REVISED CC-COM-12-2013-04951 SUPPORTING INFORMATION

'Janus-type' Organopotassium Chemistry by Deprotonation of Mesoionic Imidazolium Aminides and Amino N-Heterocyclic Carbenes: Coordination and Organometallic Polymers

Andreas A. Danopoulos and Pierre Braunstein

Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg 4 rue Blaise Pascal, 67081 Strasbourg, France E-mail: danopoulos@unistra.fr, braunstein@unistra.fr

Contents:

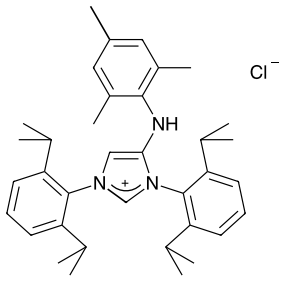
1. Synthesis and characterization

1.1 General methods

Elemental analyses were carried out by the microanalytical laboratory of London Metropolitan University. All manipulations involving organometallics were performed under nitrogen or argon in a Braun glove-box or using standard Schlenk techniques as specified below. Solvents were dried using standard methods and distilled under nitrogen prior use or passed through columns of activated alumina and subsequently purged with nitrogen or argon. The solvents used for the synthesis of the Li^+ and K^+ salts after drying were stored over K mirror in the glove box until use. The starting materials were prepared according to literature procedures: benzyl potassium[1] N,N'-bis-(2,6-di*iso*propylphenyl)-formamidine,[2] 1,3-(bis-di*iso*propylphenyl)-4-(2,6-di*iso*propylanilido)-imidazolium.[3] (mesityl)-(chloromethyl)-imidoyl chloride and (4-*tert*,-butyl-phenyl)-(chloromethyl)-imidoyl chloride were prepared by similar methodology to the one used for (2,6-di*iso*propylphenyl chloromethyl imidoyl chloride.[4] (4-*tert*,-butyl-phenyl)-(chloromethyl)-imidoyl chloride (b.p. 85 - 88 °C at 0.31 mbar) has limited shelf life and should be used straight after its isolation. Solid Me_3SiCH_2Li was obtained by evaporation of the pentane under reduced pressure from commercial (Aldrich) solutions. N,N,N',N'-tetramethylethylenediamine (tmeda) was dried by distillation from KH under N_2.

1.2 Synthesis of amino imidazolium halides

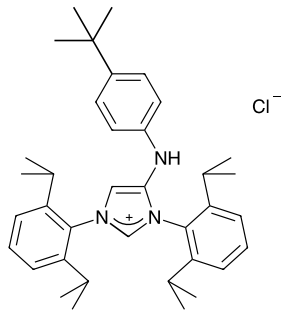
1.2.1 1,3-(bis-di*iso*propylphenyl)-4-(mesitylamino)-imidazolium chloride $(2H)^+Cl^-$



This compound was prepared following the method reported previously,[3] from N, N'-bis-(2,6-di*iso*propylphenyl)-formamidine (3.65 g, 0.01 mol), (chloromethyl)-(mesityl)-imidoyl chloride (2.30 g, 0.01 mol) and Et_3N (1.12 g, 0.011 mol, 1.1 eq.) in ethylacetate (100 ml), by refluxing for 48 h. Yield 4.05 g, *ca.* 72%. ^1H NMR ($CDCl_3$): δ 10.60 (broad s, 1H, imidazolium C-H), 7.62 (t, ^3J = 7.6 Hz, 1H, DiPP), 7.46 (t, ^3J = 7.6 Hz, 1H, DiPP), 7.42 (d, ^3J = 7.6 Hz, 2H, DiPP), 7.25 (d, J = 7.6 Hz, 2H, DiPP), 6.89 (s, 2H, mesityl), 5.96 (broad s, 1H, NH), 5.87 (d, ^4J = 1.9 Hz, 1H, backbone imid), 2.68 (sept, ^3J = 7.0 Hz, 2H, C*H*$(CH_3)_2$), 2.54 (sept, ^3J = 7.0 Hz, 2H,

C*H*(CH_3)$_2$), 2.23 (s, 3H, *p*-Me), 2.21 (s, 6H, *o*-Me), 1.43 ((d, ^3J = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.35, 1.31 and 1.23 (three doublets, 18H, ^3J = 7.0 Hz, CH(C*H*$_3$)$_2$).

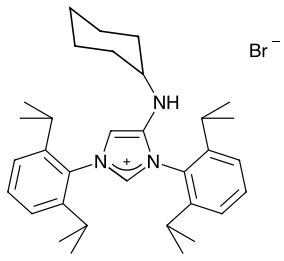
1.2.2 1,3-(bis-di*iso*propylphenyl)-4-(4-*tert*.butyl-anilino)-imidazolium chloride · CH_2Cl_2 $(3H)^+Cl^-$



This compound was prepared following the method reported previously,[3] from N, N'-bis-(2,6-di*iso*propylphenyl)-formamidine (1.85 g, 5.0 mmol), (chloromethyl)-(4-*tert*.butyl-phenyl)-imidoyl chloride (1.22 g, 5.0 mmol) and Et_3N (0.66 g, 6.0 mmol, 1.1 eq.) in ethylacetate (60 ml), by refluxing for 48 h. Yield 1.84 g, *ca.* 65%. ^{1}H NMR ($CDCl_3$): δ 9.60 (broad s, 1H, imidazolium C-H), 7.64 (s, 1H, aromatic), 7.47 (m, 2H, aromatic), 7.28 and 7.25 (two d, ^3J = 7.8 Hz, 4H, DiPP), 7.16 (d, ^3J = 9.2 Hz, 2H, aromatic), 6.99 (d, ^3J = 9.1 Hz, 2H, aromatic), 5.22 (s, 2H, C*H*$_2$Cl$_2$), 2.68 (sept, ^3J = 6.6 Hz, 4H, C*H*(CH_3)$_2$), 1.25 - 1.14 (overlapping four doublets, ^3J = 6.6 Hz, and one singlet, 33H, CH(C*H*$_3$)$_2$) and *t*-Bu).

1.2.3 1,3-(bis-di*iso*propylphenyl)-4-(cyclohexylamino)-imidazolium bromide $(4H)^+Br^-$

This compound was prepared by modification of the literature method[5] as detailed below: N,N'-bis-(2,6-di*iso*propylphenyl)-formamidine (7.52 g, 20.0 mmol), 2-chloro-N-cyclohexyl acetamide (2.95 g, 20 mmol), KI (0.33 g, 2.0 mmol) and Et_3N (4.10 g, 40.0 mmol) were heated at 100 °C in 50 ml DMF for 12 h. To the brown solution, after cooling to room temperature, was added ether (200 ml) and hydrolyzed by the addition of H_2O. After separation of the phases ,the organic extracts were dried over $MgSO_4$ and the volatiles were removed under reduced pressure giving rise to an oily residue. This was dissolved into the minimum volume of hot ethanol. After cooling the ethanol solution in ice (0 °C) the separated colorless, crystalline unreacted formamidine (*ca*. 0.85 g) was recovered and can be recycled. From the filtrate after evaporation of the volatiles under reduced pressure N-((cyclohexyl)-carbamoylmethyl)-N,N'-bis-(2,6-di*iso*propylphenyl)



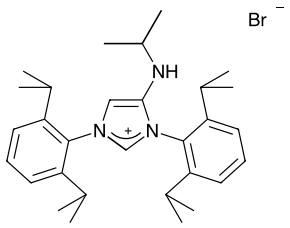
formamidine was obtained as a brown oil which was used further in the cyclization step without additional purification. Yield: 6.80 g 68% based on the 2-chloro-N-cyclohexyl acetamide. ^{1}H NMR ($CDCl_3$): 8.10 (br d, 1H, formamidine CH), 7.33 - 6.96 (m, 6 H, DiPP aromatic), 4.27 (s, 2H, -C*H*$_2$CONH-), 3.74 (m, 1H, cyclohexyl), 3.19 and 3.08 (two septets, ^3J = 7.1 Hz, 2H each, *o*-C*H*$(CH_3)_2$), 1.94 and 1.70 (two multiplets, 2H each, cyclohexyl), 1.70 (m, 1H, cyclohexyl), 1.29 - 1.01 (four doublets, ^3J = 7.1 Hz, and overlapping multiplets, 30H, CH(C*H*$_3)_2$ and cyclohexyl).

For the cyclization the N-((cyclohexyl)-carbamoylmethyl)-N,N'-bis-(2,6-di*iso*propylphenyl) formamidine (5.10 g, 10 mmol) and 2,6-lutidine (1.60 g, 15 mmol) were dissolved in dry CH_2Cl_2 (40 ml) and the solution was cooled to -78 °C. To this was added dropwise by a syringe triflic anhydride (3.10 g, 11 mmol) and the reaction mixture was allowed to warm to room temperature overnight. Then it was hydrolyzed by addition of saturated aqueous $NaHCO_3$. The phases were separated, the organic phase dried over $MgSO_4$ and evaporated to dryness. The oily residue was dissolved in the minimum of CH_2Cl_2; dropwise addition of ether precipitated the imidazolium triflate as a beige powder that was collected by filtration and dried under vacuum. Yield: 4.75 g, 75%. ^{1}H NMR ($CDCl_3$): 8.88 (broad s, 1H, imidazolium C-H), 7.62 (t, ^3J = 7.4 Hz, 1H, DiPP), 7.54 (t, ^3J = 7.4 Hz, 1H, DiPP), 7.39 (d, ^3J = 7.4 Hz, 2H, DiPP), 7.32 (d, ^3J = 7.4 Hz, 2H, DiPP), 6.60 (d, ^4J = 1.9 Hz, 1H, backbone imid C-H), 3.56 (broad d, ^3J = 7.9 Hz, 1H, NH), 3.08 (m, 1H, cyclohexyl), 2.54 and 2.48 (sept, 2H each, ^3J = 7.1 Hz, C*H*$(CH_3)_2$), 1.97 and 1.72 (m, 2H each, cyclohexyl), 1.62 (m, 1H, cyclohexyl), 1.33 - 1.08 (overlapping four doublets, ^3J = 7.1 Hz, and three multiplets, 30H, CH(C*H*$_3)_2$) and cyclohexyl).

Anion exchange was affected by dissolving the triflate salt in a solution of LiBr in methanol. After stirring for *ca.* 1 h and evaporation of the volatiles, the residue was partitioned between CH_2Cl_2 and H_2O. The organic phase was separated, dried with $MgSO_4$ and evaporated to dryness to give the bromide salt in quantitative yield. ^{1}H NMR ($CDCl_3$): 9.01 (broad s, 1H, imidazolium C-H), 7.62 (t, ^3J = 7.4 Hz, 1H, DiPP), 7.53 (t, ^3J = 7.4 Hz, 1H, DiPP), 7.39 (d, ^3J = 7.4 Hz, 2H, DiPP), 7.32 (d, ^3J = 7.4 Hz, 2H, DiPP), 6.64 (d, J = 1.9 Hz, 1H, backbone imid C-H), 3.63 (broad d, ^3J = 7.9 Hz, 1H, NH), 3.08 (m, 1H, cyclohexyl), 2.55 and 2.49 (sept, ^3J = 7.1 Hz, 2H each, C*H*$(CH_3)_2$), 1.97 and

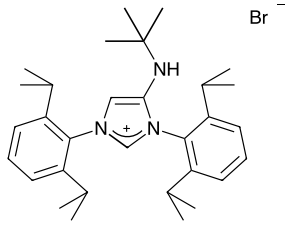
1.71 (m, 2H each, cyclohexyl), 1.60 (m, 1H, cyclohexyl), 1.33 - 1.08 (overlapping four doublets, ^3J = 7.1 Hz, and three multiplets, 30H, CH(CH_3)$_2$) and cyclohexyl).

1.2.4 1,3-(bis-di*iso*propylphenyl)-4-(*iso*propylamino)-imidazolium bromide (5H)$^+$Br$^-$



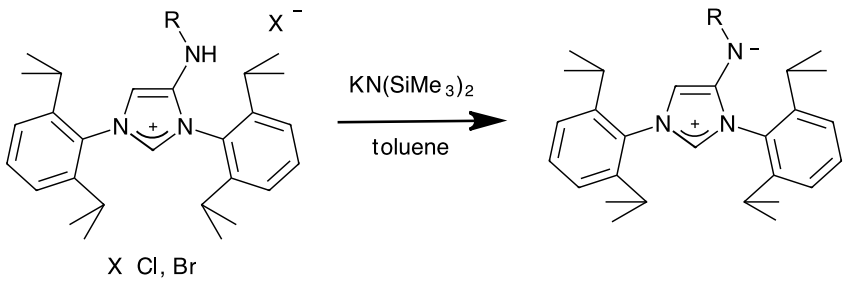
This compound was prepared as above in two steps from bis-(2,6-di*iso*propylphenyl)-formamidine (7.52 g, 20.0 mmol) and 2-chloro-N-isopropyl acetamide (2.71 g, 20.0 mmol). Overall yield (in two steps): 5.30 g, 48%. ^{1}H NMR ($CDCl_3$): 8.61 (broad s, 1H, imidazolium C-H), 7.62 (t, ^3J = 7.7 Hz, 1H, DiPP), 7.54 (t, ^3J = 7.7 Hz, 1H, DiPP), 7.39 (d, ^3J = 7.7 Hz, 2H, DiPP), 7.32 (d, ^3J = 7.7 Hz, 2H, DiPP), 6.63 (d, ^4J = 1.9 Hz, 1H, backbone imid C-H), 3.61 (broad d, ^3J = 8.4 Hz, 1H, NH), 3.48 (sept, ^3J = 6.2 Hz, 1H, NHC*H*(CH$_3$)$_2$)), 2.54 and 2.48 (sept, J = 6.7 Hz, 2H each, C*H*(CH$_3$)$_2$), 1.33 - 1.18 (four overlapping doublets, ^3J = 6.7 Hz, 30H, CH(CH_3)$_2$).

1.2.5 1,3-(bis-di*iso*propylphenyl)-4-(*tert*-butylamino)-imidazolium bromide (6H)$^+$Br$^-$

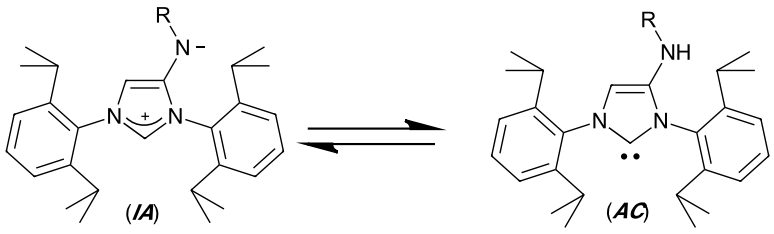


This compound was prepared as above in two steps from bis-(2,6-di*iso*propylphenyl)-formamidine (3.76 g, 10.0 mmol) and 2-chloro-N-butyl acetamide (1.49 g, 10.0 mmol). Overall yield (in two steps): 2.85 g, 53%. ^{1}H NMR ($CDCl_3$): 9.54 (broad s, 1H, imidazolium C-H), 7.62 (t, ^3J = 7.9 Hz, 1H, DiPP), 7.54 (t, ^3J = 7.9 Hz, 1H, DiPP), 7.40 (d, ^3J = 7.9 Hz, 2H, DiPP), 7.33 (d, ^3J = 7.9 Hz, 2H, DiPP), 6.51 (d, ^4J = 1.8 Hz, 1H, backbone imid C-H), 3.36 (broad s, 1H, NH), 2.54 and 2.45 (sept, 2H each, ^3J = 7.2 Hz, C*H*(CH$_3$)$_2$), 1.30 (s, 9H, *t*-Bu), 1.29 - 1.23 (four overlapping doublets, ^3J = 7.2 Hz, 24H, CH(CH_3)$_2$).

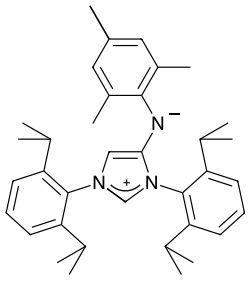
1.3 General method for the first deprotonation of the 4-amino-imidazolium halide salts



To a vigorously stirred suspension of the imidazolium halide, prepared as described above, (20.0 mmol) in toluene (100 ml) cooled to -50 / -60 °C was added a solution of $KN(SiMe_3)_2$ (24.0 mmol) in the same solvent (20 ml). After completion of the addition the heterogeneous reaction mixture was allowed to reach room temperature and stirred overnight, during which period it adopted an intense yellow or yellow-green coloration. After filtration of the reaction mixture through Celite and washing of the filtered solids with hot toluene until the washings were almost colorless, the combined toluene phases were evaporated to dryness under reduced pressure to give the deprotonated species. In specific cases (see below), the NMR spectra showed the establishment of a solvent and R-substituent dependent equilibrium (depicted below) between the amino carbene (***AC***) and the imidazolium aminide (***IA***) (see experimental description below for the specific cases and text for discussion).

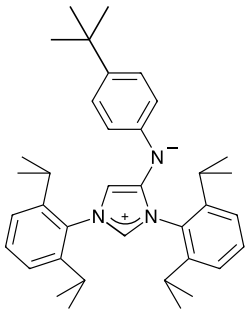


1.3.1 1,3-(bis-di*iso*propylphenyl)-4-(mesitylanilido)-imidazolium 2(*IA*)



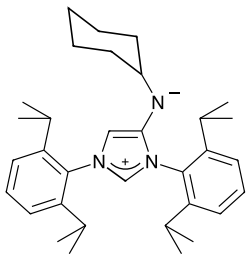
It was prepared by following the general method from **(2H)$^+$Cl$^-$** (2.79 g, 5.0 mmol) and $KN(SiMe_3)_2$ (1,20 g, 6.0 mmol). Yield: 1.69 g, 65%). Analysis: Found (Calc. for $C_{36}H_{47}N_3$ (%): C, 82.65 (82.87), H, 9.00 (9.08), N, 7.93 (8.05). ^{1}H NMR (C_6D_6): 7.25 (t, ^3J = 6.8 Hz, 1H, DiPP), 7.15 (d, ^3J = 6.8 Hz, 2H, DiPP), 7.06 (t, ^3J = 6.8 Hz, 1H, DiPP), 7.01 (d, ^3J = 6.8 Hz, 2H, DiPP), 6.87 and 6.85 (two s, 1H each, mesityl), 6.02 (d, 1H, ^4J = 2.4 Hz, CH-imid), 5.13 (d, 1H, ^4J = 2.4 Hz, CH-imid backbone), 3.36 (sept, ^3J = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 2.81 (sept, ^3J = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 2.48 (s, 6H, *o*-CH_3 mesityl), 2.31 (s, 3H, *p*-CH_3 mesityl), 1.42, 1.12, 1.02 and 0.99 (four doublets, ^3J = 6.9 Hz, 6H each CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (C_6D_6): 150.99, 149.77, 147.49, 145.80, 137.86, 132.95, 131.92, 130.96, 130.28, 129.90, 129.34, 129.28, 125.63, 123.94, 123.89, 93.09, 29.02, 28.53, 25.06, 24.92, 24.56, 23.70, 21.40, 19.02. Therefore, in this case the **(*AC*)** tautomer is not observed.

1.3.2 1,3-(bis-di*iso*propylphenyl)-4-(4-*tert*.butyl-anilido)-imidazolium 3(*IA*)



It was prepared by following the general method from **(3H)$^+$Cl$^-$** (2.86 g, 5.0 mmol) and $KN(SiMe_3)_2$ (1.20 g, 6.0 mmol). Yield: 1.54 g, of yellow-brown powder, 58%). X-Ray quality crystals were obtained by slow diffusion of pentane into THF solution of **3(*IA*)** at -40 °C. Analysis: Found (Calc. for $C_{37}H_{49}N_3$ (%): C, 82.53 (82.94), H, 9.15 (9.22), N,7.68 (7.84). ^{1}H NMR (C_6D_6): 7.35 - 6.90 (overlapping m, 10H, aromatic DiPP and *t*-Bu-Ph), 6.43 (d, 1H, ^4J = 2.0 Hz, CH-imid), 6.05 (d, 1H, ^4J = 2.0 Hz, CH-imid backbone), 3.10 (sept, 2H, ^3J = 6.9 Hz, C*H*$(CH_3)_2$), 2.86 (sept, ^3J = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 1.37 (s, 9H, *t*-Bu), 1.43, 1.18, 1.08 and 1.06 (four doublets, ^3J = 6.9 Hz, 6H each, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (C_6D_6): 152.03, 150.03, 146.73, 145.62, 137.87, 137.54, 132.66, 131.60, 130.21, 128,96, 125.25, 123.73, 123.54, 120.28, 95.40, 33.72, 31.78, 29.06, 28.34, 24.86, 23.96, 23.63, 21.02. Therefore, in this case the **(*AC*)** tautomer is not observed.

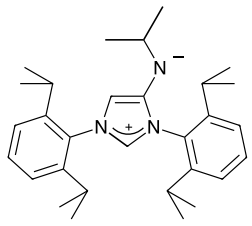
1.3.3 [1,3-(bis-di*iso*propylphenyl)-4-(cyclohexylaminide) imidazolium] - [1,3-(bis-di*iso*propylphenyl)-4-(cyclohexylamine) -imidazol-2-ylidene] equilibrium mixture 4(***IA*** ⇌ ***AC***)



It was prepared by following the general method from **(4H)$^+$Br$^-$** (2.83 g, 5.0 mmol) and $KN(SiMe_3)_2$ (1.20 g, 5.0 mmol). Yield: 1.58 g, 65%). Analysis: Found (Calc. for $C_{33}H_{47}N_3$ (%): C, 81.22 (81.60), H, 9.70 (9.75), N, 8.61 (8.65). ^{1}H NMR (C_6D_6): 7.37 - 6.91 (overlapping multiplet, 6H, DiPP aromatic), 6.04 (s, 0.3H, backbone NHC), 5.98 and 5.49 (two d, ^4J = 2 Hz, 1H each, C2-H imidazolium and backbone imidazolium), 3.33 - 2.92 (overlapping multiplets, in total 6.5 H, 2 x C*H*$(CH_3)_2$, ^3J = 7.4 Hz, DiPP of the imidazolium, 0.3 x 2 x 2 C*H*$(CH_3)_2$ of the NHC, 1H of cyclohexyl of the imidazolium and 0.3 x 1H of the cyclohexyl of the NHC), 2.66 - 2.46 (br m, 0.6H 2 cyclohexyl H of the NHC), 2.22 (d, br, ^2J = 12.2 Hz, 2H, cyclohexyl H of the imidazolium), 1.88 (m, 2H cyclohexyl H of the imidazolium), 1.81 - 1.04 (overlapping doublets, ^3J = 7.4 Hz, and multiplets, 42 H, including the CH(C*H*$_3)_2$ DiPP of the imidazolium (24 H), the CH(C*H*$_3)_2$ DiPP of the NHC (24 x 0.3 = 7.2 H), the cyclohexyl of the imidazolium (8 H) and of the NHC (8 x 0.3 = 2.4H) and 0.3 H from the N*H*Cy of the NHC. Therefore based on the ^{1}H-NMR data in C_6D_6 **4(*IA* ⇌ *AC*)** is present in an equilibrium involving **(*IA*)** and **(*AC*)** in a ratio [***AC***] / [***IA***] = 0.3.

$^{13}C\{^1H\}$ NMR (C_6D_6): 214.51 (C_{NHC}), 153.24, 147.35, 146.95, 146.26, 145.76, 139.69, 139.51, 134.70, 133.37, 132.24, 129.84, 129.18, 123.74, 123.63, 123.41, 123.26, 119.29, 99.34, 89.45, 59.65, 54.45, 34.86, 32.72, 28.88, 28.62, 28.48, 28.25, 27.00, 26.14, 25.13, 24.95, 24.81, 24.34, 24.13, 23.81, 23.65, 23.42, 23.01.

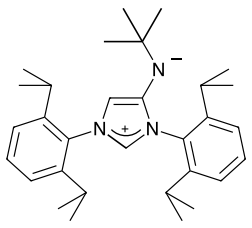
1.3.4 [1,3-(bis-di*iso*propylphenyl)-4-(*iso*propylaminide)-imidazolium] - [1,3-(bis-di*iso*propylphenyl)-4-(*iso*propylamine)-imidazol-2-ylidene] equilibrium mixture 5(***IA*** ⇌ ***AC***)



It was prepared by following the general method from (**5H)$^+$Br$^-$** (2.62 g, 5.0 mmol) and $KN(SiMe_3)_2$ (1.20 g, 6.0 mmol). Yield: 1.38 g of yellow powder, 62%). X-ray quality crystals were obtained by slow evaporation of THF solutions at -40 °C. Analysis: Found (Calc. for $C_{30}N_{43}N_3$ (%): C, 80.58 (80.85), H, 9.70 (9.72), N, 9.28 (9.43). ^{1}H NMR (C_6D_6): 7.38 - 6.93, m, 6H, overlapping aromatics of DiPP), 5.98 (br s, 1.3 H: 1 x 0.3 backbone NHC and 1H C2-H imidazolium), 5.39 (br, d, ^4J = 1.8 Hz, 1H, backbone imidazolium), 3.45 (sept, ^3J = 6.4 Hz, 1H, NC*H*$(CH_3)_2$, 3.21 (three partially overlapping septets, ^3J = 6.9 Hz, 2 x 2H x 0.3 C*H*$(CH_3)_2$ NHC DiPP and 2H C*H*$(CH_3)_2$ imidazolium DiPP), 2.99 (sept, 2H, C*H*$(CH_3)_2$ DiPP of the imidazolium), 2.85 (multiplet, 1 x 2H x 0.3 NC*H*$(CH_3)_2$ of the NHC DiPP), 2.45 (s, br, 1H x 0.3 N*H*CH$(CH_3)_2$ of the NHC), 1.50, 1.42, 1.20, 1.14, 1.10 (five doublets, 30H, 4 x CH(C*H*$_3)_2$ of the DiPPs and 1 x NCH(C*H*$_3)_2$ of the imidazolium), 1.36, 1.34, 1.30, 1.27, 0.74 five doublets partially overlapping, 0.3 x 30H, 4 x CH(C*H*$_3)_2$ of the DiPPs, ^3J = 6.9 Hz, and 1 x NHCH(C*H*$_3)_2$ ^3J = 6.4 Hz, of the NHC). Therefore based on the ^{1}H-NMR data in C_6D_6 **5(*IA* ⇌ *AC*)** is present in an equilibrium involving (***IA***) and (***AC***) in a ratio [(***AC***)] / [(***IA***)] = 0.3

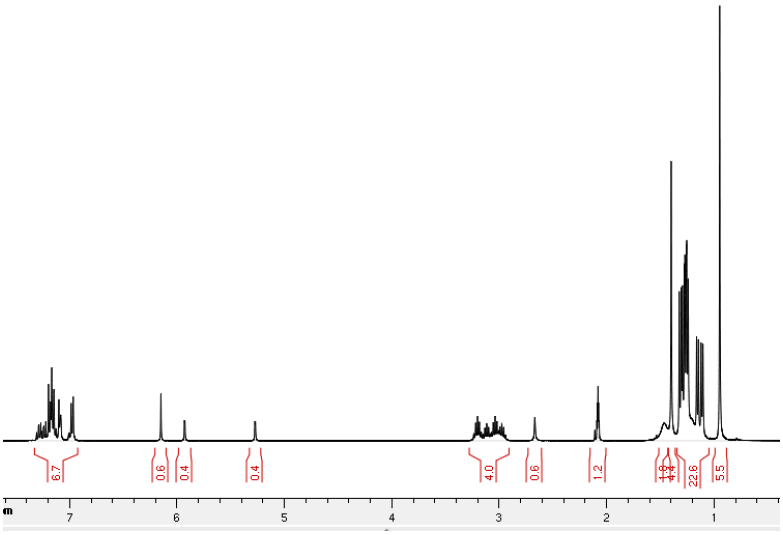
$^{13}C\{^1H\}$ NMR (C_6D_6): No C_{NHC} is observed.153.46, 146.95, 145.74, 133.34, 132.13, 129.82, 123.60, 123.45, 119.37, 89.57, 50.57, 28.84, 28.26, 24.99, 24.30, 24.17, 23.72, 23.65.

1.3.5 [1,3-(bis-di*iso*propylphenyl)-4-(*tert*-butylaminide)-imidazolium] - [1,3-(bis-di*iso*propylphenyl)-4-(*tert*-butylamine)-imidazol-2-ylidene] equilibrium mixture 6(*IA* ⇌ *AC*)



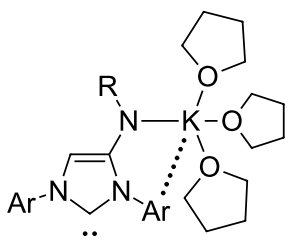
It was prepared by following the general method from **(6H)$^+$Br$^-$** (2.69 g, 5.0 mmol) and $KN(SiMe_3)_2$ (1.20 g, 6.0 mmol). Yield: 1.52 g of yellow air sensitive powder, 68%). X-ray quality crystals were obtained by dissolution in pentane and cooling at -40 °C for 2 days. Analysis: Found (Calc. for $C_{31}H_{45}N_3$ (%): C, 80.87 (80.99), H,9.79 (9.87), N, 9.05 (9.14). ^{1}H NMR (C_6D_6): 7.33 - 6.93 (m, 6H, overlapping aromatic DiPP from NHC and imidazolium), 6.15 (s, 1H x 60%, backbone imid-C-*H* of the NHC), 5.33 and 5.27 (d, each 1H x 40%, ^4J = 1.8 Hz, C-*H* imidazolium and backbone imid-C-*H* of the imidazolium), 3.28 - 2.91 (m, four overlapping septets

of the C*H*$(CH_3)_2$ of the NHC, ^3J = 6.9 Hz, and the imidazolium), 2.67 (br s, 1H x 60%, N - *H* of the NHC), 1.40 and 0.95 (two s, 9H x 40% *t*Bu of the imidazolium, 9H x 60% *t*-Bu of the NHC, respectively), 1.35 - 1.10 six overlapping doublets ^3J=6.9 Hz, and broad features 24 H, CH(C$H_3)_2$.



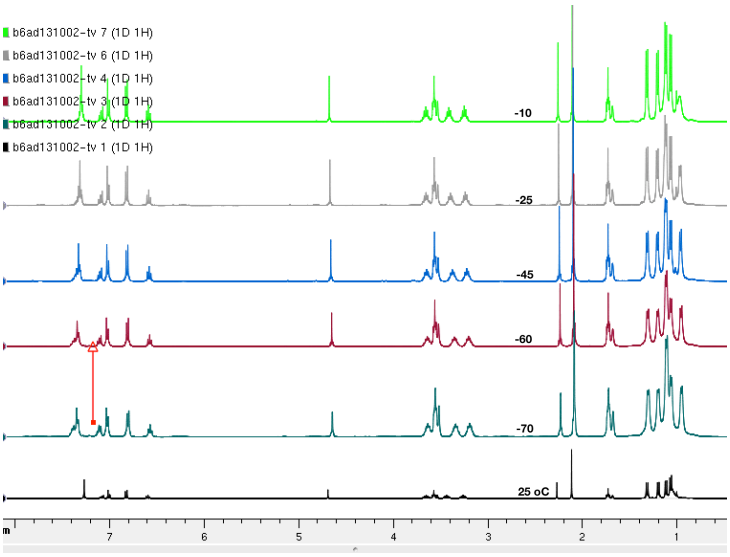
$^{13}C\{^1H\}$ NMR (toluene-d^8): Underlined peaks have been assigned with certainty to the NHC. 214.11 (C_{NHC}), {101.96 (backbone imid-C), 91.49}, {51.30, 50.90 *C*$(CH_3)_3$}, 29.62, 29.23, 2892, 28.76, 28.66,25.03, 24.77, 24.65, 23.85, 23.15. Based on the integration of relevant C signals the ratio [carbene] / [imidazolium] is *ca.* 65 / 35 which is in agreement with the information from ^{1}H-NMR spectra. ^{1}H NMR (d^8-THF): It is broad and featureless over the -50 °C to 25 °C range. $^{13}C\{^1H\}$ NMR (d^8-THF): 213.77, 150.91, 147.38, 146.37, 134.89, 134.20, 133.17, 130.15, 129.06, 128.78, 123.96, 123.70, 123.22, 121.58, 102.09, 90.91, 51.00, 50.80, 29.06, 28.82, 28.52, 23.40, 22.77. The ratio of backbone imid-C that have been used above to evaluate the position of the equilibrium, is approximately [carbene] / [imidazolium] = 1.9.

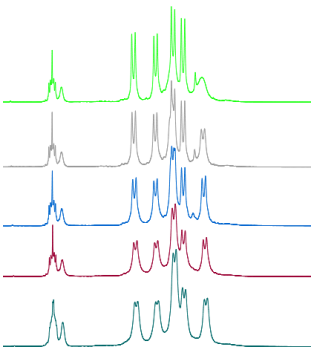
1.4 Deprotonation of the 1,3-(bis-di*iso*propylphenyl)-4-(2,6-di*iso*propylanilide)-imidazolium 3(*IA*) with stoichiometric KCH_2Ph. Complex 7



To a solution of **1(*IA*)** (0.30 g, 0.54 mmol) in THF (20 ml) at room temperature was added a solution of KCH_2Ph (0.09 g, 1.25 equiv.) in THF (5 ml). The solution adopted a yellow-orange coloration. It was stirred for 3 h, concentrated to approx. 10 ml and filtered if necessary. Diffusion of

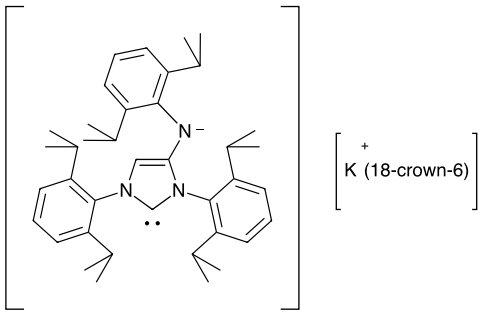
pentane vapor into the THF solution gave lemon yellow crystals of **9**. X-ray quality crystals were obtained by prolonged (4 weeks) cooling of a THF solution of **9** at -40 °C, when prisms grew on the glass wall just above the solution. Elemental analysis for this complex could not be obtained due to the ready solvent loss and extreme air sensitivity. ^{1}H NMR (d^{8}-THF): 7.33 (s, br, 3H, aromatics of the DiPP interacting with K), 7.14, (1H, t, ^{3}J = 7.3 Hz, DiPP aromatic), 7.07 (2H, d, ^{3}J = 7.3 Hz, DiPP aromatic), 6.88 (2H, d, ^{3}J = 7.4 Hz, DiPP arom.), 6.65 (1H, t, ^{3}J = 7.4 Hz, DiPP arom.), 4.75 (s, 1H, backbone imidazol C-H), 3.71, 3.49, 3.32 (2H each, sept. ^{3}J = 6.8 Hz, C*H*(CH$_3$)$_2$), 1.38, 1.26, 1.17 (6H each, d, ^{3}J = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.13 (18H, d overlapping with a broad feature, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (d^{8}-THF): 205.99, 154.95, 154.31, 148.68, 146.68, 144.67, 142.00, 141.80, 126.91, 126.73, 122.96, 122.64, 122.48, 119.41, 90.73, 58.40, 45.69, 28.76, 27.93, 27.33, 25.65, 23.99, 22.43.



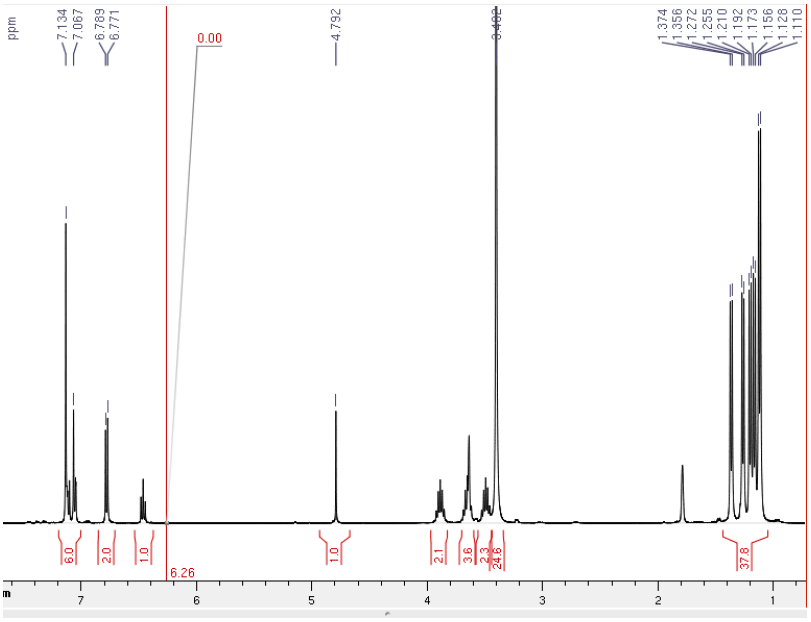


The complex is nonrigid at room temperature. This is confirmed by the broadness of the signals assignable to the aromatic and the CH(C*H*$_3$)$_2$ of the DiPP interacting with the K. Lowering of the temperature results in partial de-coalescence of the signals as shown in the stacked plot of the spectra below; the observed spectral changes are reversible on rewarming to room temperature. The nonrigidity may originate from the time averaged interaction of the K with the *ipso*-C and one of the C atom substituted with *o*-Pr^{i} (see static picture in the solid state).

1.5 Deprotonation of the 1,3-(bis-di*iso*propylphenyl)-4-(2,6-di*iso*propylanilide)-imidazolium 3(*IA*) by stoichiometric KCH_2Ph / 18-crown-6. Complex 8

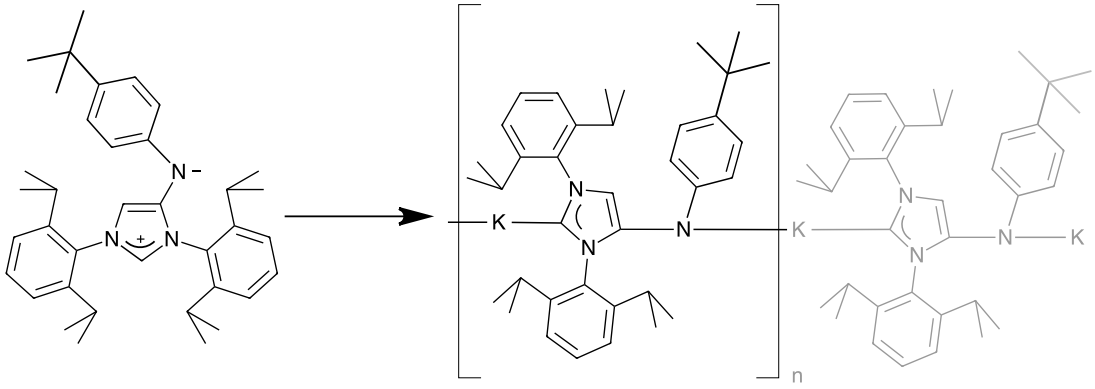


To a solution of 4-(2,6-di*iso*propylphenylimino)-1,3-(bis-di*iso*propylphenyl)-imidazolium **1(*IA*)** (0.56 g, 1.0 mmol) in THF (10 ml) was added at room temperature solid KCH_2Ph (0.17 g, 1.25 mmol). The initially yellow solution turned immediately orange. To this was added pre-dried solid 18-crown-6 (0.26 g, 1.0 mmol) resulting in a light yellow coloration. After stirring for 4 h the volatiles were removed under reduced pressure and the solid residue was extracted in THF (12 ml) and filtered if necessary. Slow diffusion of pentane vapor into the THF gave after one week at room temperature yellow crystals. Yield: 0.42 g, ca 51%. Elemental analysis data could not be obtained due to the extreme moisture and oxygen sensitivity of the compound. ^{1}H NMR (d^8-THF): 7.13 - 7.00 (m, 6H, DiPP aromatics), 6.78 (d, ^3J = 7.6 Hz, 2H, DiPP aromatics), 6.46 (t, ^3J = 7.6 Hz, 1H, DiPP aromatics), 4.76 (s, 1H, backbone NHC), 3.89 (septet, ^3J = 6.8 Hz, 2H, C*H*$(CH_3)_2$,), 3.64 (septet, ^3J = 6.8 Hz, partially overlapping with THF, 2H, C*H*$(CH_3)_2$), 3.49 (septet, *J* = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 3.40 (s, 24 H, crown ether), 1.36, 1.26, 1.20, 1.16 (doublets, ^3J = 6.8 Hz, 6H each,, CH(C*H*$_3)_2$), 1.12 (doublet, ^3J = 6.8 Hz, 12H, CH(C*H*$_3)_2$)). ^{13}C{^{1}H} NMR (d^8-THF): 207.17,

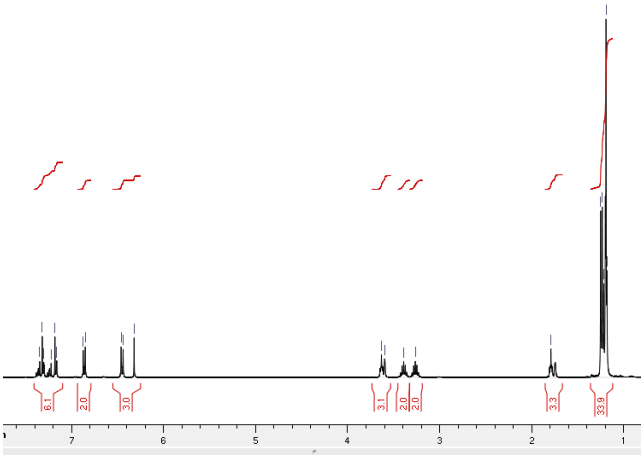


157.44, 153.56, 148.35, 147.29, 143.67, 142.79, 142.64, 126.06, 125.62, 122.15, 121.67, 116.40, 87.94, 70.45, 28.56, 27.76, 27.29, 25.22, 23.11.

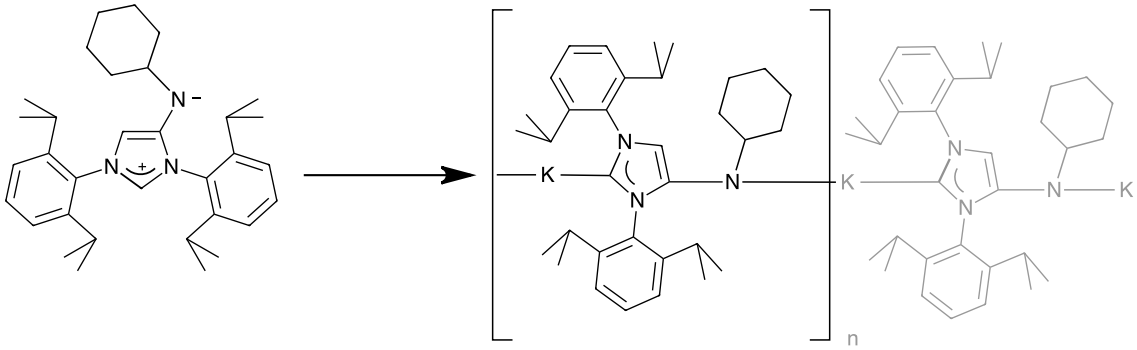
1.6 Deprotonation of the 1,3-(bis-di*iso*propylphenyl)-4-(*tert*-butylanilide)-imidazolium 5(*IA*) by stoichiometric KCH_2Ph. Complex 9

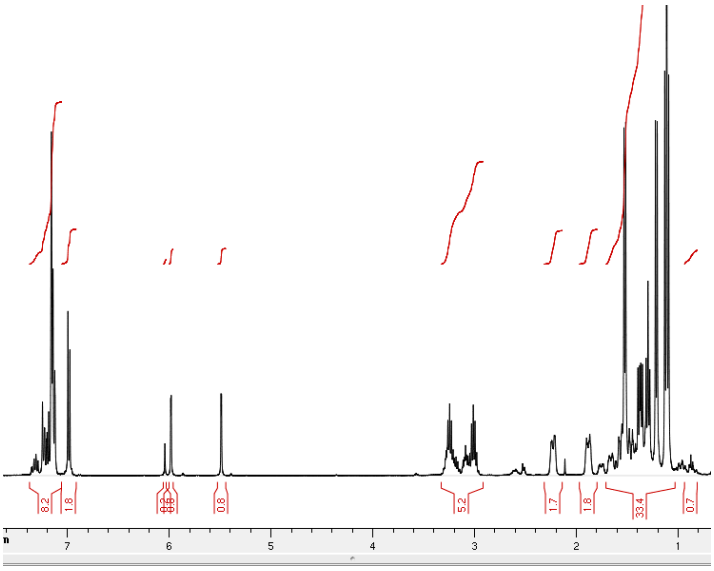


This was prepared by a method similar to that reported for complex **7** above from **3(*IA*)** (0.54 g, 1.0 mmol) and KCH_2Ph (0.16 g, 1.2 mmol) in THF (20 ml). Yellow crystals (also suitable for X-ray study) by layering the THF solution with pentane. Elemental analysis data could not be obtained due to the extreme moisture and oxygen sensitivity of the compound. Yield: 0.45 g, ca. 78%. ^{1}H NMR (d^8-THF): 7.40 - 7.15 (m, 6H, DiPP arom.), 6.67 and 6.45 (d, J = 9.0 Hz, 2H each, *t*Bu-Ph arom.), 6.32 (s, 1H, backbone imidazol proton), 3.60 (THF), 3.39 and 3.26 (sept. ^3J = 6.9 Hz, 2H each C*H*$(CH_3)_2$ of DiPP), 1.74 (THF), 1.28 - 1.14 (three overlapping doublets ^3J = 6.9 Hz, and one singlet 33H, CH(C*H*$_3)_2$ of DiPP and *t*-Bu of *t*-Bu-Ph). ^{13}C{^{1}H} NMR (d^8-THF): 208.64, 154.82, 149.25, 148,53, 146.85, 141.78, 141.72, 132.49, 127.15, 125.28, 122.85, 122.75, 117.12, 95.55, 33.51, 31.75, 28.66, 28.33, 25.85, 23.96, 23.66, 22.71.



1.7 Deprotonation of the 4(*IA* ⇌ *AC*) by stoichiometric KCH_2Ph. Complex 10

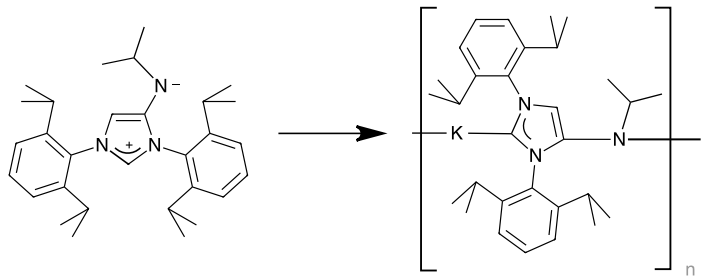


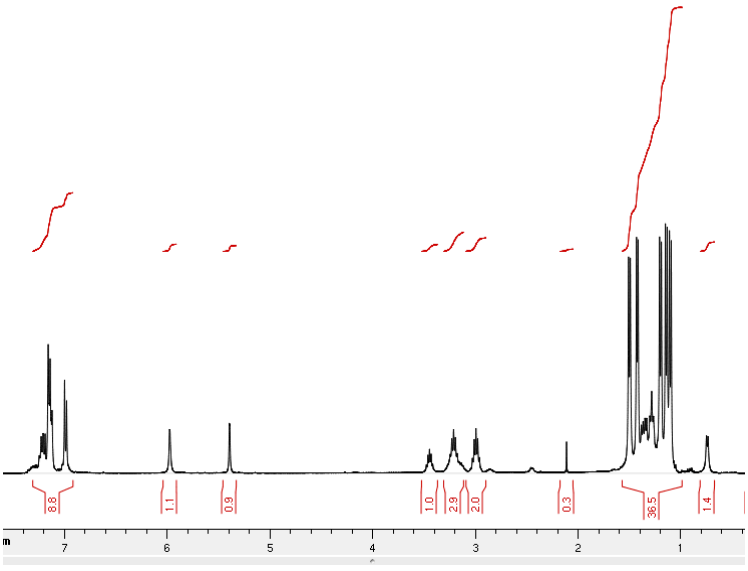


To a solution of **4(*IA* ⇌ *AC*)** (0.48 g, 1.0 mmol) in THF (20 ml) was added at room temperature solid KCH_2Ph (0.16 g, 1.2 mmol). After stirring for 2-5 min, a yellow precipitate started forming. Stirring was continued for additional 12 h and equal volume of pentane was added. The suspension was allowed to settle for a 15 min and the yellow precipitate was collected on a frit and dried. Yield: 0.40 g, 77%. X-ray quality crystals were obtained by dissolving the yellow precipitate in hot THF and allowing pentane vapor to slowly diffuse into the cooled THF solution; the yellow crystals appeared after one week. Elemental analysis data could not be obtained due to the extreme moisture and oxygen sensitivity of the compound. ^{1}H NMR (d^8-THF): 7.54 - 7.10 (m, 6H, DiPP aromatic), 5.21 (s, 1H, backbone imidazol C-H), 3.52 (septet, ^3J = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 3.39 (septet, ^3J = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 2.59 (m, 1H, cyclohexyl), 2.13 (br d, 2H cyclohexyl), 2.38 (br m, 4H, cyclohexyl), 1.44 - 1.18 (overlapping d, ^3J = 6.8 Hz, and br m, 29H, cyclohexyl and

CH(C*H*$_3$)$_2$ of the DiPP). ^{13}C{^{1}H} NMR (d^8-THF): The quality of the spectrum is affected by the low solubility of the compound in THF at room temperature. 156.70, 148.89, 147.41, 146.97, 123,31, 122.72, 122.42, 87.39, 34.51, 25.88, 22.72.

1.8 Deprotonation of the 5(*IA* ⇌ *AC*) by stoichiometric KCH_2Ph. Complex 11



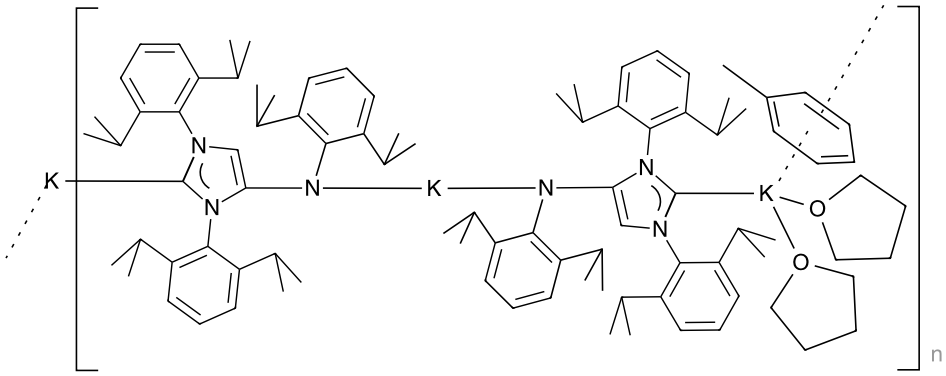


This was prepared in a way similar to the cyclohexylimino analogue from **5(*IA* ⇌ *AC*)** (0.44 g, 1.0 mmol) and KCH_2Ph (0.16 g, 1.2 mmol) in THF. The product was isolated as a yellow powder. It was not structurally characterized but based on its similar solubility properties with **10** and the NMR data given below we presume that it adopts a polymeric structure analogous to **12**. Yield: 0.30 g, 67%. Elemental analysis data could not be obtained due to the extreme moisture and oxygen sensitivity of **11**. ^{1}H NMR (d^8-THF): 7.33 - 7.12 (m, 6H, aromatic DiPP), 5.18 (s, 1H, backbone imidazol C-H), 3,46 and 3.37 (septet, ^3J = 7.1 Hz, 2H each, C*H*(CH$_3$)$_2$ of DiPP), 2.97 (septet, ^3J = 7.1 Hz, 1H, C*H*(CH$_3$)$_2$ of amido NPr^i), 1.28, 1.26, 1.23, 1.20, (d, *J* = 7.1 Hz, 6H each, CH(C*H*$_3$)$_2$ of DiPP), 0.94 (d, *J* = 6.1 Hz, 1H, CH(C*H*$_3$)$_2$ of amido NPr^i). ^{13}C{^{1}H} NMR (d^8-THF): 205.75, 156.91, 148.88, 146.89, 142.70, 142.42, 126.61, 126.62, 122.80, 122.56, 87.84, 51.20, 28.41, 28.12, 23.88, 22.85.

1.9 Deprotonation of the 6(*IA* ⇌ *AC*) by stoichiometric KCH_2Ph.

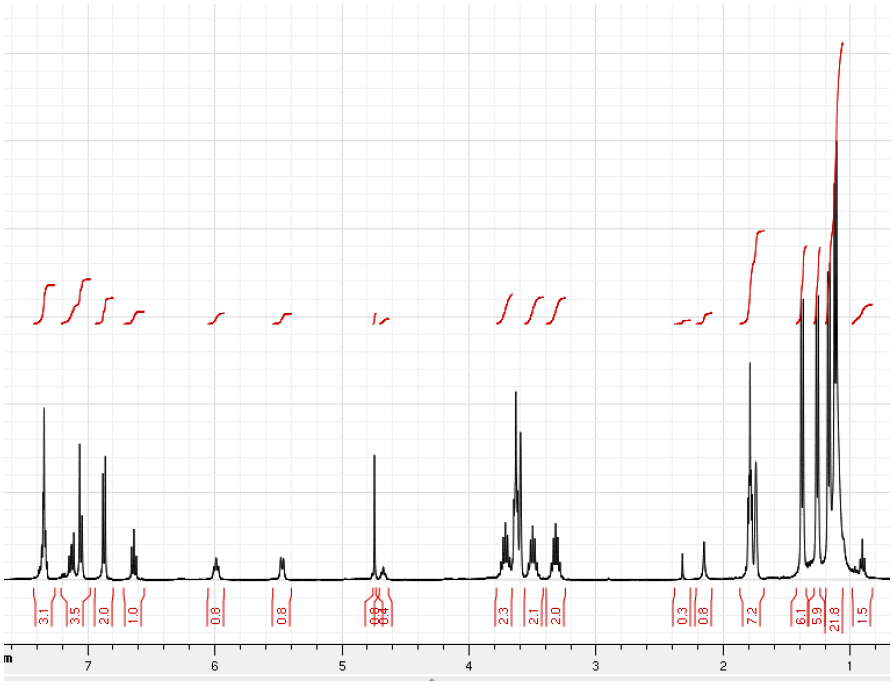
In a Young's NMR tube was placed **6(*IA* ⇌ *AC*)** (20 mg) and KCH_2Ph (20 mg, *ca.* 3 equiv,) and THF-d^8 (0.6 ml). The solution adopted an intense orange coloration and was used for NMR studies. ^1H NMR (d^8-THF): 7.50 - 6.97 (m, 6H, DiPP aromatic), 5.16 (s, 1H, backbone imidazol C-H), 3.46 and 3.36 (septet, ^3J = 6.8 Hz, 2H each,C*H*$(CH_3)_2$ of DiPP), 1.40 - 1.16 (d, 24H, ^3J = 6.8 Hz CH(C*H*$_3)_2$ of DiPP), 1.10 (s, 9H, *t*-Bu). In addition there are signals due to the presence of toluene (following deprotonation of **6(*IA* ⇌ *AC*)**) and excess of KCH_2Ph. In the $^{13}C\{^1H\}$ NMR spectrum (d^8-THF) there is a C_{NHC} at 197.54. The isolation of the species responsible for these NMR spectra failed.

1.10 Deprotonation of [1,3-(bis-di*iso*propylphenyl)-4-(2,6-di*iso*propylanilido)]-imidazolium 3(*IA*) with excess KCH_2Ph. Complex 12



To a solution of 1,3-(bis-di*iso*propylphenyl)-4-(2,6-di*iso*propylanilido)-imidazolium (0.56 g, 1.0 mmol) in THF (10 ml) was added at room temperature solid KCH_2Ph (0.22 g, 1.7 mmol). The initially yellow solution turned immediately intense orange. Crystallization was carried out by slow vapor diffusion of pentane into a dilute THF solution at 5 °C or by cooling at -40 °C. The product in THF solution at room temperature decomposes after approximately one week but is stable at -40 °C for at least six months under an inert atmosphere. Yield: *ca.* 0.42 g, 65% based on the imidazolium.

^{1}H NMR (d^{8}-THF): 7.34 (m, 3H, aromatic DiPP), 7.13 (t, ^{3}J = 6.2 Hz, 1H, aromatic DiPP), 7.05 (d, 2H, ^{3}J = 6.2 Hz, aromatic DiPP), 6.87 (d, ^{3}J = 5.7 Hz, 2H, aromatic DiPP), 6.63 (t, ^{3}J = 5.7 Hz, 1H, aromatic DiPP), 6.08 (two AB d, 2H x 50% *o*-H in $KCH_2C_6H_5$), 5.55 (two AB d, 2H x 50%, *m*-H in $KCH_2C_6H_5$), 4.74 (s, 1H, backbone imidazol C-H), 4.67 (t, 1H x 50%, *p*-H in $KCH_2C_6H_5$), 3.71(sept., ^{3}J = 6.4 Hz, 2H, C*H*$(CH_3)_2$ of DiPP), 3.59 (THF) 3.50 (sept., ^{3}J = 6.4 Hz, 2H, C*H*$(CH_3)_2$ of DiPP), 3.32 (sept., ^{3}J = 6.4 Hz, 2H, C*H*$(CH_3)_2$ of DiPP), 2.26 (s, 2H x 50%, $KCH_2C_6H_5$), 1.74 (THF) 1.38 (d, ^{3}J = 6.4 Hz, 6H, CH(C*H*$_3)_2$ of DiPP), 1.26 (d, ^{3}J = 6.4 Hz, 6H, CH(C*H*$_3)_2$ of DiPP), 1.17 and 1.12 (two partially overlapping d, ^{3}J = 6.4 Hz, 24H, CH(C*H*$_3)_2$ of DiPP).



^{13}C{^{1}H} NMR (d^{8}-THF): 206.14, 155.00, 154.32, 148.93, 146.87, 144.71, 142.11, 141.84, 129.30, 128.36, 126.85, 126.69, 122.96, 122.64, 122.46, 119.39, 90.72, 28.80, 27.93, 27.33, 25.85, 23.96, 22.42.

1.11 Table S1. Tabulation of ^{13}C-NMR chemical shifts for the C_{NHC} in the anionic NHC species and their precursors

Compound	δC_{NHC}	Comment
4(*IA* ⇌ *AC*) (C_6D_6)	214.51	R = Cy
6(*IA* ⇌ *AC*) (C_6D_6)	214.11	R = *t*-Bu
7 (THF - d^8)	205.99	R = DiPP / free C_{NHC} donor
8 (THF - d^8)	207.11	R = DiPP / free C_{NHC} donor
9 (THF - d^8)	208.64	R = *t*-Bu-Ph / Janus polymer
11 (THF - d^8)	205.75	R = *i*-Pr
12 (THF - d^8)	206.14	R = DiPP / Copolymer

2. X-ray crystallography

2.1 General methods

Summary of the crystal data, data collection and refinement for compounds **7, 8, 9, 10** and **12** and the imidazoliums **5(*IA*)** and **6(*IA*)** are given in Table S2 and S3, respectively. The crystals were mounted on a glass fiber with grease, from Fomblin vacuum oil. Data sets were collected on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å) unless otherwise stated (see specific comments for each data set given below). The cell parameters were determined (APEX2 software[6]) from reflections taken from tree sets of 12 frames, each at 10 s exposure. The structures were solved by direct methods using the program SHELXS-97.[7] The refinement and all further calculations were carried out using SHELXL-97.[8] The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2.

The following specific comments apply for the structures:

Complex 7 · THF: Data were collected with the Cu micro source because of the low diffracting power of the crystal. The THF molecules are very 'agitated' so several alerts are generated in the checkcif. Two THF molecules are disordered over two positions.

Complex 8: The asymmetric unit contains one anionic ligand and half a molecule of "C24H48K2O12". This molecule is very disordered. The atoms C35, C36, C40, C41, C44, C45, C46, C47, C48, C49, C51, O1, O5 and O6 are disordered on two positions. The Alert B in checkcif (Short intra contact H43A --- H44C) is due to the fact that the atom C44 is disordered.

Complex 10: The methyls C11 and C12 are disordered on two positions.

Complex 12: Data were collected with the Cu micro source because of the low diffracting power of the crystal. The asymmetric unit contains one ligand coordinated to two K atoms, K1 in special position, and K2 coordinated to two THF and half a molecule of $C_6H_5CH_2$. Due to the symmetry, the carbon C51 of $C_6H_5CH_2$ is in half occupancy. Two hydrogen atoms were placed on C51 but

were not located experimentally. SQUEEZE instruction was used to eliminate the residual density. which corresponds to one disordered molecule of pentane.

5(*IA*) · THF: The asymmetric unit contains one molecule of ligand and one molecule of THF. The carbon C34 of THF is disordered on two positions.

2.2 Summary of crystal data

Table S2 Crystal data for the K complexes **7**, **8**, **9**, **10** and **12**

	7 · THF	**8**	**9**	**10**	**12**
Chemical formula	$C_{55}H_{84}KN_3O_4$	$C_{102}H_{152}K_2N_6O_{12}$	$C_{41}H_{56}KN_3O$	$C_{33}H_{46}KN_3$	$C_{101}H_{142}K_3N_6O_4$
CCDC Number	965581	965582	965583	965584	965585
Formula Mass	890.35	1732.50	645.99	523.83	1621.51
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
a (Å)	23.271(5)	20.9918(6)	15.3219(5)	20.871(4)	10.7003(3)
b (Å)	10.689(5)	20.7930(5)	14.8804(4)	13.134(2)	15.9846(5)
c (Å)	22.09.7(5)	23.1690(6)	21.0810(5)	23.056(4)	32.2059(10)
α (°)	90.00	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	126.430(2)	100.135(4)	104.187(2)
γ (°)	90.00	90.00	90.00	90.00	90.00
Unit cell volume/*Å*^{3}	5496(3)	10112.9(5)	3867.13(19)	6221.2(19)	5340.5(3)
Temperature/*K*	173(2) K	173(2)	173(2)	173(2)	173(2)
Space group	Pna21	Pbca	P 21/c	C 2/c	P 21/c
Formula units / cell, *Z*	4	4	4	4	2
Absorption coeff., μ/mm^{-1}	1.174	0.153	0.170	0.195	1.484
No. of reflections measured	30001	55913	33852	35945	34275
No. of independent reflections	8960	12218	11263	7508	9316
R_{int}	0.0342	0.0532	0.0360	0.1190	0.0322
Final R_1 values ($I > 2\sigma(I)$)	0.0658	0.0709	0.0721	0.0658	0.0806
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1858	0.1645	0.1891	0.1445	0.2093
Final R_1 values (all data)	0.0776	0.1389	0.1105	0.1378	0.0904
Final $wR(F^2)$ values (all data)	0.1975	0.2090	0.2155	0.1783	0.2156
Goodness of fit on F^2	1.049	1.022	1.035	1.008	1.048

Table S3 Crystal data for the imidazolium aminides **5(*IA*)** and **6(*IA*)**

	5(*IA*) · THF	**6(*IA*)**
Chemical formula	$C_{34}H_{51}N_3O$	$C_{31}H_{45}N_3$
CCDC Number	965579	965580
Formula Mass	517.78	459.70
Crystal system	Monoclinic	Triclinic
a (Å)	10.1224(6)	10.3078(5)
b (Å)	14.9203(9)	10.9366(5)
c (Å)	21.5368(12)	14.0780(7)
α (°)	90	74.9360(10)
β (°)	90.4090	78.7450(10)
γ (°)	90	74.2170(10)
Unit cell volume/$Å^3$	3252.6(3)	1461.44(12)
Temperature/*K*	173(2)	173(2)
Space group	*P 21/c*	*P -1*
Formula units / cell, *Z*	4	2
Absorption coeff., μ/mm^{-1}	0.063	0.061
No. of reflections measured	24446	19814
No. of independent reflections	7875	8531
R_{int}	0.0874	0.0308
Final R_1 values ($I > 2\sigma(I)$)	0.0647	0.0696
Final $wR(F^2)$ values (I > 2σ(I))	0.1337	0.1801
Final R_1 values (all data)	0.1667	0.1059
Final wR(F^2) values (all data)	0.1694	0.2006
Goodness of fit on F^2	0.972	1.068

2.3 The structure of 7 · THF

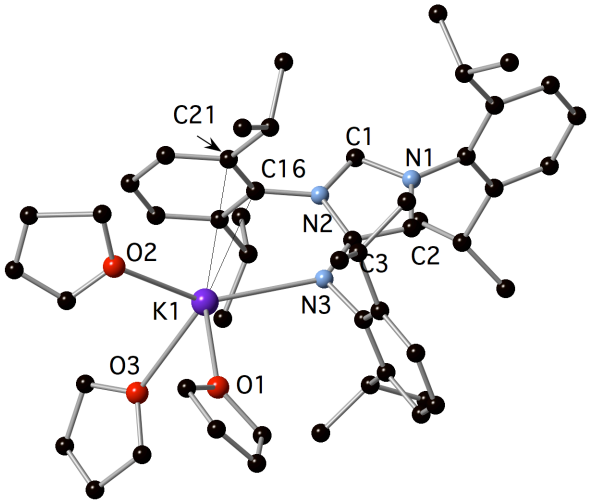
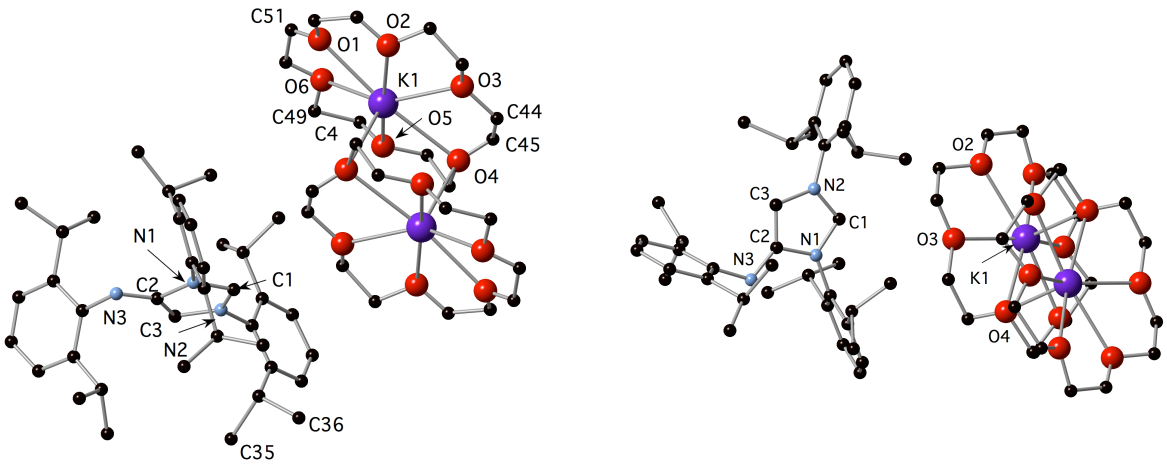


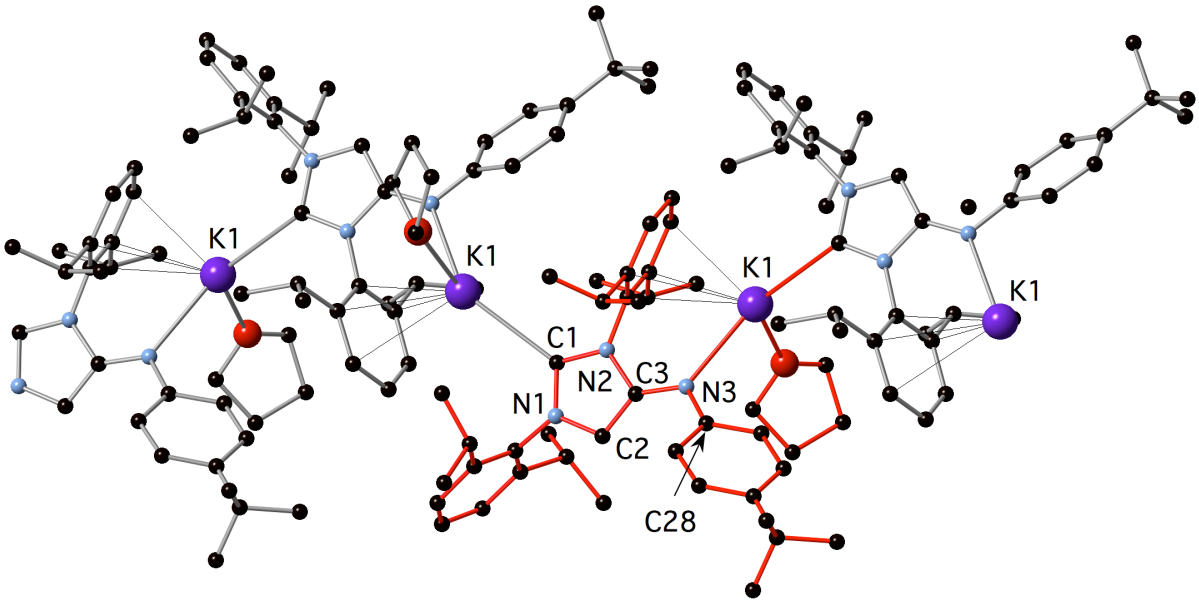
Figure S1 The structure of **7**. One THF molecule in the asymmetric unit is omitted. Only one position of the disordered coordinated THF ligands incorporating O2 and O3 are shown. Important bond lengths (Å) and angles (°): C1 - N1 1.347(4), C1 - N2 = 1.389(4), C2 - C3 = 1.365(4), C2 - N1 = 1.420(4), N3 - K1 = 2.710(3), O1 - K1 = 2.696(4), O2 - K1 = 2.732(4), O3 - K1 = 2.732(4), C16 - N2 = 1.421(4), C16 - K1 = 3.334(3), C21 - K1 = 3.318(3), N3 - K1 = 2.710(3), C16 - N2 = 1.421(4), N1 - C1 - N2 = 101.3(3), C3 - C2 - N1 = 106.5(3), N3 - C3 - C2 = 135.3(3), N3 - C3 - N2 = 120.5(3), C2 - C3 - N2 = 104.2(3), O1 - K1 - N3 = 99.39(12) O1 - K1 - O3 = 81.84(18), N3 - K1 - O3 = 125.45(13), O1 - K1 - O2 = 80.48(14), N3 - K1 - O2 = 140.21(12), O3 - K1 - O2 = 94.11(16), O1 - K1 - C21 = 146.71(15), N3 - K1 - C21 = 67.23(8), O3 - K1 - C21 = 131.13(14), O2 - K1 - C21 = 91.06(12), O1 - K1 - C16 = 153.69(12), N3 - - K1 - C16 = 55.25(8), O3 - K1 - C16 = 117.28(13), O2 - K1 - C16 = 113.67(11), C21 - K1 - C16 = 24.28(8), O1 - K1 - C20 = 148.28(14), N3 - K1 - C20 = 91.07(9), O3 - K1 - C20 = 115.98(14), O2 - K1 - C20 = 72.60(12), C21 - K1 - C20 = 23.90(9), C16 - K1 - C20 = 41.52(9), O1 - K1 - C44 = 73.9(3), N3 - K1 - C44 = 158.6(3), O3 - K1 - C44 = 74.4(3), O2 - K1 - C44 = 20.1(3), C21 - K1 - C44 = 107.1(3), C16 - K1 - C44 = 126.7(3), O1 - K1 - C17 = 162.89(12), N3 - K1 - C17 = 69.58(8), O3 - K1 - C17 = 93.86(14), O2 - K1 - C17 = 116.45(12), C21 - K1 - C17 = 42.12(8), C16 - K1 - C17 = 23.53(8), C20 - K1 - C17 = 47.80(9), C44 - K1 - C17 = 121.1(3).

2.4 The structure of 8



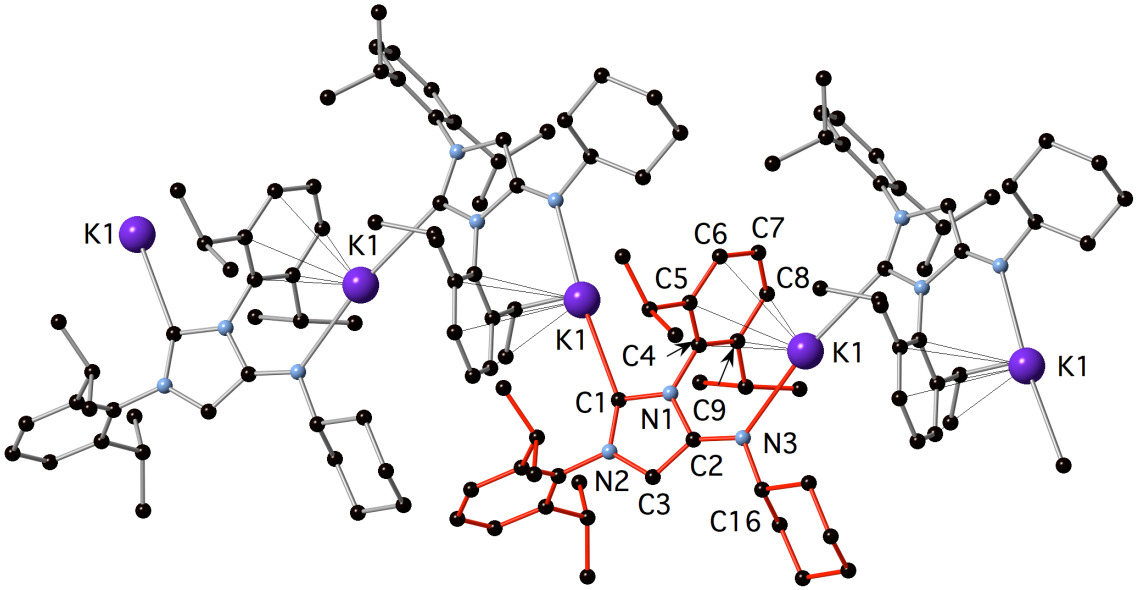
Figures S2A and S2B Two views of the structure of **8**. The asymmetric unit contains one anionic ligand and half a molecule of 'C24H48K2O12'. One of the disordered positions of C35, C36, C40, C41, C44, C45, C46, C47, C48, C49, C51, O1, O5 and O6 is shown. Important bond lengths (Å) and angles (°): C1 - N2 = 1.337(3), C1 - N1 = 1.386(3), C2 - N3 = 1.334(3), C2 - C3 = 1.368(4), C2 - N1 = 1.415(3), C3 - N2 = 1.413(3), O1 - K1 = 2.756(7), O2 - K1 = 2.765(3), O3 - K1 = 2.710(3), O4 - K1 = 2.876(3), O4 - K1 = 2.932(2), O5 - K1 = 2.860(7), O6 - K1 = 2.778(6), N2 - C1 - N1 = 101.6(2), N3 - C2 - C3 = 136.2(2), N3 - C2 - N1 = 120.3(2), C3 - C2 - N1 = 103.5(2), C2 - C3 - N2 = 107.0(2).

2.5 The structure of 9



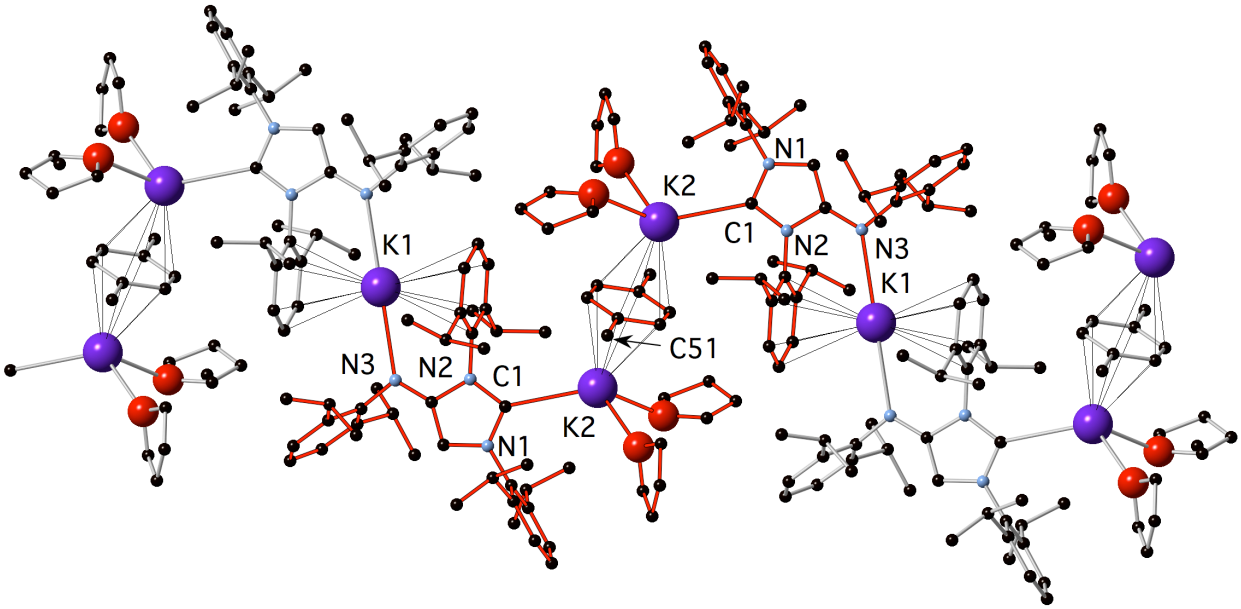
Figures S3 The structure of the polymer chain in **9**. Four consecutive repeat units are shown with one depicted in red showing the metal binding sites. Important bond lengths (Å) and angles (°): C1 - N1 = 1.354(3), C1 - N2 = 1.384(2),C1 - K1 = 3.021(2), C2 - C3 = 1.368(3), C2 - N1 = 1.408(2), C3 - N3 = 1.358(2), C3 - N2 = 1.416(2), C1 - N1 = 1.354(3), C1 - N2 = 1.384(2), C1 - K1 = 3.021(2), C2 - C3 = 1.368(3), C2 - N1 = 1.408(2), C3 - N3 = 1.358(2), C3 - N2 = 1.416(2), C16 - K1 = 3.2882(19), C18 - K1 = 3.425(3), C19 - K1 = 3.422(3), N1 - C1 - N2 = 101.37(16), N1 - C1 - K1 = 126.53(13), N2 - C1 - K1 = 129.55(13), C3 - C2 - N1 = 106.94(17), N3 - K1 - C1 = 143.31(6), O1 - K1 - C1 = 119.48(6).

2.6 The structure of 10



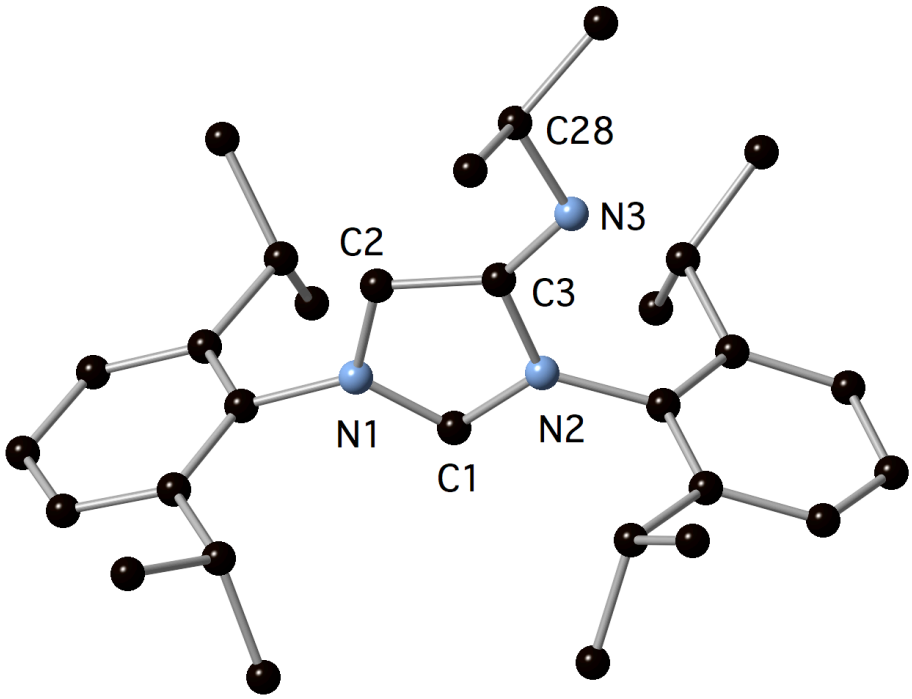
Figures S4 The structure of the polymer chain in **10**. Four consecutive repeat units are shown with one depicted in red showing the metal binding sites. Important bond lengths (Å) and angles (°): C1- N2 = 1.350(3), C1 - N1 = 1.370(3), C1 - K1 = 2.924(2), C2 - N3 = 1.332(3), C2 - C3 = 1.384(3), C2 - N1 = 1.419(3), C3 - N2 = 1.408(3), C4 - K1 = 3.490(2), C6 - K1 = 3.308(3), C7 - K1 = 3.355(3), C8 - K1 = 3.334(3), C9 - K1 = 3.250(3), N2 - C1 - N1 = 101.55(19), N2 - C1 - K1 = 148.69(17), N1 - C1 - K1 = 109.66(13), N3 - C2 - C3 = 137.4(2), N3 - C2 - N1 = 120.26(19), C3 - C2 - N1 = 102.32(19), C2 - C3 - N2 = 107.39(19), N3 - K1 - C4 = 129.39(6), C1 - K1 - C4 = 43.82(6).

2.7 The structure of 12



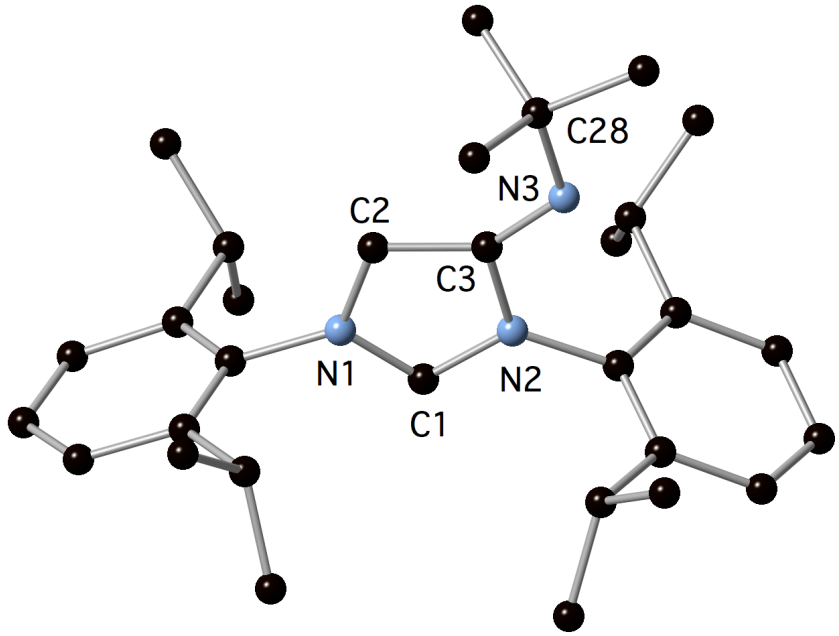
Figures S5 The structure of the polymer chain in **12**. Three consecutive repeat units are shown with one depicted in red showing the metal binding sites. Due to the symmetry, the carbon C51 of $C_6H_5CH_2$ is in half occupancy. Important bond lengths (Å) and angles (°): C1 - N1 = 1.336(4), C1 - N2 = 1.394(4), C1 - K2 = 2.934(3), C2 - C3 = 1.365(4), C2 - N1 = 1.419(4), C3 - N3 = 1.335(4), C3 - N2 = 1.412(4), C4 - C9 = 1.389(5), C4 - C5 = 1.396(5), C4 - N1 = 1.434(4), K1 - N3 = 2.904, K1 - C16 = 3.268(3), K1 - C17 = 3.289(3), K1 - C21 = 3.342(3), K1 - C18 = 3.373(3), K1 - C20 = 3.440(3), K2 - C48 = 3.141(4), K2 - C49 = 3.223(4), K2 - C50 = 3.284(5), N1 - C1 - N2 = 101.5(2), N1 - C1 - K2 = 125.69(19), N2 - C1 - K2 = 132.38(18), C3 - C2 - N1 = 106.9(2), N3 - C3 - C2 = 135.6(3), N3 - C3 - N2 = 120.5(2), C2 - C3 - N2 = 103.9(2), C9 - C4 - C5 = 123.2(3), C9 - C4 - N1 = 118.3(3), C5 - C4 - N1 = 118.3(3).

2.8 The structure of 5(*IA*) · THF



Figures S6 The structure of **5(*IA*)** in **5(*IA*) · THF**. One THF molecule of crystallisation in the asymmetric unit is omitted. Important bond lengths (Å) and angles (°): C1 - N1 = 1.317(2), C1 - N2 = 1.351(2), C2 - N1 = 1.389(2), C2 - C3 = 1.410(3), C3 - N3 = 1.301(2), C3 - N2 = 1.425(2), C4 - C9 = 1.395(3), C28 - N3 = 1.458(3), N1 - C1 - N2 = 107.90(17), N1 - C2 - C3 = 107.91(16), N3 - C3 - C2 = 137.41(19), N3 - C3 - N2 = 119.67(16), C1 - N1 - C2 = 110.47(15), C1 - N1 - C4 = 124.93(16), C2 - N1 - C4 = 124.44(15), C1 - N2 - C3 = 110.80(15), C1 - N2 - C16 = 124.64(16), C3 - N2 - C16 = 124.56(15), C3 - N3 - C28 = 113.91(16).

2.9 The structure of 6(*IA*)



Figures S7 The structure of **6(*IA*)**. Important bond lengths (Å) and angles (°): C1 - N1 = 1.3182(19), C1 - N2 = 1.3524(17), C2 - N1 = 1.3876(18), C2 - C3 = 1.4223(18), C3 - N3 = 1.2977(18), C3 - N2 = 1.4297(19), C28 - N3 = 1.470(2), N1 - C1 - N2 = 108.03(12), N1 - C2 - C3 = 108.14(13), N3 - C3 - C2 = 139.29(14), N3 - C3 - N2 = 118.40(12), C2 - C3 - N2 = 102.30(11), N3 - C28 - C29 = 112.06(16), N3 - C28- C31 = 106.08(14), C29 - C28 - C31 = 108.32(17), N3 - C28 - C30 = 111.54(15), C29 - C28 - C30 = 110.62(17), C31 - C28 - C30 = 107.99(17).

Bibliography

1 P. J. Bailey, R. A. Coxall, C. M. Dick, S. Fabre, L. C. Henderson, C. Herber, S. T. Liddle, D. Loroño-González, A. Parkin and S. Parsons, *Chem. Eur. J.* 2003, **9**, 4820.

2 K. Hirano, S. Urban, C. Wang and F. Glorius, *Org. Lett.* 2009, **11**, 1019.

3 A. A. Danopoulos, K. Y. Monakhov and P. Braunstein, *Chem. Eur. J.* 2013, **19**, 450.

4 S. Conde-Guadano, M. Hanton, R. P. Tooze, A. A. Danopoulos and P. Braunstein, *Dalton Trans.* 2012, **41**, 12558.

5 V. Cesar, J.-C. Tourneux, N. Vujkovic, R. Brousses, N. Lugan and G. Lavigne, *Chem. Commun.* 2012, **48**, 2349.

6 Bruker AXS Inc., Madison, USA, 2006.

7 G. M. Sheldrick, *Acta Cryst. Section A* 1990, **46**, 467-473.

8 G. M. Sheldrick, University of Göttingen, Göttingen, .