Alkali Metal Complexes of a Bis(diphenylphosphino) methane Functionalized Amidinate Ligand: Synthesis and Luminescence
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Experimental Section

**General procedures**

All manipulations were performed under exclusion of moisture and oxygen in flame-dried Schlenk-type glassware or in an argon-filled MBraun glovebox. THF, Et₂O and n-pentane were dried using an MBraun solvent purification system (SPS-800). THF was additionally distilled under nitrogen from potassium and benzophenone before storage over 4 Å molecular sieves. Deuterated solvents were obtained from Carl Roth GmbH (99.5 atom % D). Prior to use, THF-d₈ and C₆D₆ were stored over a Na/K alloy. NMR spectra were recorded on a Bruker Avance II 300 MHz or Avance 400 MHz spectrometer. ¹H and ¹³C{¹H} NMR chemical shifts were referenced to the residual ¹H and ¹³C resonances of the deuterated solvents and are reported relative to tetramethysilane (TMS). ³¹P{¹H} resonances are reported relative to external 85 % phosphoric acid and ⁷Li resonances to 9.7 M LiCl in D₂O. Diffusion coefficients were measured with Diffusion Ordered NMR Spectroscopy (DOSY) experiments, using a Bruker Smart VT unit to control the temperature which was calibrated to be exactly 298 K. IR spectra were obtained on a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLaTGS detector and a diamond ATR (attenuated total reflection) unit. Elemental analyses were carried out with a Micro Cube from Elementar Analysensysteme GmbH. EI mass spectra were obtained from a Thermofischer DFS mass spectrometer. PL measurements were performed with a Horiba Jobin Yvon Fluorolog-322 spectrometer (for details refer to SI).

[Rb{N(SiMe₃)₂}] and [Cs{N(SiMe₃)₂}] were prepared according to literature procedures. [K{N(SiMe₃)₂}] (97%) and n-butyllithium solution (2.5 M in hexanes) were purchased from Sigma-Aldrich. [Na{N(SiMe₃)₂}] (98%) was purchased from Alfa Aesar. Bis(diphenylphosphino)methane (97%) was purchased from abcr. Bis(2,6-diisopropylphenyl)carbodiimide (98%) was purchased from TCI. They were all used as received.

**Synthesis**

**General Information**

Synthesis or crystallization in THF and Et₂O leads to solvent coordination of the respective alkali metal ions, therefore the solvents cannot always be completely removed in vacuum. Hence, residues of THF and Et₂O are observed in the corresponding NMR and IR spectra as well as in elemental analysis. All relevant spectra
are given in the SI. Complexes 3-6 were also synthesized from reactions in toluene or benzene. In this case, it was possible to synthesize solvent free samples. Higher yields can be achieved if compounds 3-6 are dried after washing with n-pentane, instead of crystallizing. For elemental analysis, all compounds expect 1 were mortared and dried under reduced pressure for at least two days.

In some $^{13}$C($^1$H) NMR spectra virtual triplet resonances (vt) are observed, which are due to specific C-P couplings. This fine structure splitting has been reported previously for organophosphorus metal complexes.\textsuperscript{[2-3]} In some cases, these resonances cannot be fully resolved. For complexes 1 and 2, $^{31}$P decoupling was applied, to simplify the evaluation of the $^{13}$C($^1$H)h NMR spectra. The corresponding NMR spectroscopy data is labelled as $^{13}$C($^1$H, $^{31}$P). Unless otherwise stated, all NMR spectroscopy measurements were performed at 298 K.

$\text{[Li}(\text{DPPM-CH(N-Dipp)_{2}})\text{(thf)}\text{]}$ (1)

Bis(diphenylphosphino)methane (2.50 g, 6.50 mmol, 1.00 eq.) was dissolved in freeze-pumped THF (40 mL) and the corresponding solution was cooled to 78 °C. Thereupon, 2.60 mL $n$-BuLi (2.5 M, 6.50 mmol, 1.00 eq.) were added to the solution, which then was adjusted to ambient temperature and subsequently stirred for 16 h. A freshly degassed solution of bis(2,6-diisopropylphenyl)-carbodiimide (2.36 g, 6.50 mmol, 1.00 eq.) in THF (20 mL) was added slowly at -78 °C, resulting in a pale-yellow solution. The reaction mixture was allowed to warm to ambient temperature and stirred for additional 6 h. Removal of the volatile components under reduced pressure and subsequent washing of the remaining solid with n-pentane (2 x 20 mL) afforded an off-white powder. Single crystals of $\text{[Li}(\text{DPPM-CH(N-Dipp)_{2}})\text{(thf)}\text{]}$ (1), suitable for X-ray analysis, were obtained by slow diffusion of n-pentane into a THF solution. Crystalline yield: 3.21 g (60 %).

$^1$H NMR (C$_6$D$_6$, 300 MHz): $\delta$ [ppm] = 0.79 – 0.88 (m, 4H, thf-CH$_2$), 0.91 (d, $^3$J$_{H,H}$ = 6.7 Hz, 6H, $^1$Pr-Dipp-CH$_2$), 1.17 – 1.28 (m, 12H, $^1$Pr-Dipp-CH$_3$), 1.53 (d, $^3$J$_{H,H}$ = 6.9 Hz, 6H, $^1$Pr-Dipp-CH$_3$), 2.50 – 2.74 (m, 4H, thf-CH$_2$), 3.61 (sept, $^3$J$_{H,H}$ = 6.9 Hz, 2H, $^1$Pr-Dipp-CH), 3.93 (sept, $^3$J$_{H,H}$ = 6.8 Hz, 2H, $^1$Pr-Dipp-CH), 4.48 (t, $^2$J$_{H,P}$ = 3.9 Hz, 1H, DPPM-CH), 6.79 (t, $^3$J$_{H,H}$ = 7.6 Hz, 1H, Dipp-CH$_{ar}$), 6.89 – 7.19 (m, 17H, CH$_{ar}$), 7.29 – 7.39 (m, 4H, CH$_{al}$), 7.65 – 7.74 (m, 4H, CH$_{ar}$). $^{31}$P($^1$H) NMR (C$_6$D$_6$, 121 MHz): $\delta$ [ppm] = -3.2 (PPh$_2$). $^{13}$C($^1$H, $^{31}$P) NMR (C$_6$D$_6$, 101 MHz) $\delta$ [ppm] = 22.7 (CH$_3$), 23.5 (CH$_3$), 24.8 (thf-CH$_2$), 26.1 (CH$_3$), 26.5 (Dipp-CH), 28.1 (Dipp-CH), 38.3 (DPPM-CH), 68.2 (thf-CH$_2$), 121.5 (CH$_{ar}$), 123.0 (CH$_{ar}$), 123.7 (Dipp-CH$_{ar}$), 124.5 (Dipp-CH$_{ar}$), 127.3 (CH$_{ar}$), 127.5 (CH$_{ar}$), 133.7 (CH$_{al}$), 135.7 (CH$_{al}$), 138.5 (DPPM-C$_6$), 141.0 (DPPM-C$_6$), 142.0 (Dipp-C$_6$), 143.4 (Dipp-}
$C_{1}$, 148.2 (Dipp-$C_{1}$), 153.1 (Dipp-$C_{1}$), 164.7 (NCN$_{2}$). In the $^{31}$P coupled $^{13}$C($^1$H) NMR spectrum, characteristic couplings of the carbon resonances DPPM-CH ($\delta = 38.3$ ppm; $^3J_{C,P} = 40.5$ Hz) and NC$_2$N ($\delta = 145.9$ ppm; $^3J_{C,P} = 13.4$ Hz) are observed. $^7$Li NMR (C$_5$D$_{10}$, 117 MHz): $\delta$ [ppm] = -1.6. IR (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3343 (vw), 3074 (vw), 2935 (vs), 2865 (m), 1613 (vs), 1583 (m), 1487 (m), 1459 (s), 1432 (vs), 1381 (w), 1357 (w), 1329 (m), 1310 (m), 1256 (vw), 1243 (vw), 1228 (vw), 1193 (w), 1141 (vw), 1093 (vw), 1069 (vw), 1027 (vw), 1000 (vw), 953 (vv), 933 (vv), 916 (vw), 882 (vw), 862 (vw), 808 (vw), 794 (vw), 756 (vw), 738 (s), 696 (s), 670 (vw), 605 (vw), 497 (w), 479 (vw), 430 (vw). Elemental analysis calcd (%) for [C$_{50}$H$_{35}$LiN$_2$P$_2$·C$_4$H$_8$O] (825.00 g·mol$^{-1}$): C 78.62, H 7.70, N 3.40; found C 78.14, H 7.47, N 3.51.

**DPPM-C(N-Dipp)$_2$H (2)**

Lithium compound 1 (2.00 g, 2.42 mmol 1.00 eq.) was dissolved in 40 mL diethyl ether and transferred into a separating funnel. Subsequent addition of degassed water (5 mL) resulted in a protonation of the ligand. The organic layer was separated, dried over sodium sulphate and was subsequently filtered. The solvent was removed under reduced pressure to obtain an off-white solid. Single crystals of DPPM-C(N-Dipp)$_2$H (2), suitable for X-ray analysis, were obtained by slow evaporation of diethyl ether. Crystalline yield: 1.45 g (80%).

$^1$H NMR (C$_5$D$_{10}$, 400 MHz): $\delta$ [ppm] = 0.82 (d, $^3J = 6.6$ Hz, 6H, $^1$Pr-Dipp-CH$_3$), 1.17 (d, $^3J = 6.6$ Hz, 6H, $^1$Pr-Dipp-CH$_3$), 1.30 (d, $^3J = 6.9$ Hz, 6H, $^1$Pr-Dipp-CH$_3$), 1.39 (d, $^3J = 6.7$ Hz, 6H, $^1$Pr-Dipp-CH$_3$), 3.14 – 3.29 (m, 2H, $^1$Pr-Dipp-CH), 3.63 – 3.79 (m, 2H, $^1$Pr-Dipp-CH), 4.34 – 4.39 (m, 1H, DPPM-CH), 4.96 (s, 1H, NH), 6.89 – 6.99 (m, 15H, CH$_{2}$), 7.90 – 7.14 (m, 1H, CH$_{2}$), 7.19 – 7.27 (m, 6H, CH$_{2}$), 7.43 – 7.52 (m, 4H, CH$_{2}$). $^{31}$P($^1$H) NMR (C$_5$D$_{10}$, 121 MHz): $\delta$ [ppm] = -5.2 (PPh$_3$). $^{13}$C($^1$H, $^{31}$P) NMR (C$_5$D$_{10}$, 101 MHz) $\delta$ [ppm] = 21.9 (CH$_3$), 22.8 (CH$_3$), 25.9 (overlapping CH$_3$ resonances), 28.7 (Dipp-CH), 29.0 (Dipp-CH), 38.3 (DPPM-CH), 123.8 (CH$_{2}$), 123.9 (CH$_{2}$), 124.3 (CH$_{2}$), 128.5 (CH$_{2}$), 128.7 (CH$_{2}$), 134.1 (CH$_{2}$), 135.7 (CH$_{2}$), 136.6 (DPPM-C$_2$), 138.4 (DPPM-C$_2$), 140.5 (Dipp-C$_2$), 143.6 (Dipp-C$_2$), 147.3 (Dipp-C$_2$), 156.8 (NC$_2$N). In the $^{31}$P coupled $^{13}$C($^1$H) NMR spectrum, characteristic couplings of the carbon resonances DPPM-CH ($\delta = 38.3$ ppm; $^3J_{C,P} = 37.4$ Hz) and NC$_2$N ($\delta = 156.8$ ppm; $^3J_{C,P} = 11.2$ Hz) are observed. IR (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3347 (vw), 3333 (vw), 3073 (vw), 3052 (vw), 2964 (vs), 2924 (w), 2866 (w), 1646 (vw), 1613 (vs), 1582 (m), 1482 (vw), 1457 (m), 1483 (s), 1382 (vw), 1362 (vw), 1332 (m), 1256 (vw), 1238 (vw), 1197 (vw), 1181 (vw), 1142 (vw), 1092 (vw), 1058 (vw), 1026 (vw), 1000 (vw), 934 (vw), 864 (vw), 839 (vw), 803 (vv), 776 (vw), 763 (vw), 738 (m), 724 (w), 694 (s), 672 (vw), 607 (vw), 527 (vw), 507 (vv), 492 (w), 476 (vw), 432 (vw). Elemental analysis calcd (%) for [C$_{50}$H$_{35}$N$_2$P$_2$] (746.96 g·mol$^{-1}$): C 80.40, H 7.56, N 3.75; found C 80.29, H 7.21, N 3.84.
[Na(DPPM-C(N-Dipp)₂)(thf)₂] (3)

Compound 2 (0.150 g, 0.201 mmol, 1.00 eq.) and sodium bis(trimethylsilyl)amide (0.037 g, 0.201 mmol, 1.00 eq.) were dissolved in 10 mL of THF at -78 °C and subsequently stirred for three days at ambient temperature. The solvent was removed under reduced pressure and the resulting solid washed with n-pentane (3 x 10 mL). Single crystals of [Na(DPPM-C(N-Dipp)₂)(thf)₂] (3), suitable for X-ray analysis, were obtained by slow diffusion of n-pentane into a THF solution. Crystalline yield: 102 mg (55%).

^1H NMR (C₆D₆, 400 MHz): \( \delta \) [ppm] = 0.85 (d, \( ^{3}J = 6.5 \) Hz, 6H, \(^{1}Pr\text{-Dipp-CH}_3\) and overlapping thf-CH₃), 1.19 – 1.24 (m, 14H, \(^{1}Pr\text{-Dipp-CH}_3\)), 3.14 – 3.19 (m, 8H, thf-CH₃), 3.69 (sept, \( ^{3}J = 6.9 \) Hz, 2H, \(^{1}Pr\text{-Dipp-CH}_3\)), 4.01 (sept, \( ^{3}J = 6.8 \) Hz, 2H, \(^{1}Pr\text{-Dipp-CH}_3\)), 4.56 (t, \( ^{3}J = 3.9 \) Hz, 1H, DPPM-CH), 6.75 (t, \( ^{3}J = 7.5 \) Hz, 1H, CH₃), 6.94 – 7.05 (m, 13H, CH₃), 7.08 – 7.12 (m, 4H, CH₃), 7.36 – 7.42 (m, 4H, CH₃), 7.68 – 7.75 (m, 4H, CH₃). ^31P[^1H] NMR (C₆D₆, 162 MHz): \( \delta \) [ppm] = -3.3 (PPPh₃). ^13C[^1H] NMR (C₆D₆, 101 MHz) \( \delta \) [ppm] = 23.2 (CH₃), 23.3 (CH₃), 25.5 (thf-CH₃), 25.9 (CH₃), 26.7 (CH₃), 27.7 (CH₃, overlapping with Dipp-CH), 28.0 (CH₃, overlapping with Dipp-CH), 38.4 (t, \( ^{1}JC,P = 22.5 \) Hz, CH₃), 135.8 (d, \( ^{1}JC,P = 25.1 \) Hz, CH₃), 139.0 (d, \( ^{1}JC,P = 21.1 \) Hz, DPPM-CH), 141.4 (d, \( ^{1}JC,P = 22.9 \) Hz, DPPM-CH), 142.7 (Dipp-CH), 143.3 (Dipp-CH), 149.4 (Dipp-CH) 154.5 (Dipp-CH), 162.4 (t, \( ^{2}JC,P = 13.0 \) Hz, NC₃N).

IR (ATR): \( \tilde{\nu} \) [cm⁻¹] = 3070 (vw), 3054 (vw), 2958 (s), 2930 (m), 2865 (m), 1613 (s), 1583 (w), 1500 (vs), 1459 (w), 1431 (vs), 1378 (m), 1355 (vw), 1319 (m), 1254 (vw), 1242 (w), 1230 (vw), 1191 (vw), 1142 (vw), 1094 (vw), 1066 (w), 1054 (w), 1030 (vw), 944 (vw), 916 (vw), 884 (vw), 796 (vw), 753 (vw), 737 (m), 694 (m), 496 (vw) 478 (vw). Elemental analysis calcd (%) for [C₅₀H₅₅N₃P₃Na] (768.94 g·mol⁻¹): C 78.10, H 7.21, N 3.64; found C 78.71, H 6.92, N 3.39.

[K(DPPM-C(N-Dipp)₂)L₂] (L = thf, Et₂O) (4)

Compound 2 (0.150 g, 0.201 mmol, 1.00 eq.) and potassium bis(trimethylsilyl)amide (0.040 g, 0.201 mmol 1.00 eq.) were dissolved in 10 mL of THF at -78 °C and stirred for 30 minutes. The solution was allowed to warm to room temperature and stirred overnight. Subsequently, the solvent was removed under reduced pressure and the resulting solid washed with n-pentane (2 x 10 mL). Single crystals of [K(DPPM-C(N-Dipp)₂)L₂] (4), suitable for X-ray analysis, were obtained by slow diffusion of n-pentane into a THF solution (L = thf) or by slow evaporation of diethyl ether (L = Et₂O). Crystalline yield: 146 mg (78 %). NMR spectroscopy of 4 was performed from the thf coordinated species.
1H NMR (CD$_2$D$_6$, 400 MHz): $\delta$ [ppm] = 0.70 – 0.96 (m, 6H, 'Pr-Dipp-CH$_3$), 1.02 – 1.21 (m, 6H, 'Pr-Dipp-CH$_3$), 1.23 – 1.41 (m, 14H, 'Pr-Dipp-CH$_3$ with CH$_2$-thf), 1.43 – 1.64 (m, 6H, 'Pr-Dipp-CH$_3$), 3.28 – 3.42 (m, 8H, CH$_2$-thf), 3.62 – 3.81 (m, 2H, 'Pr-Dipp-CH), 3.82 – 4.02 (m, 2H, 'Pr-Dipp-CH), 4.46 (t, $^3$J$_{H,P} = 3.9$ Hz, 1H, DPPM-CH), 6.60 – 6.75 (m, 1H, CH$_ar$), 6.88 – 7.11 (m, 17H, CH$_ar$), 7.31 – 7.40 (m, 4H, CH$_ar$), 7.65 – 7.76 (m, 4H, CH$_ar$). – Due to dynamic processes in solution, rather broad resonances are observed in the 1H and 13C(1H) NMR spectra of compound 4, complicating resonance assignment. These effects can be partially suppressed by low temperature NMR spectroscopy (refer to compounds 5 and 6). $^{31}$P(1H) NMR (CD$_2$D$_6$, 162 MHz): $\delta$ [ppm] = -1.7 (PPh$_3$). $^{13}$C(1H) NMR (CD$_2$D$_6$, 101 MHz) $\delta$ [ppm] = 23.5 (CH$_3$), 25.7 (CH$_3$, overlapping with CH$_2$-thf), 27.6 (CH$_3$, overlapping with Dipp-CH), 38.2 (t, $^1$J$_{C,P} = 40.7$ Hz, DPPM-CH), 67.7 (CH$_2$-thf), 119.4 (CH$_ar$), 121.1 (CH$_ar$), 122.5 (CH$_ar$), 123.7 (CH$_ar$), 133.8 (d, $^3$J$_{C,H} = 21.6$ Hz, CH$_ar$), 135.8 (d, $^3$J$_{C,H} = 24.0$ Hz, CH$_ar$), 139.0 (d, $^3$J$_{C,H} = 20.1$ Hz, DPPM-C$_6$), 141.5 (d, $^3$J$_{C,H} = 22.9$ Hz, DPPM-C$_6$), 142.3 (Dipp-C$_6$), 144.0 (Dipp-C$_6$), 149.3 (Dipp-C$_6$), 156.3 (Dipp-C$_6$), 161.9 (t, $^2$J$_{C,H} = 13.5$ Hz, NC$_N$). – Due to dynamic processes in solution and overlapping solvent signals not all CH$_3$ and CH resonances of the Dipp groups are detected. IR (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3050 (vw), 3020 (vw), 2998 (vw), 2959 (m), 2926 (w), 2864 (w), 1614 (w), 1582 (w), 1482 (vw), 1432 (s), 1423 (m), 1381 (w), 1362 (w), 1326 (w), 1306 (w), 1270 (vw), 1253 (vw), 1234 (vw), 1184 (vw), 1168 (vw), 1156 (vw), 1142 (vw), 1094 (vw), 1057 (vw), 1041 (vw), 1026 (vw), 1000 (vw), 964 (vw), 936 (vw), 383 (vw), 862 (vw), 840 (vw), 809 (vw), 795 (vw), 781 (vw), 763 (vw), 751 (w), 737 (s), 726 (w), 693 (s), 673 (vw), 539 (vw), 509 (vw), 498 (vw), 474 (vw), 433 (vw). Elemental analysis calcd (%) for [C$_{50}$H$_{59}$N$_2$P$_2$K] (785.05 g·mol$^{-1}$): C 76.50, H 7.06, N 3.57; found C 76.73, H 6.86, N 3.18.

[Rb{DPPM-C(N-Dipp)$_2$}(thf)$_3$] (5)

Compound 2 (0.150 g, 0.201 mmol, 1.00 eq.) and rubidium bis(trimethylsilyl)amide (0.049 g, 0.201 mmol, 1.00 eq.) were dissolved in 15 mL of THF at -78 °C and stirred for 15 minutes. The solution was allowed to warm to room temperature and stirred for another two days. Subsequently, the solution was filtered and the solvent removed under reduced pressure. The remaining solid was washed with n-pentane (2 x 10 mL). Single crystals of [Rb{DPPM-C(N-Dipp)$_2$}(thf)$_3$] (5), suitable for X-ray analysis, were obtained by slow diffusion of n-pentane into a THF solution. Crystalline yield: 76.0 mg (36 %).

1H NMR (THF-$d_8$, 400 MHz, 245 K): $\delta$ [ppm] = 0.76 – 0.88 (m, 6H, 'Pr-Dipp-CH$_3$), 0.90 – 1.01 (m, 6H, 'Pr-Dipp-CH$_3$), 1.05 – 1.17 (m, 6H, 'Pr-Dipp-CH$_3$), 1.19 – 1.33 (m, 6H, 'Pr-Dipp-CH$_3$), 3.33 – 3.46 (m, 2H, 'Pr-Dipp-CH), 3.81 – 3.92 (m, 2H, 'Pr-Dipp-CH), 4.03 – 4.10 (m, 1H, DPPM-CH), 6.64 – 7.15 (m, 22H, CH$_ar$), 7.19 – 7.37 (m, 4H, CH$_ar$). $^{31}$P(1H) NMR (THF-$d_8$, 162 MHz): $\delta$ [ppm] = 0.0 (PPh$_3$). $^{13}$C(1H) NMR (THF-$d_8$, 101 MHz) $\delta$ [ppm] =
23.1 (CH₃), 23.9 (CH₃), 24.5 (CH₃), 28.2 (CH₃), 29.0 (Dipp-CH), 38.7 (t, 1J_C,P = 42.2 Hz, DPPM-CH), 123.5 (CH₆), 127.5 (CH₆), 127.6 (CH₆), 128.3 (CH₆), 129.2 (CH₆), 131.4 (vt, 1J_C,P = 11.2 Hz, CH₆), 135.3 (vt, 1J_C,P = 13.2 Hz, C₆), 135.3 (vt, 1J_C,P = 12.2 Hz, CH₆), 139.6 (C₆), 139.9 (C₆), 142.4 (C₆), 142.6 (C₆), 161.4 (t, 2J_C,P = 14.1 Hz, NC₆N).

Underlying solvent resonances (thf) hamper the accurate assignment of the Dipp-CH and CH₃ resonances in the ¹³C{¹H} NMR spectrum. In addition, due to dynamic processes in solution broad resonances are obtained in the ¹H and ¹³C{¹H} NMR spectra of compound 5, complicating resonance assignment. IR (ATR): ̃v [cm⁻¹] = 3050 (vw), 2960 (m), 2936 (vw), 2925 (vw), 2863 (vw), 1584 (vw), 1478 (vs), 1429 (s), 1423 (s), 1369 (w), 1354 (vw), 1314 (vw), 1305 (vw), 1253 (vw), 1233 (vw), 1223 (vw), 1190 (vw), 1171 (vw), 1142 (vw), 1093 (vw), 1026 (vw), 943 (vw), 861 (vw), 806 (vw), 792 (vw), 780 (vw), 761 (vw), 736 (m), 695 (m), 515 (vw), 497 (vw), 485 (vw), 470 (vw), 430 (vw), 407 (vw). Elemental analysis calcd (%) for [Cs₅H₅S₃N₅P₂Rb] (831.42 g·mol⁻¹): C 72.23, H 6.67, N 3.37; found C 72.70, H 6.23, N 3.15.

[Cs(DPPM-C(N-Dipp)₂)(thf)₃] (6)

Compound 2 (0.150 g, 0.201 mmol, 1.00 eq.) and caesium bis(trimethylsilylamide) (0.065 g, 0.201 mmol, 1.00 eq.) were dissolved in 10 mL of THF at ambient temperature and stirred for 16 h. Subsequently, the solvent was removed under reduced pressure and the remaining solid washed with n-pentane (2 x 10 mL). Then, compound 6 was crystallized by slow diffusion of n-pentane into a THF solution. However, no single crystals of [Cs(DPPM-C(N-Dipp)₂)(thf)₃] (6), suitable for X-ray analysis, were obtained. Crystalline yield: 79.0 mg (36%).

¹H NMR (THF-d₈, 400 MHz, 233 K): ⁰δ [ppm] = 0.87 (d, 3J = 6.7 Hz, 6H, 'Pr-Dipp-CH₃), 0.97 (d, ³J = 6.6 Hz, 6H, 'Pr-Dipp-CH₃), 1.12 (d, ³J = 6.8 Hz, 6H, 'Pr-Dipp-CH₃), 1.26 (d, ³J = 6.7 Hz, 6H, 'Pr-Dipp-CH₃), 3.29 – 3.40 (m, 2H, 'Pr-Dipp-CH), 3.80 – 3.90 (m, 2H, 'Pr-Dipp-CH), 4.00 (t, ²J_H,P = 3.9 Hz, 1H, DPPM-CH), 6.70 (t, ³J_C,H), 6.76 (t, ³J_C,H), 6.80 – 6.92 (m, 10H, CH₆), 6.93 – 7.06 (m, 10H, CH₆), 7.19 – 7.25 (m, 4H, CH₆).³¹P{¹H} NMR (THF-d₈, 162 MHz, 298 K): ⁰δ [ppm] = 0.6 (PPh₃).¹³C{¹H} NMR (THF-d₈, 101 MHz, 223 K) ⁰δ [ppm] = 23.9 (CH₃), 23.9 (CH₃), 24.1 (CH₃), 27.8 (CH₃), 28.8 (CH₃, overlapping with Dipp-CH), 28.2 (CH₃, overlapping with Dipp-CH), 38.4 (t, ¹J_C,P = 39.4 Hz, DPPM-CH), 119.9 (CH₆), 120.2 (CH₆), 123.3 (CH₆), 124.0 (CH₆), 127.6 (CH₆), 128.1 (d, ¹J_C,P = 9.6 Hz, CH₆), 134.2 (d, ¹J_C,P = 22.2 Hz, CH₆), 136.0 (d, ¹J_C,P = 21.9 Hz, C₆), 142.0 (d, ¹J_C,P = 21.6 Hz, C₆), 142.4 (C₆), 143.8 (C₆), 150.5 (C₆), 157.1 (C₆), 161.0 (t, ²J_C,P = 13.6 Hz, NC₆N). – Due to dynamic processes in solution not all Dipp-CH resonances are detected or are partially overlapping with CH₃ resonances. IR (ATR): ̃v [cm⁻¹] = 3053 (vw), 2956 (m), 2923 (w), 2869 (w), 1584 (vw), 1474 (vs), 1445 (w), 1430 (s), 1421 (m), 1372 (w), 1357 (w), 1335 (vw), 1303 (vw), 1253 (vw), 1229 (vw), 1190 (vw), 1170 (vw), 1150 (vw), 1130 (vw), 1107 (vw), 1092 (vw), 1073 (vw), 1057 (vw), 1046 (vw), 1023 (vw), 1008 (vw), 989 (vw), 950 (vw), 896 (vw), 861 (vw), 806 (vw), 792 (vw), 780 (vw), 761 (v), 736 (m), 695 (m), 515 (vw), 497 (vw), 485 (vw), 470 (vw), 430 (vw), 407 (vw).
1142 (vw), 1092 (vw), 1070 (vw), 1040 (vw), 944 (vw), 934 (vw), 857 (vw), 806 (vw), 790 (vw), 778 761 (w), 752 (w), 737 (m), 696 (m) 509 (vw), 498 (vw), 477 (vw), 426 (vw), 411 (vw). Elemental analysis calcd (%) for [CsH55N2P2Cs] (878.86 g·mol⁻¹): C 68.33, H 6.31, N 3.19; found C 67.32, H 6.19, N 3.09.

[Cs-PPh2CH2-C(N-Dipp)2]₆ [7]

During the synthesis of [Cs(DPPM-C(N-Dipp)2)(thf)]₆ (6) a decomposition in solution is observed by NMR spectroscopy, which was subsequently studied on a larger scale. In this process, one of the PPh₂ groups of the DPPM moiety is cleaved, resulting in the formation of a monophosphine-functionalized caesium amidinate. Whereas a six-membered ring structure [Cs-PPh₂CH₂-C(N-Dipp)]₆ (7) is present in the solid state, a monomer species is assumed in solution. Single crystals of 7, suitable for X-ray analysis, were obtained by slow diffusion of n-pentane into a THF solution. Crystalline yield: 56.0 mg (40 %) after approx. one week, with regards to 0.150 g of compound 2 (0.201 mmol, 1.00 eq.) and 0.065 g of caesium bis(trimethylsilyl)amide (0.201 mmol, 1.00 eq.) as starting materials in THF solution. – The decomposition process is not considered a reproducible synthetic procedure.

1H NMR (THF-d₈, 400 MHz): δ [ppm] = 0.94 – 1.10 (m, 12H, i-Pr-Dipp-CH₃), 1.14 – 1.37 (m, 12H, i-Pr-Dipp-CH₃), 2.75 (s, 2H, CH₂), 3.59 – 3.64 (m, 4H, Dipp-CH₂), 6.58 – 6.73 (m, 2H, CH₉), 6.81 – 7.00 (m, 4H, CH₉), 7.02 – 7.16 (m, 6H, CH₉), 7.40 – 7.51 (m, 4H, CH₉). – The resonance for the Dipp-CH moiety is partially superimposed by the thf resonance at δ = 3.6 ppm. 31P{¹H} NMR (THF-d₈, 162 MHz): δ [ppm] = -20.4 (PPh₂).

13C{¹H} NMR (THF-d₈, 101 MHz) δ [ppm] = 23.1 (CH₃), 24.7 (CH₃), 25.5 (Dipp-CH, overlapping with thf resonance), 28.1 (CH₃), 28.9 (CH₃), 35.7 (d, ¹J₃,P = 13.1 Hz, PPh₂-CH₂), 119.3 (CH₉), 120.2 (CH₉), 123.1 (CH₉), 127.5 (CH₉), 128.2 (CH₉), 134.0 (d, ¹J₃,P = 16.6 Hz, CH₉), 142.6 (C₉), 143.2 (C₉), 145.3 (C₉), 145.5 (C₉), 159.0 (NC₆N). – Due to dynamic processes in solution no triplet resonance splitting is detected for the quarternary NC₆N resonance. IR (ATR): ν [cm⁻¹] = 3068 (vw), 2957 (m), 2927 (w), 2864 (w), 1637 (vw), 1585 (vw), 1494 (vs), 1465 (w), 1433 (m), 1422 (w), 1384 (w), 1355 (w), 1310 (vw), 1256 (vw), 1235 (w), 1205 (vw), 1190 (vw), 1173 (vw), 1157 (vw), 1131 (vw), 1094 (vw), 1069 (vw), 1042 (vw), 1026 (vw), 954 (vw), 932 (vw), 910 (vw), 884 (vw), 857 (vw), 826 (vw), 805 (vw), 789 (vw), 777 (vw), 758 (vw), 744 (vw), 734 (vw), 696 (w), 563 (vw), 501 (vw), 479 (vw), 441 (vw), 420 (vw). Elemental analysis calcd (%) for [Cs₃H₆₅N₃P₃Cs] (694.68 g·mol⁻¹): C 65.70, H 6.67, N 4.03; found C 65.23, H 6.18, N 3.68.
Single Crystal X-ray Diffraction

Suitable crystals for X-ray diffraction were selected under an optical microscope equipped with polarizing filters, covered in mineral oil (Aldrich) and mounted on a MiTeGen holder. The crystals were transferred directly to the cold stream of a STOE IPDS 2 or a STOE StadiVari diffractometer equipped with a Mo-sealed tube or Mo-Genix 3D HF X-ray source, respectively. All structures were solved by using the program SHELXS/T[4-5] and OLEX2.[6] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on $F^2$ by using the program SHELXL.[4-5] In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. 2091287-2091292. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +(+44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Details:

[DPPM-C(N-Dipp)$_2$H] (2): Single crystals of compound 2 generally proved to be weakly diffracting, rendering appropriate data acquisition difficult. A problem that could not be resolved despite several attempts of recrystallization.

Alert level B:

Problem:

PLAT029_ALERT_3_B: diffrn_measured_fraction_theta full value Low. 0.943

Response:

Crystals diffracted extremely weakly. Multiple attempts were made to grow better diffracting crystals. All results were consistent with the model in this report. However, all yielded serious problems due to weak diffraction.
Problem:
PLAT911_ALERT_3_B: Missing FCF Refl Between Thmin & STh/L= 0.598 876
Response:
Some reflections had to be omitted in the refinement for technical reasons.

\[ K\{\text{DPPM-C(N-Dipp)}\}_2\{\text{Et}_2\text{O}\}_3 \] (4):
The molecular solid state structure of compound 4 exhibits a positionally disordered \text{Et}_2\text{O} ligand in an approximate ratio of 75/25 coordinated to the potassium ion. Moderate to strong SADI and SIMU restraints were used to model the disordered ligand. It should be noted here, that close inspection of the residual electron density distribution indicates a third possible position for the ligand. However, this could not be modelled satisfactorily due to the low correlated chemical occupancy of the third position.

\[ \text{Rb}\{\text{DPPM-C(N-Dipp)}\}_3\{\text{thf}\}_3 \] (5):
The molecular solid state structure of compound 5 features three positionally disordered Rb-coordinated THF ligands. These were modelled using FragmentDB[7] (within OLEX² 1.3).[6]

Alert level B:
Problem:
PLAT220_ALERT_2_B: NonSolvent Resd 1 C Ueq(max)/Ueq(min) Range 6.2
Response:
The large ratio of observed U values is likely caused by the disordered THF-ligands coordinating the Rb cation.

\[ \text{Cs-PPh}_2\text{CH}_2\text{-C(N-Dipp)}_6 \] (7):
The crystal structure of 7 contains half a molecule of THF and half a molecule of \text{n}-pentane in the asymmetric unit, which could not be modeled satisfactorily. Therefore, the corresponding electron density was removed from the electron density map using the solvent-mask algorithm of OLEX².[6]
**Table S1.** Crystal data and structure refinement of 1-3.

| Compound | [Li(DPPM-C(N-Dipp)$_2$)(thf)] (1) | DPPM-C(N-Dipp)$_2$H (2) | [Na(DPPM-C(N-Dipp)$_2$)(thf)$_2$] (3) |
|----------|----------------------------------|--|----------------------------------|
| Formula  | C$_{54}$H$_{63}$LiN$_2$OP$_2$     | C$_{50}$H$_{56}$N$_2$P$_2$ | C$_{58}$H$_{71}$N$_2$NaO$_2$P$_2$ |
| D$_{calc}$/ g·cm$^{-3}$ | 1.168                          | 1.150                        | 1.203                           |
| μ/mm$^{-1}$ | 0.133                          | 0.136                        | 0.139                           |
| Formula Weight | 824.94                        | 746.90                        | 913.09                           |
| Colour | clear colourless                | clear colourless             | clear colourless                |
| Shape | fragment-shaped                | rod-shaped                   | block-shaped                    |
| Size/mm$^3$ | 0.46×0.30×0.16                | 0.77×0.38×0.18               | 0.78×0.50×0.23                 |
| T/K     | 100                             | 220                          | 150                             |
| Crystal System | triclinic                  | monoclinic                  | triclinic                       |
| Space Group | P-1                      | P$_2_1/n$                    | P-1                             |
| a/Å    | 12.1672(5)                      | 10.5915(2)                   | 10.7197(10)                    |
| b/Å    | 13.0208(5)                      | 21.1687(6)                   | 13.1897(11)                    |
| c/Å    | 17.7874(7)                      | 38.6540(10)                  | 19.016(3)                      |
| α/°    | 107.568(3)                      | 100.901(9)                   | 106.020(9)                     |
| β/°    | 94.861(3)                       | 95.312(2)                    | 93.313(7)                      |
| γ/°    | 115.592(3)                      | 8629.3(4)                    | 2520.3(5)                      |
| V/Å$^3$ | 2345.9(2)                      | 8629.3(4)                    | 2520.3(5)                      |
| Z      | 2                               | 8                            | 2                               |
| Z'     | 1                               | 2                            | 1                               |
| Wavelength/Å | 0.71073                  | 0.71073                      | 0.71073                         |
| Radiation type | Mo Kα                   | Mo Kα                        | MoKα                            |
| Q$_{min}$ | 1.240                      | 1.098                        | 1.583                           |
| Q$_{max}$ | 30.188                      | 25.164                       | 26.788                          |
| Measured Refl. | 25330                        | 38690                        | 21094                           |
| Independent Refl. | 11738                      | 14621                        | 10655                           |
| Reflections with I > 2(I) | 8428                        | 8700                         | 8249                            |
| R$_{int}$ | 0.0355                     | 0.0322                       | 0.0273                          |
| Parameters | 549                         | 989                          | 594                             |
| Restraints | 0                           | 0                            | 0                               |
| Largest Peak | 0.528                      | 0.232                        | 0.475                           |
| Deepest Hole | -0.346                     | -0.203                       | -0.509                          |
| GoOF | 1.037                          | 0.869                        | 1.082                           |
| wR$_2$ (all data) | 0.1356                     | 0.0862                       | 0.1257                          |
| wR$_2$ | 0.1233                         | 0.0801                       | 0.1207                          |
| R$_1$ (all data) | 0.0776                     | 0.0713                       | 0.0559                          |
| R$_1$ | 0.0492                         | 0.0362                       | 0.0421                          |
Table S2. Crystal data and structure refinement of 4-5 and 7.

| Compound | [K(DPPM-C(N-Dipp))₂(Et₂O)₂] [4] | [Rb(DPPM-C(N-Dipp))₂(thf)] [5] | [Cs-PPh₂CH₂-C(N-Dipp)]₆ [7] |
|----------|----------------------------------|---------------------------------|-------------------------------|
| Formula  | C₅₈H₇₅KN₂O₂P₂                  | C₆₂H₇₉N₂O₂P₂Rb                  | C₂₂₈H₇₆Cs₂N₁₂P₆              |
| Dcalc./ g·cm⁻³ | 1.185                         | 1.241                           | 1.244                         |
| μ/mm⁻¹   | 0.205                          | 0.986                           | 1.067                         |
| Formula Weight | 933.24                        | 1047.68                         | 4167.87                       |
| Colour   | clear colourless               | clear colourless                | colourless                    |
| Shape    | rod-shaped                     | fragment-shaped                 | irregular                     |
| Size/mm³ | 0.54×0.30×0.15                 | 0.77×0.52×0.34                  | 0.57×0.43×0.22                |
| T/K      | 150                            | 150                             | 150                           |
| Crystal System | triclinic                     | monoclinic                     | trigonal                      |
| Space Group | P-1                          | P2₁/c                           | R-3                           |
| a/Å      | 10.8336(5)                     | 16.7203(18)                     | 25.5219(6)                    |
| b/Å      | 13.1765(5)                     | 12.1349(5)                      | 25.5219(6)                    |
| c/Å      | 19.4699(8)                     | 27.653(2)                       | 29.5909(8)                    |
| α/°      | 99.154(3)                      |                                 | 90                            |
| β/°      | 105.698(3)                     | 92.522(7)                       | 90                            |
| γ/°      | 95.028(3)                      |                                 | 120                           |
| V/Å³     | 2616.4(2)                      | 5605.4(8)                       | 16692.2(9)                    |
| Z        | 2                              | 4                               | 3                             |
| Z'       | 1                              | 1                               | 0.16667                       |
| Wavelength/Å | 0.71073                        | 0.71073                         | 0.71073                       |
| Radiation type | Mo Kα                         | Mo Kα                           | Mo Kα                         |
| Qₐₙo/°   | 1.580                          | 1.474                           | 1.596                         |
| Qₐₙo/°   | 29.554                         | 29.313                          | 29.201                        |
| Measured Refl. | 28640                         | 76545                           | 36851                         |
| Independent Refl. | 14472                         | 15167                           | 9824                          |
| Reflections with I > 2(I) | 9258                          | 10698                           | 7009                          |
| R₁(int)  | 0.0236                         | 0.0745                          | 0.0792                        |
| Parameters | 626                           | 774                             | 387                           |
| Restraints | 24                            | 396                             | 0                             |
| Largest Peak | 0.590                         | 1.540                           | 1.522                         |
| Deepest Hole | -0.303                        | -0.943                          | -0.909                        |
| Goof     | 0.938                          | 1.035                           | 1.010                         |
| wR² (all data) | 0.1207                        | 0.1602                          | 0.1227                        |
| wR²      | 0.1124                         | 0.1467                          | 0.1090                        |
| R₁ (all data) | 0.0758                        | 0.0863                          | 0.0642                        |
| R₁       | 0.0446                         | 0.0574                          | 0.0420                        |
Solid State Structures

**Fig. S1.** Molecular structure of 1 in the solid state, displayed with an ellipsoid probability of 30 %. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-Li 1.951(3), P1-C2 1.898(2), P2-C2 1.878(2), N1-C1 1.342(2), N2-C1 1.314(2), N2-C3 1.410(2), C1-C2 1.537(2), Li-O 1.882(3), Li-C3 2.347(4); P1-C2-P2 116.79(8), N1-C1-N2 122.50(13), N1-C1-C2 123.32(14), N2-C1-C2 114.17(13), C1-N1-Li 120.00(14), C1-N2-C3 114.57(13).

**Fig. S2.** Molecular structure of 2 in the solid state, displayed with an ellipsoid probability of 30 %. Carbon bound hydrogen atoms are omitted for clarity. The asymmetric unit contains two independent molecules of 1, one of which is shown in this figure (respective bond lengths and angles are similar). Selected bond lengths [Å] and angles [°]: P1-C2 1.905(2), P2-C2 1.886(2), N1-C1 1.365(2), N2-C1 1.295(2), C1-C2 1.513(2); P1-C2-P2 112.50(9), N1-C1-N2 122.6(2), N1-C1-C2 119.9(2), N2-C1-C2 117.3(2).
**Fig. S3.** Molecular structure of 3 in the solid state, displayed with an ellipsoid probability of 30 %. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-Na 2.374(2), P1-C2 1.905(2), P2-C2 1.877(2), N1-C1 1.339(2), N2-C1 1.313(2), N2-C3 1.407(2), C1-C2 1.543(2), Na-O1 2.359(2), Na-C3 2.815(2); P1-C2-P2 115.60(8), N1-C1-N2 123.43(14), N1-C1-C2 123.41(13), N2-C1-C2 113.09(14), C1-N2-C3 118.50(13), C1-N1-Na 125.45(10).

**Fig. S4.** Molecular structure of 4 in the solid state, displayed with an ellipsoid probability of 30 %. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-K 2.7879(11), P1-C2 1.8970(14), P2-C2 1.8784(14), N1-C1 1.334(2), N2-C1 1.320(2), C1-C2 1.544(2), K-O1 2.8499(12), K-C3 3.0906(14), K-C6 3.342(2); P1-C2-P2 116.64(7), N1-C1-N2 123.71(12), N1-C1-C2 124.20(12), N2-C1-C2 112.07(11), C1-N2-C3 119.03(11), C1-N1-K 126.30(9).
**Fig. S5.** Molecular structure of 5 in the solid state, displayed with an ellipsoid probability of 30%. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-Rb 2.973(2), P1-C2 1.893(2), P2-C2 1.873(2), N1-C1 1.333(3), N2-C1 1.317(3), C1-C2 1.548(3), Rb-O1A 3.064(8), Rb-C3 3.289(2); P1-C2-P2 115.66(12), N1-C1-N2 125.6(2), N1-C1-C2 122.3(2), N2-C1-C2 112.0(2), C1-N2-C3 121.2(2), C1-N1-Rb 125.02(14).

**Fig. S6.** Asymmetric unit of 7, displayed with an ellipsoid probability of 30%. Hydrogen atoms and solvent molecules (THF, n-pentane) are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-Cs 3.069(2), P-C2 1.843(3), N1-C1 1.324(3), N2-C1 1.327(4), C1-C2 1.520(3), N2-C3 1.411(3), Cs-C3 3.573(2), Cs-C6 3.591(3); N1-C1-N2 125.2(2), N1-C1-C2 120.5(2), N2-C1-C2 114.3(2), C1-C2-P 114.1(2), C1-N1-Cs 133.3(2), C1-N2-C3 117.5(2).
Fig. S7. Molecular structure of 7 in the solid state, displayed with an ellipsoid probability of 30 %. Hydrogen atoms and solvent molecules (THF, n-pentane) are omitted for clarity. Formation of a six-membered ring structure in the solid-state due to intermolecular interactions between Cs-N2 (green, dotted) and Cs-P (pink, dotted). Respective atom distances [Å] and angles [°]: Cs-P 3.776, Cs-N2 3.188(2); N1-Cs-N2 171.08(5).
NMR Spectra

NMR spectra were recorded on a Bruker Avance II 300 MHz or Avance 400 MHz. $^1$H and $^{13}$C\{\(^1\)H\} NMR chemical shifts were referenced to the residual $^1$H and $^{13}$C resonances of the deuterated solvents and are reported relative to tetramethylsilane (TMS). $^{31}$P\{\(^1\)H\} resonances are reported relative to external 85 % phosphoric acid and $^7$Li resonances to 9.7 M LiCl in D\(_2\)O.

Fig. S8. $^1$H NMR spectrum of [Li(DPPM-C(N-Dipp)_2)(thf)] (1) in C\(_6\)D\(_6\) (300 MHz, 298 K).
Fig. S9. $^{13}\text{C}^{[\text{H}, 31\text{P}]}$ NMR spectrum of [Li(DPPM-C(N-Dipp)$_2$)(thf)] (1) in C$_6$D$_6$ (101 MHz, 298 K).

Fig. S10. $^{31}\text{P}^{[\text{H}]}$ NMR spectrum of [Li(DPPM-C(N-Dipp)$_2$)(thf)] (1) in C$_6$D$_6$ (121 MHz, 298 K).
**Fig. S11.** $^7$Li NMR spectrum of [Li(DPPM-C(N-Dipp)$_2$)(thf)] (1) in C$_6$D$_6$ (117 MHz, 298 K).

**Fig. S12.** $^1$H NMR spectrum of DPPM-C(N-Dipp)$_2$H (2) in C$_6$D$_6$ (400 MHz, 298 K).
**Fig. S13.** $^{13}$C($^1$H, $^{31}$P) NMR spectrum of DPPM-C(N-Dipp)$_2$H (2) in C$_6$D$_6$ (101 MHz, 298 K).

**Fig. S14.** $^{31}$P($^1$H) NMR spectrum of DPPM-C(N-Dipp)$_2$H (2) in C$_6$D$_6$ (121 MHz, 298 K).
Fig. S15. $^1$H NMR spectrum of [Na{DPPM-C(N-Dipp)$_2$}(thf)$_2$] (3) in C$_6$D$_6$ (400 MHz, 298 K).

Fig. S16. $^{13}$C($^1$H) NMR spectrum of [Na{DPPM-C(N-Dipp)$_2$}(thf)$_2$] (3) in C$_6$D$_6$ (101 MHz, 298 K).
Fig. S17. $^{31}$P($^1$H) NMR spectrum of [Na(DPPM-C(N-Dipp)$_2$)(thf)$_2$] (3) in C$_6$D$_6$ (162 MHz, 298 K).

Fig. S18. $^1$H NMR spectrum of [K(DPPM-C(N-Dipp)$_2$)(thf)$_2$] (4) in C$_6$D$_6$ (400 MHz, 298 K).
Fig. S19. $^{13}$C{${}^1$H} NMR spectrum of [K(DPPM-C(N-Dipp)$_2$)(thf)$_2$] (4) in C$_6$D$_6$ (101 MHz, 298 K).

Fig. S20. $^{31}$P{${}^1$H} NMR spectrum of [K(DPPM-C(N-Dipp)$_2$)(thf)$_2$] (4) in C$_6$D$_6$ (162 MHz, 298 K).
Fig. S21. $^1$H NMR spectrum of [Rb(DPPM-C(N-Dipp)$_2$](thf)$_3$ (5) in THF-$d_8$ (400 MHz, 245 K).

Fig. S22. $^{13}$C($^1$H) NMR spectrum of [Rb(DPPM-C(N-Dipp)$_2$](thf)$_3$ (5) in THF-$d_8$ (101 MHz, 298 K).
Fig. S23. $^{31}\text{P}^{[1\text{H}]}$ NMR spectrum of [Rb(DPPM-C(N-Dipp)$_2$)(thf)$_3$] (5) in THF-$d_8$ (162 MHz, 298 K).

Fig. S24. $^1\text{H}$ NMR spectra of [Rb(DPPM-C(N-Dipp)$_2$)(thf)$_3$] (5) in THF-$d_8$, recorded at varying temperatures (400 MHz, ranging from 245 K to 283 K).
Fig. S25. $^1$H NMR spectrum of [Cs(DPPM-C(N-Dipp)$_2$)](thf)$_x$ (6) in THF-$d_8$ (400 MHz, 233 K).

Fig. S26. $^{13}$C($^1$H) NMR spectrum of [Cs(DPPM-C(N-Dipp)$_2$)](thf)$_x$ (6) in THF-$d_8$ (101 MHz, 223 K).
Fig. S27. $^{31}$P$^{[1]}$H NMR spectrum of [Cs(DPPM-C(N-Dipp)$_2$](thf)$_x$] (6) in THF-$d_8$ (162 MHz, 298 K).

Fig. S28. $^1$H NMR spectra of [Cs(DPPM-C(N-Dipp)$_2$](thf)$_x$] (6) in THF-$d_8$, recorded at varying temperatures (400 MHz, ranging from 233 K to 298 K).
Fig. S29. $^1$H NMR spectrum of [Cs-PPh$_2$CH$_2$-C(N-Dipp)$_2$] (7) in THF-$d_8$ (400 MHz, 298 K). [*] residual n-pentane, [#] residual THF. A monomer species of 7 is considered to be present in solution.

Fig. S30. $^{13}$C($^1$H) NMR spectrum of [Cs-PPh$_2$CH$_2$-C(N-Dipp)$_2$] (7) in THF-$d_8$ (101 MHz, 298 K). A monomer species of 7 is considered to be present in solution.
Fig. S31. $^{31}\text{P}[\text{H}]$ NMR spectrum of [Cs-PPh$_2$CH$_2$-C(N-Dipp)$_2$] (7) in THF-$d_8$ (162 MHz, 298 K). A monomer species of 7 is considered to be present in solution.
Fig. S32. $^{31}$P[¹H] NMR scale experiment (in THF-d₈) monitoring the reaction of Cs-complex 6 over time. The spectrum at $t = 1$ h shows that the reaction of 2 with [Cs(N(SiMe₃)₂)] is completed after one hour with conversion to [Cs(DPPM-C(N-Dipp))(thf)] (6). With time, compound 6 (*) decomposes, leading to the formation of the amidinate [Cs-PPh₂CH₂-C(N-Dipp)]₆ (7), among others. Small signals of 7 (#) can already be observed after only a few hours, which amplify over days. For research purposes, after one week, the NMR sample was heated at 50 °C for another week, resulting in slightly amplified resonances of decomposition. After four weeks (additional two weeks at r.t.), a mixture of different species was visible, with the main decomposition product being 7. It is important to note that the NMR scale experiment does not fully reflect the actual synthesis, since, for example, only small amounts of the reactants were used, and the solution was not stirred. This can explain faster decomposition processes, which we experienced in laboratory scale synthesis. [*] compound 6, [#] decomposition product 7.
DOSY Measurements

General remarks:

Molecules are distinguished according to their diffusion coefficient ($D$), which correlates with their hydrodynamic radius ($R_h$).[8-10] Hereby, the diffusion coefficient $D$ is dependent on the concentration of the sample. Calculations of the hydrodynamic radii were carried out, applying the Stokes-Einstein equation. For calculations, the dynamic viscosity $\eta$ of the pure solvent (THF) was applied, neglecting a slight change in viscosity due to the dissolved sample. Additionally, it has to be considered that the Stokes-Einstein Equation assumes spherical molecules, which need to be significantly larger than the solvent molecules.[11]

Importantly, received values for $D$ (and the respective radii) from DOSY measurements are not absolute numbers and should only be used in comparison to other measurements (applying the same solvent and concentration). All samples were recorded at least twice, resulting in similar results in each case (only one measurement is presented).

Compound 7 was analysed in THF-$d_8$ ($c ~ 10 \text{ mg}\cdot\text{mL}^{-1}$), employing a dynamic viscosity of $\eta = 0.000473 \frac{N}{m^2}s$ (at 298 K).[12] Measurements in C$_6$D$_6$ were not feasible due to limited solubility of 7.

\[
\text{Stokes – Einstein Equation:} \quad D = \frac{k_B \cdot T}{6\pi \cdot \eta \cdot R_h} ; \quad R_h = \frac{k_B \cdot T}{6\pi \cdot \eta \cdot D}
\]

\[
k_B = 1.38 \cdot 10^{-23} J \cdot K^{-1} ; \quad T = 298 K ; \quad \eta (\text{THF}) = 0.473 \text{ cP} = 0.473 \text{ mPa} \cdot \text{s (at 298 K)}
\]

\[
1 \text{ Pa} = 1 \frac{N}{m^2} ; \quad 1 J = 1 N \cdot m
\]

\[
R_h = \frac{1.38 \cdot 10^{-23} J \cdot 298 K}{6\pi \cdot 0.000473 \frac{N}{m^2}s} \cdot \frac{1}{D}
\]

\[
R_h = \frac{4.1124 \cdot 10^{-21} m^2}{0.0089158 \text{ N}s} \cdot \frac{1}{D}
\]

\[
R_h = 4.612 \cdot 10^{-19} \frac{m^3}{s} \cdot \frac{1}{D}
\]
\[ [\text{Cs-PPh}_2\text{CH}_2\text{-C(N-Dipp)}_2] (1/6 \cdot 7): \quad D_{av} = 6.78 \cdot 10^{-10} \text{m}^2/\text{s}; \]

\[ R_h = 6.80 \cdot 10^{-10} \text{m} = 6.80 \, \text{Å} \]
Fig. S33. DOSY report of [Cs-PPh₂CH₂-C(N-Dipp)₂] (7), measured in THF-d₈ (peaks 16 and 19) at 298 K.

Compound 1 was analysed in C₆D₆ (c ~ 10 mg·mL⁻¹), employing a dynamic viscosity of \( \eta = 0.000608 \frac{N}{m^2 s} \) (at 298 K).

\[
Stokes - Einstein Equation: \quad D = \frac{k_B \cdot T}{6\pi \cdot \eta \cdot R_h} \quad ; \quad R_h = \frac{k_B \cdot T}{6\pi \cdot \eta \cdot D}
\]

\( k_B = 1.38 \cdot 10^{-23} \) J/K; \( T = 298 \) K; \( \eta \) (benzene) = 0.608 cP = 0.608 mPa·s (at 298 K)

\[
1 \text{ Pa} = 1 \frac{N}{m^2} ; \quad 1 \text{ J} = 1 \text{ N} \cdot \text{m}
\]
\[ R_h = \frac{1.38 \cdot 10^{-23} J \cdot 298 K}{6\pi \cdot 0.000608 \frac{N}{m^2 s} \cdot \frac{1}{D}} \]

\[ R_h = \frac{4.1124 \cdot 10^{-21} \frac{m^2}{s} \cdot \frac{1}{D}}{0.0114605 \text{ Ns} \cdot \frac{1}{D}} \]

\[ R_h = 3.588 \cdot 10^{-19} \frac{m^3}{s} \cdot \frac{1}{D} \]

[Li(DPPM-C(N-Dipp)_2)(thf)] (1):

\[ D_{av.} = 6.13 \cdot 10^{-10} \frac{m^2}{s}; \]

\[ R_h = 5.85 \cdot 10^{-10} m = 5.85 \text{ Å} \]
### Fig. S34. DOSY report of [Li(DPPM-C(N-Dipp)₂)(thf)] (1), measured in C₆D₆ at 298 K.

| Peak name | F2 [ppm] | D [m²/s] | error    |
|-----------|----------|----------|----------|
| 1         | 7.695    | 5.89 e-10 | 1.567 e-11 |
| 2         | 7.690    | 5.82 e-10 | 1.606 e-11 |
| 3         | 7.341    | 6.04 e-10 | 7.186 e-12 |
| 4         | 7.170    | 5.57 e-10 | 2.895 e-11 |
| 5         | 7.151    | 6.12 e-10 | 2.685 e-11 |
| 6         | 7.099    | 6.15 e-10 | 1.119 e-11 |
| 7         | 6.931    | 5.94 e-10 | 1.450 e-11 |
| 8         | 6.926    | 5.86 e-10 | 1.118 e-11 |
| 9         | 6.790    | 6.17 e-10 | 6.628 e-12 |
| 10        | 4.479    | 5.94 e-10 | 2.363 e-11 |
| 11        | 3.933    | 5.94 e-10 | 1.381 e-11 |
| 12        | 3.613    | 6.10 e-10 | 5.228 e-12 |
| 13        | 2.645    | 6.66 e-10 | 1.703 e-11 |
| 14        | 1.537    | 6.17 e-10 | 1.168 e-11 |
| 15        | 1.520    | 6.19 e-10 | 1.091 e-11 |
| 16        | 1.240    | 6.23 e-10 | 5.333 e-12 |
| 17        | 1.235    | 6.10 e-10 | 3.013 e-12 |
| 18        | 0.922    | 6.07 e-10 | 1.540 e-11 |
| 19        | 0.905    | 6.01 e-10 | 1.316 e-11 |
| 20        | 0.852    | 6.63 e-10 | 2.010 e-11 |
IR Spectra (ATR)

IR spectra were obtained on a Bruker Tensor 37 FTIR spectrometer, equipped with a room temperature DLaTGS detector and a diamond ATR (attenuated total reflection) unit.

Fig. S35. IR spectrum of [Li(DPPM-C(N-Dipp)₂)(thf)] (1).
Fig. S36. IR spectrum of DPPM-C(N-Dipp)₂H (2).

Fig. S37. IR spectrum of [Na(DPPM-C(N-Dipp)₂)(thf)₂] (3).
Fig. S38. IR spectrum of \([\text{K}(\text{DPPM-C(N-Dipp)2})(\text{thf})_2]\) (4).

Fig. S39. IR spectrum of \([\text{Rb}(\text{DPPM-C(N-Dipp)2})(\text{thf})_3]\) (5).
Fig. S40. IR spectrum of [Cs(DPPM-C(N-Dipp)$_2$)(thf)$_x$] (6).

Fig. S41. IR spectrum of [Cs-PPh$_2$CH$_2$-C(N-Dipp)$_2$] (7).
Photoluminescence Spectra

Photoluminescence measurements

PL measurements were performed with a Horiba Jobin Yvon Fluorolog-322 spectrometer equipped with an optical cryostat based on a pulse tube cryocooler (Cryomech) operating within a temperature range of 5-300 K. A Hamamatsu R9910 photomultiplier was used as detector for the emission spectral range of about 300-830 nm. The solid samples (crystalline powders) were measured as dispersions in a thin layer of viscous heavy mineral oil (Sigma Aldrich) placed between two 1 mm quartz plates (Material: Spectrosil® 2000). The latter were mounted on the cold finger of the cryostat. All emission spectra were corrected for the wavelength-dependent response of the spectrometer and detector (in relative photon flux units). Emission decay traces were recorded by connecting a photomultiplier to a 500 MHz LeCroy LT322 oscilloscope (via a 50, 500, 2.500 or 10.000 Ohm load depending on the decay time scale) and using a nitrogen laser (~2 nsec, ~5 µJ per pulse) for pulsed excitation at 337 nm. PL efficiencies of solid complexes at ambient temperature were determined using an integrating sphere out of optical PTFE, which was installed into the sample chamber of the spectrometer, according to the method of de Mello et al.\textsuperscript{[13]} The uncertainty of this measurement was estimated to be ±10%.

For the PL measurements of 1-7 merely crystalline species were applied (after drying in vacuum). For compounds 1 and 3-6 the respective thf adducts were used.
Fig. S42. Photoluminescence emission (PL) and excitation (PLE) spectra of compound 1 in a temperature range of 6 K to 295 K.

Fig. S43. Photoluminescence emission (PL) and excitation (PLE) spectra of compound 2 in a temperature range of 12 K to 295 K.
Fig. S44. Photoluminescence emission (PL) and excitation (PLE) spectra of compound 3 in a temperature range of 6 K to 295 K.

Fig. S45. Photoluminescence emission (PL) and excitation (PLE) spectra of compound 4 in a temperature range of 6 K to 295 K.
**Fig. S46.** Photoluminescence emission (PL) and excitation (PLE) spectra of compound 5 in a temperature range of 6 K to 295 K.

**Fig. S47.** Photoluminescence emission (PL) and excitation (PLE) spectra of compound 6 in a temperature range of 6 K to 295 K.
Fig. S48. Photoluminescence emission (PL) and excitation (PLE) spectra of compound 7 in a temperature range of 6 K to 295 K.
**Fig. S49.** Integral PL intensities versus temperature in the range of 6-295 K.
Fig. S50. CIE 1931 graph for compounds 1-7 at 20 K.

Fig. S51. CIE 1931 graph for compounds 1-7 at 295 K.
Table S3. Photoluminescence data for compounds 1-4.

| Compound | 1  | 2  | 3  | 4  |
|----------|----|----|----|----|
| Metal atoms | Li | /  | Na | K  |
| \( \lambda_{\text{PLE}}^a \) [nm] | 339 | 320 | 361 | 375 |
| \( \lambda_{\text{PL}} (6/295 \text{ K})^b \) [nm] | 463 | 461 | 478 | 436 |
| \( \lambda_{\text{PL, Max}} (6 \text{ K})^c \) [nm] | 465 | 469 | 478 | 411/436/464 |
| \( \lambda_{\text{PL, Max}} (295 \text{ K})^c \) [nm] | 461 | 372 | 486 | 431/435 |
| FWHM (20 K)^d [nm] | 96 | 92 | 145 | / |
| FWHM (295 K)^d [nm] | 111 | /  | 166 | / |
| \( \lambda_{\text{PLE}} (\phi)^e \) [nm] | 350 | 350 | 365 | 375 |
| \( \phi (\text{RT})^f \) [%] | <1 | <1 | <1 | ~ 2 |

[a] Adjusted wavelengths of excitation for the measurement of the PL spectra. [b] Adjusted wavelengths for the measurement of the PLE spectra at 20 and 295 K, respectively. [c] Maxima of the PL spectra. The most intense is underlined. [d] Full width at half maximum of the whole emission bands. [e] Wavelength of excitation for the quantum yield determination. [f] PL quantum yields at ambient temperature.

Table S4. Photoluminescence data for compounds 5-7.

| Compound | 5  | 6  | 7  |
|----------|----|----|----|
| Metal atoms | Rb | Cs | Cs |
| \( \lambda_{\text{PLE}}^a \) [nm] | 387 | 351 | 330 |
| \( \lambda_{\text{PL}} (6/295 \text{ K})^b \) [nm] | 524 | 478 | 454 |
| \( \lambda_{\text{PL, Max}} (6 \text{ K})^c \) [nm] | 519 | 475 | 456 |
| \( \lambda_{\text{PL, Max}} (295 \text{ K})^c \) [nm] | 517 | 484 | 393/467 |
| FWHM (20 K)^d [nm] | 119 | 111 | 68 |
| FWHM (295 K)^d [nm] | 121 | 142 | 40 |
| \( \lambda_{\text{PLE}} (\phi)^e \) [nm] | 382 | 369 | 369 |
| \( \phi (\text{RT})^f \) [%] | <1 | <1 | <1 |

[a] Adjusted wavelengths of excitation for the measurement of the PL spectra. [b] Adjusted wavelengths for the measurement of the PLE spectra at 20 and 295 K, respectively. [c] Maxima of the PL spectra. The most intense is underlined. [d] Full width at half maximum of the whole emission bands. [e] Wavelength of excitation for the quantum yield determination. [f] PL quantum yields at ambient temperature.
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