43191700 |
| H   | 1.01157700  | 3.79215800 | -2.03538000 |
| C   | 0.06189800  | 1.96697200 | -2.64406500 |
| C   | 0.27141700  | 0.67154400 | -3.22089500 |
| C   | -0.44172600 | -0.95548200 | 0.73374500  |
| C   | -0.02284900 | -1.64684000 | -0.44233600 |
Table S1. Cartesian coordinates of the optimized structure of 3-Anth⁻.

|   |   |   |   |
|---|---|---|---|
| Sc | 0.46874100 | -0.45646900 | -0.03485700 |
| N  | 0.41879800 | 1.13342000 | 1.38415100 |
| N  | -1.22185200 | -0.14096000 | -1.29597200 |
| C  | 2.96528600 | -1.71615400 | 2.54933500 |
| H  | 2.46475600 | -2.10451300 | 3.63594900 |
| C  | 4.18771400 | -1.06149000 | 2.34278400 |
| H  | 4.63441400 | -0.93492000 | 3.65723100 |
| C  | 4.83446600 | -0.57375800 | 1.54327500 |
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\[
\begin{align*}
H & -5.76207300 & 1.79593300 & 1.29743800 \\
C & -3.10928900 & -2.66124500 & 2.42475600 \\
H & -2.39856800 & -2.37612400 & 3.20756500 \\
C & -2.72630400 & -2.37612400 & 3.20756500 \\
H & -4.06377500 & -2.89120700 & 2.90445700 \\
C & -1.29298200 & 0.51906800 & -2.60940700 \\
C & -1.41910100 & 2.05151600 & -2.52121200 \\
H & -0.59299300 & 2.45577700 & -1.93544900 \\
H & -1.37547600 & 2.48898700 & -3.52489500 \\
C & 0.03700200 & 0.21436500 & -3.30761700 \\
H & 0.06930800 & 0.21436500 & -3.30761700 \\
H & 0.86865700 & 0.60928800 & -2.71755100 \\
C & 0.16897800 & -0.86364000 & -3.41144400 \\
H & 0.06930800 & 0.60928800 & -2.71755100 \\
H & 0.16897800 & -0.86364000 & -3.41144400 \\
C & -2.41783800 & -0.08394800 & -3.46586400 \\
H & -2.40167800 & 0.35304500 & -4.46972000 \\
H & -3.40444500 & 0.09030000 & -3.03361400 \\
H & -2.72105200 & -1.16352100 & -3.55034800
\end{align*}
\]
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