Indenyl- and Fluorenyl-Functionalized N-Heterocyclic Carbene Complexes of Titanium, Zirconium, Vanadium, Chromium, and Yttrium

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Dimethylindenyl-functionalized N-heterocyclic carbene complexes of titanium(IV), titanium(III), zirconium(IV), and vanadium(III) were prepared from potassium indenylcarbenes by salt elimination reactions. X-ray diffraction studies revealed that in the complexes the ligand adopts a bidentate coordination mode. Alkanolysis of a dimethylindene-functionalized imidazolium salt with $Y(CH_2SiMe_3)_3(THF)_2$ gave rise to a dimeric yttrium bromo alkyl in which the ligand adopts a bidentate coodination mode. Aminolysis of the fluorene-functionalized imidazolium salts with $\{[Cr(N(SiMe_3)_2)_2(THF)_2\}$ led to chromium(II) complexes in which the ligand adopts a monodentate binding mode via the N-heterocyclic carbene end with dangling fluorene groups.

Introduction

We have recently communicated the facile synthesis of a series of β-(fluorenylethyl)- and β-(indenylethyl)imidazolium salts with various substituents on the imidazolium ring and their stepwise deprotonation to β-(fluorenylethyl)- and β-(indenylethyl)-N-heterocyclic carbenes and to potassium β-(fluorenylethyl)- and β-(indenylethyl)-N-heterocyclic carbenes, respectively.[1] We also demonstrated briefly the use of the new ligands in the synthesis of early transition metal complexes. We envisaged that the widely different electronic character of the anionic annulated cyclopentadienyl[2] and the neutral N-heterocyclic carbene donors,[3] in combination with the diverse strength of the metal−NHC bond across the periodic table, may lead to versatile coordination chemistry with implications to catalysis. In principle, a bidentate coordination mode (providing four, six, or eight electrons depending on the hapticity of the annulated cyclopentadienyl ring), a monodentate coordination mode (with dangling cyclopentadiene or NHC functionalities), and a bridging mode supporting homo- or heterobimetallic assemblies are conceivable. Furthermore, the dynamic behavior of the coordinated ligand in solution should be very interesting and dependent on the nature of the metal center and the co-ligands. Compared to other NHCs functionalized with anionic donors[4] (alkoxy, phenoxy, amido), the ligands reported here have wider scope, especially with late transition metals where anionic heteroatom donors are very rare.[5]

In this paper we wish to report (i) the synthesis of β-ethyl- and γ-propyl-4,7-dimethylindene-functionalized imidazolium salts and their deprotonation to the corresponding potassium β-ethyl- and γ-propyl-dimethylindenyl-functionalized N-heterocyclic carbenes; (ii) the synthesis of Ti, Zr, and V complexes by salt metathesis reactions (iii) the synthesis of one Y alkyl complex by an alkanolysis reaction; and (iv) the synthesis of Cr complexes by aminolysis reactions, the latter featuring a monodentate (from the NHC site) ligand with dangling annulated cyclopentadiene.

Results and Discussion

Pro-ligand and Ligand Synthesis. The imidazolium proligands were successfully obtained in high yields by a method analogous to that previously reported,[1] i.e., quaternization of the β-bromoethyl- and γ-bromopropyl-(4,7)-dimethylindene with alkyl- or arylimidazoles in refluxing dioxane for approximately 1 week (Scheme 1).

The products were isolated as white hygroscopic powders and characterized by analytical and spectroscopic methods. Our results contrast the recently reported failure by Shen[6] to isolate γ-indenylpropyl(arylimidazolium) salts by quaternization reactions. The structures of the imidazolium salts **1d**, **1f**, and **1g** have been determined crystallographically and are included as Supporting Information.

The deprotonation of the imidazolium proligands by $KN(SiMe_3)_2$ was carried out in two steps in benzene and gave moderate to good yields (50−80% in two steps) of the potassium salts of the indenyl- or fluorenyl-functionalized N-heterocyclic carbenes. The first equivalent of base attacked exclusively the imidazolium proton at C2, producing the neutral, benzene-

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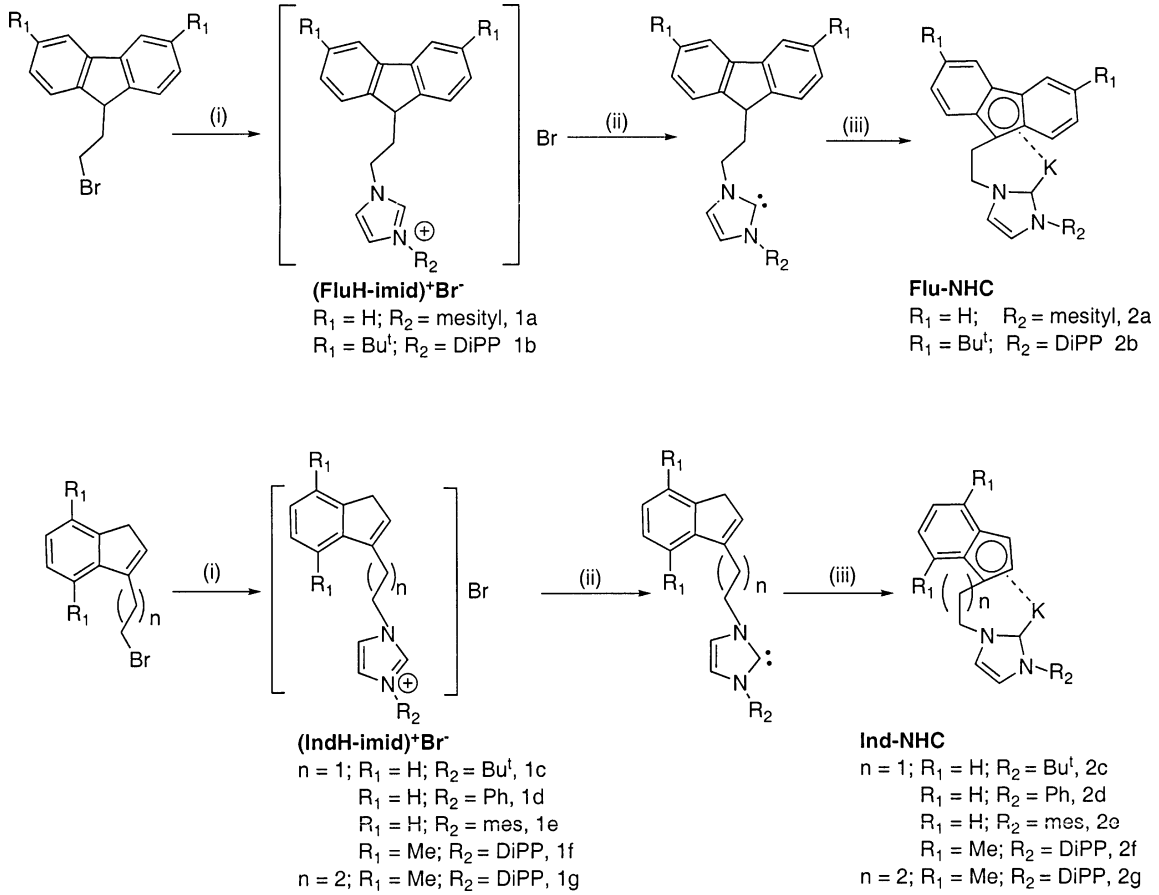
Scheme 1. Synthesis of Indene- and Fluorene-Based Ligands Described in the Paper[a]



[a] Reagents and Conditions: (i) alkyl- or arylimidazole, dioxane reflux, 3−5 days; (ii) 1 equiv of $KN(SiMe_3)_2$ in benzene; (iii) 1 equiv of $KN(SiMe_3)_2$ in benzene.

soluble fluorenylethyl-, indenylethyl-, or indenylpropyl-functionalized N-heterocyclic carbene; minor amounts of the spiroindene were also produced at this stage. Separation of the insoluble potassium halides from the crude reaction mixtures was followed by treatment with a second equivalent of $KN(SiMe_3)_2$, which, after deprotonation of the five-membered ring of the fluorene or indene system, gave the benzene-insoluble potassium fluorenylethyl-, indenylethyl-, or indenylpropyl-NHCs. These were isolated by filtration as analytically pure, extremely air-sensitive powders, soluble in polar nonprotic solvents (pyridine, THF, etc.). The observed order of deprotonation of the two C−H acidic sites is the reverse of the one expected based on the known thermodynamic pK_a involved (Bordwell pK_a values for methylindene and dialkylimidazolium salts in DMSO are 22.4 and 24.0, respectively).[7] This may be due to the kinetic nature of the products formed under the deprotonation conditions employed here (see Supporting Information in ref. 1).

Vanadium, Titanium, Zirconium, and Yttrium Complexes. The potassium 4,7-dimethylindenyl NHCs serve as convenient reagents for the introduction of the ligand to a variety of early transition metals. The reactions were carried out in THF without any obvious adverse effect on the yield of the reaction or incorporation of the (hard) THF in the coordination sphere of the metal. High oxidation state, easily reducible group 4 and group 5 metal halides (e.g., $TiCl_4$, $TiCl_4(THF)_2$, VCl_4, $NbCl_5$, $TaCl_5$) were not suitable as starting materials for this reaction due to competing reduction.

The paramagnetic V(III) (**3**) and Ti(III) (**4**) complexes obtained by the reaction of **2f** with $VCl_3(THF)_3$ and $TiCl_3(THF)_3$, respectively, were characterized by analytical and crystallographic techniques. The ORTEP diagrams of the molecules are shown in Figures 1 and 2.

Both complexes exhibit distorted tetrahedral geometries, assuming that the indenyl group occupies one coordination site defined by the centroid of the five-membered ring. The ligand adopts a bidentate coordination mode. The metrical data in both complexes are similar, with slightly longer bond distances and larger coordination angles being observed for **4**. In particular, the M−C_{NHC} bonds [2.126(5) Å for **3** and 2.196(5) Å for **4**] are slightly shorter than values reported in the literature for vanadium and titanium metal complexes in the same oxidation states.[8] Interestingly, the V−C_{NHC} bond length is dependent on the nature of the co-ligands, as can be easily seen by comparison of the structure of **3** with the recently reported analogue incorporating a coordinated dimethylamido group;[1] in the latter complex the V−C_{NHC} bond is longer by ca. 0.05 Å. The distortion on the carbene coordination imposed by the tether, as measured by the difference of the magnitude of the exocyclic and endocyclic N−C_{NHC}−M angles (ca. 10° in both complexes), is small. In addition, the angle formed by the plane of the carbene heterocycle and the ring centroid−metal−C_{NHC} plane is 54.80(13)° in **3** and 54.25(18)° in **4**. In both **3** and **4** the slip distortion is minimal (Δ = 0.089 Å for **3** and 0.064 Å for **4**).[9]

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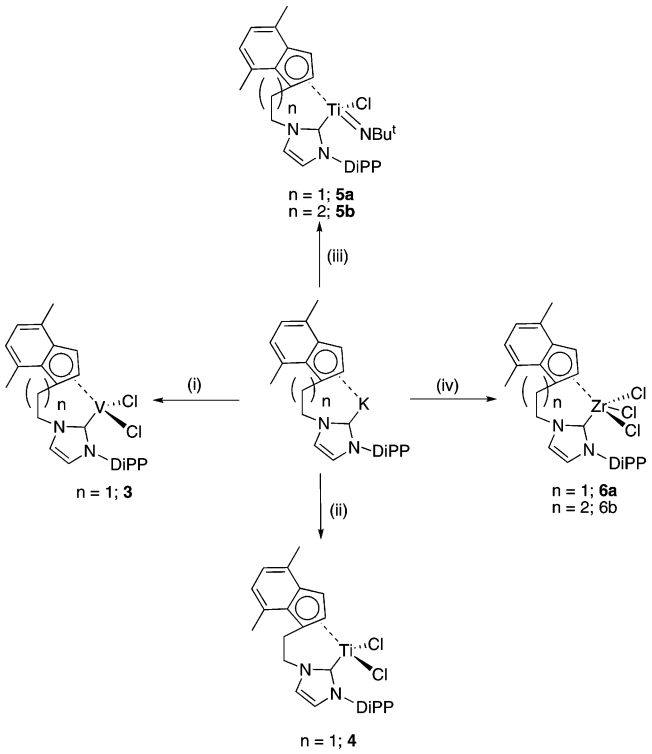
Scheme 2. Synthesis of Group 4 and 5 Metal Complexes[a]



[a] Complexes in bold have been structurally characterized. Reagents and conditions: (i) $VCl_3(THF)_3$ in THF, addition at −78 °C, slow warming to RT; (ii) $TiCl_3(THF)_3$ in THF, addition at −78 °C, slow warming to RT; (iii) $TiCl_2(NBu^t)py_3$ in THF, addition at −78 °C, warming to RT; (iv) $ZrCl_4(THT)_2$ in THF, addition at −78 °C, slow warming to RT.

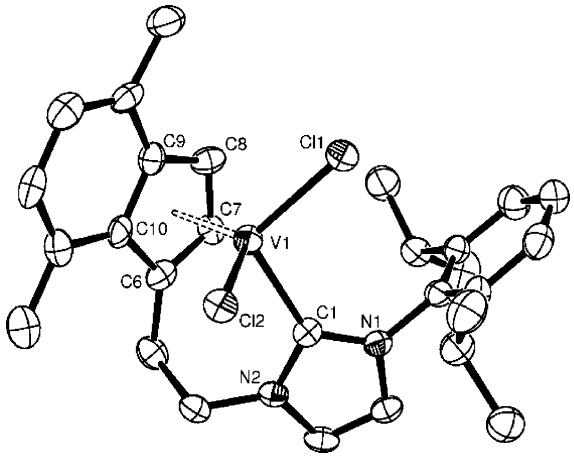


Figure 1. ORTEP representation of the structure of **3** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)−N(1) 1.352(6); C(1)−N(2) 1.363(5); C(1)−V(1) 2.126(5); C(6)−V(1) 2.288(5); C(7)−V(1) 2.260(5); C(8)−V(1) 2.285(5); C(9)−V(1) 2.337(5); C(10)−V(1) 2.362(5); Cl(1)−V(1) 2.2816(14); Cl(2)−V(1) 2.3189(15); N(1)−C(1)−N(2) 103.5(4); N(1)−C(1)−V(1) 133.8(3); N(2)−C(1)−V(1) 122.5(3); C(1)−V(1)−C(7) 84.55(18); C(1)−V(1)−Cl(1) 103.19(13); C(7)−V(1)−Cl(1) 114.01(12).

The complexes **3** and **4** constitute the only examples of half-sandwich species of V(III) and Ti(III) with *indenyl* donors bearing pendant groups. Analogues stabilized with the ligand L^N in which a *cyclopentadienyl* group is tethered to a hard amine donor via a two-C-atom linker have recently been prepared by the reaction of $VCl_3(PMe_3)_2$ with LiL^N. Even though a comparison of the effect of the NHC against the hard amine donor is not straightforward due to differences in the bite angle and the electronics of the annulated five-membered rings (indenyl versus cyclopentadienyl), it is clear that in **3** the metal center is more electron rich, as evidenced by the lower coordination number in **3** versus $[L^NVCl_2(PMe_3)]$. In addition, the dialkylamine pendant group undergoes dissociation on alkylation of the metal.[10]

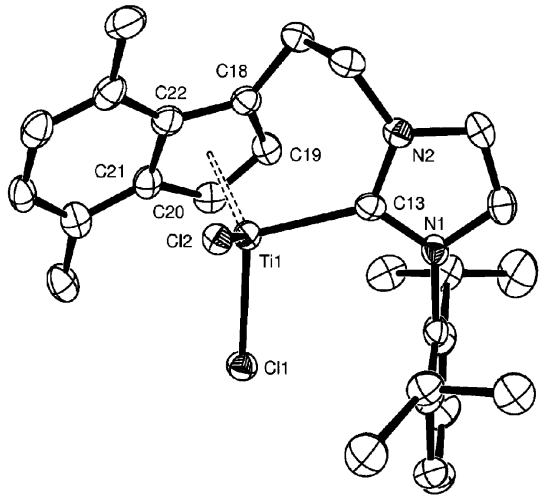


Figure 2. ORTEP representation of the structure of **4** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(13)−N(2) 1.348(7); C(13)−N(1) 1.349(7); C(13)−Ti(1) 2.196(5); Cl(1)−Ti(1) 2.3021(16); Cl(2)−Ti(1) 2.3576(16); C(18)−Ti(1) 2.337(6); C(21)−Ti(1) 2.365(6); C(22)−Ti(1) 2.365(6); Cl(1)−Ti(1)−Cl(2) 103.95(6).

Reaction of the potassium indenyl NHCs **2f** and **2g** with $Ti(NBu^t)Cl_2(py)_3$ in THF gave good yields of the titanium complexes **5a** and **5b**, respectively, which were characterized by spectroscopic, analytical, and diffraction methods. The low molecular symmetry of **5a** and **5b** was evidenced by the appearance of signals for the diastereotopic isopropyl- and indenylmethyl and the spacer methylene protons. The C_{NHC} signal in the $^{13}C\{^1H\}$ NMR spectrum was observed at δ 195.3 for **5a**, slightly shielded relative to the potassium salt **2f**. In contrast, the C_{NHC} signal for **5b** could not be observed due to the limited solubility of the complex in C_6D_6, in which it is inert. There is no NMR evidence of dissociation of the NHC in hydrocarbon solvents. ORTEP diagrams of **5a** and **5b** are shown in Figures 3 and 4, respectively.

In this case too, the complexes adopt a distorted tetrahedral geometry with the indenyl centroid occupying one coordination site. The Ti−C_{NHC} bond lengths [2.227(4) Å in **5a** and 2.226(2) Å in **5b**] are at the long end of the observed range. The difference of the endocyclic and exocyclic angles (N2−C13−Ti) and (N1−C13−Ti) [ca. 10° for **5a** and ca. 6.8° for **5b**] are in agreement with the reduced strain expected for the C3 tethered functionality. The *tert*-butyl imido group is deviating slightly from linearity in both complexes and leads to a distortion of the bonding of the indenyl system to the Ti, with the C atoms opposite the imido group being more distant from the metal [slip distortion $\Delta = 0.253$ Å for **5a** and $\Delta = 0.320$ Å for **5b**]. However, the hapticity of the five-membered rings in both complexes is still best described as 5.

Reaction of the potassium indenyl NHCs **2f** and **2g** with $ZrCl_4(THT)_2$ (THT = tetrahydrothiophene) in THF gave good

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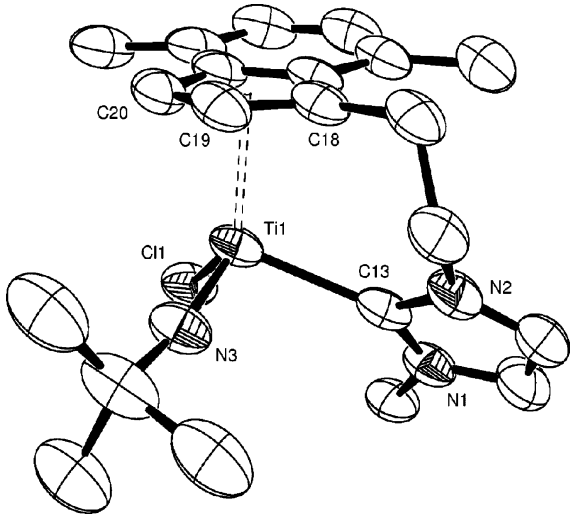

Figure 3. ORTEP representation of the structure of **5a** showing 50% probability ellipsoids. H atoms and the DiPP ring (bar *ipso* carbon) are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Cl(1)−Ti(1) 2.3209(10); N(3)−Ti(1) 1.705(3); C(13)−Ti(1) 2.227(4); C(13)−N(1) 1.362(4); C(13)−N(2) 1.365(4); C(18)−Ti(1) 2.439(3); C(19)−Ti(1) 2.360(3); C(20)−Ti(1) 2.353(4); C(21)−Ti(1) 2.538(3); C(22)−Ti(1) 2.572(3); C(29)−N(3)−Ti(1) 169.0(3).

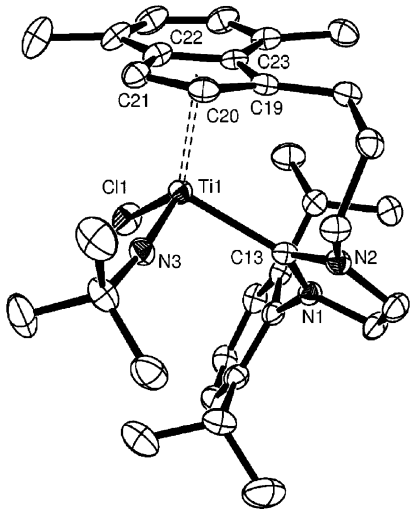

Figure 4. ORTEP representation of the structure of **5b** showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Cl(1)−Ti(1) 2.3168(7); N(3)−Ti(1) 1.703(2); C(13)−Ti(1) 2.226(2); C(13)−N(1) 1.367(3); C(13)−N(2) 1.353(3); C(19)−Ti(1) 2.497(2); C(20)−Ti(1) 2.353(2); C(21)−Ti(1) 2.323(2); C(22)−Ti(1) 2.520(2); C(29)−N(3)−Ti(1) 171.07(18).

yields of the complexes **6a** and **6b**, respectively, as yellow air-sensitive powders. Their purification was carried out by extraction into dichloromethane; however, long contact times (>1 day) with the solvent should be avoided due to partial decomposition. The complexes exhibit complicated ^{1}H NMR spectra in polar noncoordinating solvents (CD_2Cl_2, C_6D_5Cl) due to the low molecular symmetry of the species in solution. In **6a** the methyls of the Pr^i groups appear as four overlapping doublets and the protons of the C2 linker as four multiplets; in hot C_6D_5Cl the methyls of the Pr^i and the indene groups appear as 10 overlapping doublets and four singlets, respectively, which may be due to the presence of discrete diastereomers at this temperature. In addition, multiplets assignable to the protons of the bridge are also seen. The ^{1}H NMR spectrum of **6b** in

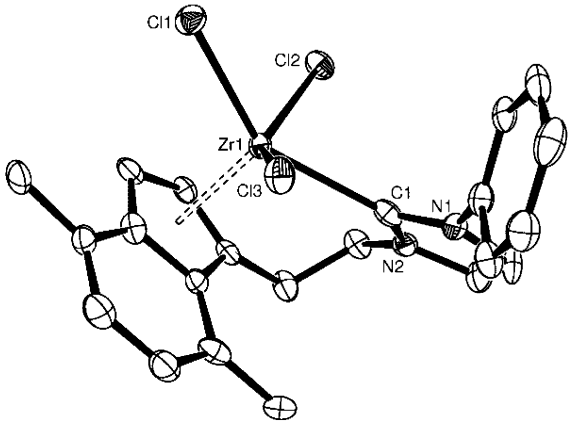

Figure 5. ORTEP representation of the structure of **6a** showing 50% probability ellipsoids. H atoms and Pr^i groups are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Zr(1)−Cl(1) 2.441(9); Zr(1)−Cl(1) 2.480(2); Zr(1)−Cl(2) 2.458(2); Zr(1)−Cl(3) 2.413(2); C(6)−Zr(1) 2.531(8); C(7)−Zr(1) 2.489(8); C(8)−Zr(1) 2.440(9); C(9)−Zr(1) 2.514(9); C(10)−Zr(1) 2.579(8); N(1)−C(1)−N(2) 105.4(7); N(1)−C(1)−Zr(1) 122.5(6); C(1)−Zr(1)−Cl(1) 145.6(2); C(1)−Zr(1)−Cl(2) 80.9(2); C(1)−Zr(1)−Cl(3) 84.3(2).

CD_2Cl_2 and C_6D_5Cl shows similar features, the methyls of the Pr^i and indenyl groups appearing as four doublets and two singlets, respectively. In the $^{13}C\{^1H\}$ NMR spectra of both complexes all backbone carbons are inequivalent; however the signal due to the coordinated C_{NHC} is observed in **6b** only in C_6D_5Cl at δ 190.1, supporting coordination of the C_{NHC} under these conditions. There is no evidence of fluxionality in solution in CD_2Cl_2. The structure of **6a** was determined crystallographically and is shown in Figure 5.

The metal adopts a distorted piano-stool geometry with a bidentate indenyl carbene. There is a certain asymmetry of the metal−indenyl ($\Delta = 0.115$) and the metal−NHC binding. The Zr $-C_{NHC}$ bond (2.441 Å) is within the previously observed range (2.43−2.46 Å) for other Zr−NHC complexes.[11] The angle formed by the NHC plane and the plane defined by C_{NHC}−Zr−centroid is 44.41(29)°, while Cl1−Zr1−C1 is 49.30°.

Comparison of the structure of **6a** with that of the complex $ZrL^PCl_3(THF)$, in which L^P is the tetramethylcyclopentadienyl tethered to the soft diphenylphosphine donor via a C2 linker, reveals again the reduced coordination number of the metal with the indenyl NHC ligands.[12] This may be due to the increased electron donation of the ligand system, even though at this stage it cannot unambiguously be attributed to a specific donor. Other cyclopentadienyl ligands tethered to harder amine donors resemble L^P,[13] while the only other known indenyl-based system resembles **6a**.[14]

When complex **6a** or **6b** is dissolved in carefully dried pyridine, a rapid decomposition takes place and the final products that could be identified spectroscopically were the imidazolium salts **1g** and **1f**. It is unclear what the origin of the proton is in these transformations, and monitoring of the reactions by NMR does not reveal the presence of any

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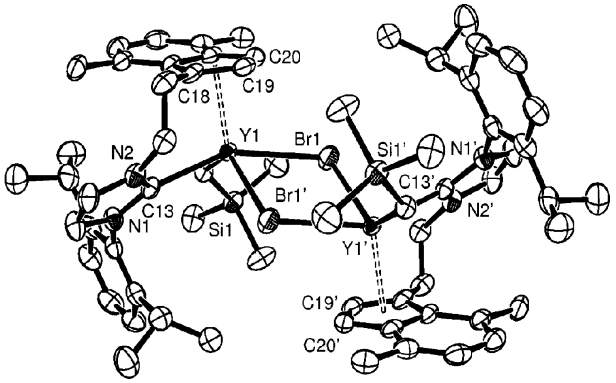

Figure 6. ORTEP representation of the structure of **7** showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Br(1)−Y(1)#1 2.8645(7); Br(1)−Y(1) 2.8747(7); Y(1)−Br(1)#1 2.8645(7); C(29)−Y(1) 2.372(5); C(13)−Y(1) 2.547(5); C(20)−Y(1) 2.613(5); C(21)−Y(1) 2.724(5); C(22)−Y(1) 2.793(5).

intermediates. Further work aiming at understanding this reactivity is in progress.

Attempts to prepare yttrium complexes by salt elimination methods were not successful, leading to insoluble possibly polymeric products. However, alkanolysis of $Y(CH_2SiMe_3)_3(THF)_2$[15] with the imidazolium salt **1f** in ether gave moderate yields of the bromide-bridged dimer **7**.

The molecule is insoluble in hydrocarbon solvents and reacts with THF within 15−20 min, giving insoluble white precipitates. It was characterized by ^{1}H NMR spectroscopy (in d_8-THF), elemental analysis, and X-ray diffraction. A diagram of the molecule is shown in Figure 6.

The structure comprises a centrosymmetric bromide-bridged dimer with bidentate ligands on the yttrium center. The coordination sphere of each metal is completed by a trimethylsilylmethyl group. The geometry around the metal is distorted square-pyramidal ($\tau = 0.38$), assuming that the five-membered ring centroid occupies one coordination site. The Y−C_{NHC} bond length at 2.547(5) Å is significantly longer than the Y−C_{alkyl} bond length [2.372(5) Å] within the measured esd's. The angle of the NHC plane with the centroid−Y−C_{NHC} plane is 50.25(14)°. The slip distortion of the indenyl ring is 0.196 Å.

Complex **8** constitutes the first example of an yttrium complex in which the coordination sphere includes both NHC and alkyl ligands. There are only three other examples of yttrium−NHC complexes involving silylamido[16a] or dialkylamido co-ligands.[16b]

Chromium Complexes. The reaction of the imidazolium salt **1b** with $Cr(N(SiMe_3)_2)_2(THF)_2$ in THF results in the formation of the paramagnetic complex **8**, which was characterized by analytical and diffraction methods. Analogous complexes have been obtained with the indene ligand. The nature of the product is the same irrespective of the ratio of the reactants. An ORTEP diagram of complex **8** is shown in Figure 7.

In this case the metalation occurs specifically at the C2-carbon of the imidazolium group, giving rise to a NHC complex with dangling fluorene groups. The geometry around the metal is square-planar. The Br−Cr−C_{NHC}−N torsion angle is 70°. The imidazol-2-ylidene rings adopt an eclipsed conformation presumably for steric reasons. The bond angles around the tetrahedral crystallographic C6 clearly indicate that the fluorenyl

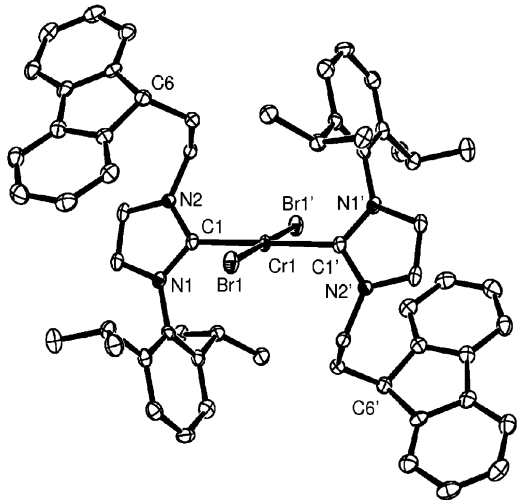

Figure 7. ORTEP representation of the structure of **8** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)−Cr(1) 2.146(3); Br(1)−Cr(1) 2.4821(5); C(1)−Cr(1)−Cr(1′) 180.000(15); Br(1)−Cr(1)−Br(1′) 180.000(13); C(1)−Cr(1)−Br(1) 90.56(8).

ring has remained protonated. The plane of the imidazol-2-ylidene ring lies 1.9° from the Cr−C_{NHC} vector. The Cr−C_{NHC} bond lengths are within the expected range (2.075−2.155 Å).[17] It is unclear why the bis-NHC species forms in preference to the mono-carbene silylamide complex. Attempts to metalate the fluorene ring in **8** by heating proved unsuccessful.

Conclusions

The chemistry of the NHC complexes of the electropositive metals is not as advanced as that of the late transition metals. The development of the cyclopentadienyl-type ligands with pendant NHCs provides a way of tailored incorporation of the NHC functionality in the coordination sphere of the electropositive metals. The wide scope of this approach has been demonstrated in the present paper. Studies of the role of the NHC as a spectator in the presence of various M−C bonds may lead to the development of catalytically active species in reactions where the early transition metals and lanthanides have shown potential, for example polymerization of functionalized and unfunctionalized alkenes, hydroamination, reduction, lactide polymerization, and Lewis acid catalysis. The introduction of chirality is another attractive feature of the ligand design. These are areas that are currently under investigation in our group.

Experimental Section

General Methods. Elemental analyses were carried out by the London Metropolitan University microanalytical laboratory. All manipulations were performed under nitrogen in a Braun glovebox or using standard Schlenk techniques, unless stated otherwise. Solvents were dried using standard methods and distilled under nitrogen prior to use. The light petroleum used throughout had a bp of 40−60 °C. The starting materials bromoethylfluorene,[18] bromoethylindene,[19] 5,7-dimethylindene,[20] di-*tert*-butylfluorene,[21] *tert*-butylimidazole, phenylimidazole, mesitylimidazole,[22] 2,6-di-

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isopropylphenylimidazole,[23] $ZrCl_4(THT)_2$[24] (THT = tetrahydrothiophene), $Ti(NBu^t)Cl_2(pyridine)_3$,[25] and $Cr(N(SiMe_3)_2)_2(THF)_2$[26] were prepared according to literature procedures. NMR data were recorded on Bruker AV-300 and DPX-400 spectrometers, operating at 300 and 400 MHz (^1H), respectively. The spectra were referenced internally using the signal from the residual protio-solvent (^1H) or the signals of the solvent (^{13}C).

1-[2-(9*H*-Fluoren-9-yl)ethyl]-3-(2,4,6-trimethylphenyl)-3*H*-imidazol-1-ium Bromide (1a). An ampule containing 9-(2-bromoethyl)-9*H*-fluorene (18 mmol, l5 g), mesitylimidazole (18 mmol, 3.4 g), and dioxane (100 mL) was heated at 100 °C for 5 days. The volatiles were removed, and the residue was dissolved in the minimum amount of dichloromethane (5 mL). The solution was then added slowly to ether (100 mL). The resulting solid was filtered, washed with ether (100 mL), and dried under reduced pressure. It was dried azeotropically with toluene and isolated as a white powder (6.6 g, 79%). It is very hygroscopic, rapidly forming an oil on exposure to air. It was stored in a glovebox.

^1H NMR ($CDCl_3$, 300 MHz): 10.36 (1H, m, imidazolium-H); 7.70 (2H, m, Ar); 7.55 (2H, m, Ar); 7.38 (2H, m, Ar); 7.30 (2H, m, Ar); 6.94 (2H, s, Ar); 6.77 (1H, m, imid-H); 6.73 (1H, m, imid-H); 4.35 (2H, t, J = 7.0 Hz, NCH_2); 4.24 (1H, t, J = 5.0 Hz, fluorenyl-H); 3.01 (2H, td, J = 7.0, 5.0 Hz, CH_2); 2.92 (3H, s, mesityl-CH_3); 1.99 (6H, s, mesityl-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 145.1 (Ar); 141.7 (Ar); 141.3 (Ar); 138.2 (Ar); 134.1 (Ar); 130.6 (ArH); 129.8 (CH, NCH); 127.8 (CH, NCH); 127.7 (ArH); 124.8 (ArH); 122.7 (ArH); 122.0 (ArH); 120.1 (ArH); 47.5 (NCH_2); 45.0 (fluorenyl-CH); 33.5 (CH_2-fluorenyl); 21.0 (CH_3); 17.8 (CH_3). MS (ES^+): 379.3 (M^+). Mp: 155 °C (CH_2Cl_2/ether).

2-(2,7-Di-*tert*-butyl-9*H*-fluoren-9-yl)ethyl 1-Bromide. Di-*tert*-butylfluorene (10.00 g, 36 mmol) was dissolved in ether (150 mL). The solution was cooled to −78 °C, and BuLi (2.5 M in hexanes, 15 mL, 36 mmol) was added. The mixture was allowed to warm to room temperature and left to stir for 2 h. The solution was recooled to −78 °C, and 1,2-dibromoethane (18.50 g, 100 mmol) was added. The reaction mixture was allowed to stir overnight, the volatiles were removed under reduced pressure, and the solid residue was recrystallized from petrol to give the product as a colorless crystalline material (8.10 g, 82%). ^1H NMR ($CDCl_3$, 300 Hz): 7.68 (2H, d, J = 8 Hz, Ar); 7.59 (2H, m, Ar); 7.45 (2H, dd, J = 7.2 Hz); 4.16 (1H, t, J = 6 Hz, fluorene-H); 3.43 (2H, t, J = 8 Hz, CH_2); 2.55 (2H, q, J = 8 Hz, CH_2); 1.45 (18H, s, ^{t}Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 150.0 (Ar); 138.5 (Ar); 124.5 (Ar); 120.7 (Ar); 119.3 (ArH); 46.5 (CH, fluorenyl-H); 37.0 ($BrCH_2$) 34.9 (C, ^{t}Bu); 31.7 (CH, ^{t}Bu); 30.9 (CH_2).

1-[2-(2,7-Di-*tert*-butyl-9*H*-fluoren-9-yl)ethyl]-3-(2,6-diisopropylphenyl)-3*H*-imidazol-1-ium Bromide (1b). Di-*tert*-butylbromoethylfluorene (8.00 g, 21 mmol), 2,6-diisopropylphenylimidazole (4.80 g, 21 mmol), and dioxane (100 mL) were heated at 100 °C under reduced pressure for 3 days. The volatiles were removed under reduced pressure, and the remaining solid residue was stirred with ether/petrol (50/50, 25 mL), isolated by filtration, and dried under vacuum. It was finally dried azeotropically with toluene to give the desired product (11.30 g, 88%). ^1H NMR ($CDCl_3$, 300 Hz): 10.39 (1H, s, imidazolium-H); 7.62 (1H, m, Ar); 7.59 (2H, m, Ar); 7.39 (3H, m, Ar); 1.17 (2H, d, J = 8 Hz); 7.10 (2H, d, J = 7 Hz, Ar); 7.03 (1H, m, Ar); 4.47 (2H, t, J = 5 Hz, NCH_2); 4.15 (1H, t, J = 5 Hz, fluorenyl-H); 2.80 (2H, q, J = 7 Hz, CH_2); 2.11 (2H, quin, J = 6 Hz, ^{i}PrH); 1.33 (18H, s, ^{t}Bu); 1.14 (6H, d, J = 6 Hz, ^{i}PrMe); 1.04 (6H, d, J = 6 Hz, ^{i}PrMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 149.5 (Ar); 145.4 (Ar); 144.8 Ar); 137.5 (Ar); 130.8 (ArH); 128.0 (ArH); 125.3 (ArH) 124.9 (ArH); 124.1 (ArH) 123.8 (ArH) 21.6 (ArH); 119.4 (ArH); 47.8 (CH_2N); 46.4 (fluorenyl-H) 34.5 (CH_2); 31.7 (^{t}BuMe); 28.5 (H, ^{i}Pr); 27.5 (C, ^{t}Bu); 24.4 (Me, ^{i}Pr); 24.2 (Me, ^{i}Pr).

3-(*tert*-Butyl)-1-[2-(3*H*-inden-1-yl)ethyl]-2*H*-imidazolium Bromide (1c). 1-(2-Bromoethyl)-1*H*-indene (4.40 g, 2.0 mmol) and *tert*-butylimidazole (2.50 g, 2.0 mmol) were dissolved in dioxane (50 mL) and heated at 110 °C for 1 week. The dioxane was removed under reduced pressure, and the resulting viscous residue was dissolved in dichloromethane. Addition of ether precipitated a viscous solid, which was dried azeotropically with toluene. After removal of the toluene under reduced pressure, the residue was washed with ether and dried under vacuum to give an off-white powder (6.0 g, 86%). ^1H NMR ($CDCl_3$, 300 MHz): 10.23 (1H, s, imidazolium-H); 7.64 (1H, t, J = 2 Hz, HC=CH); 7.39 (1H, t, J = 2 Hz, HC=CH); 7.31−7.28 (1H, m, Ar); 7.23−7.21 (1H, m, Ar); 7.12−7.03 (2H, m, Ar); 6.34 (1H, s, indene-CH); 4.66 (2H, t, J = 7 Hz, CH_2); 3.19 (2H, s, indene-CH_2); 3.13 (2H, t, J = 7 Hz, CH_2); 1.49 (9H, s, ^{t}Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 143.8 (Ar); 138.6 (ArH); 135.3 (Ar); 131.2 (ArH); 127.8 (Ar); 125.9 (ArH); 124.7 (ArH); 123.6 (ArH); 122.5 (ArH); 119.1 (ArH); 118.3, (ArH); 59.9 (Me_3C); 48.6 (CH_2); 37.7 (CH_2); 29.8 (CH_3); 28.42 (CH_2). MS (ES^+): 267.1, M^+.

3-Phenyl-1-[2-(3*H*-inden-1-yl)ethyl]-2*H*-imidazolium Bromide (1d). 1-(2-Bromoethyl)-1*H*-indene (2.20 g, 1.0 mmol) and phenylimidazole (1.40 g, 1.0 mmol) were dissolved in dioxane (50 mL) and heated to 110 °C for 1 week. X-ray quality crystals as colorless needles were obtained when the reaction mixture was cooled. The crystals were washed with ether and dried under reduced pressure. The product was dried azeotropically with toluene. Removal of the toluene gave a colorless microcrystalline material. Yield: 3.10 g, 86%. ^1H NMR ($CDCl_3$, 300 MHz): 10.84 (1H, s, imidazolium-H); 7.71 (2H, dt, J = 14, 2 Hz, Ar); 7.66−7.63 (2H, m, Ar); 7.45−7.34 (5H, m, Ar); 7.18−7.02 (2H, m, Ar); 6.41 (1H, s, indene-CH); 4.84 (2H, t, J = 7 Hz, CH_2); 3.27 (2H, s, indene-CH_2); 3.23 (2H, t, J = 7 Hz, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 Hz): 143.8 (Ar); 138.6 (Ar) 135.3 (ArH); 134.2 (Ar); 131.4 (ArH); 130.3 (ArH); 129.9 (ArH); 126.1 (ArH); 125.0 (ArH); 123.8 (ArH); 123.6 (ArH); 121.6 (ArH); 120.3 (ArH); 118.6 (ArH); 48.9 (CH_2); 37.9 (CH_2); 28.5 (CH_2).

3-(2,3,5-Trimethylphenyl)-1-[2-(3*H*-inden-1-yl)ethyl]-3*H*-imidazolium Bromide (1e). 1-(2-Bromoethyl)-1*H*-indene (2.20 g, 1.0 mmol) and mesitylimidazole (1.90 g, 1.0 mmol) were dissolved in dioxane (50 mL) and heated to 110 °C for 1 week. After removal of the volatiles under reduced pressure, the resulting residue was dissolved in dichloromethane and precipitated with ether. The solid product was isolated by filtration and dried azeotropically. Removal of the toluene gave the product as a colorless powder. Yield: 2.80 g, 68%. ^1H NMR ($CDCl_3$, 300 Hz): 9.97 (1H, t, J = 1 Hz, imidazolium-H); 7.95 (1H, t, J = 1 Hz, CH=CH); 7.37 (2H, t, J = 8 Hz, Ar); 7.22−7.10 (2H, m, Ar); 7.02 (1H, t, J = 1 Hz, CH=CH); 6.86 (2H, s, Ar); 6.44 (1H, s, indene-CH); 3.28 (4H, m CH_2); 3.23 (2H, s, indene-CH_2); 2.32 (3H, s, Me); 1.83 (6H, s, Me) $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 143.9 (Ar); 143.8 (Ar); 138.6 (ArH); 133.9 (Ar); 131.7 (ArH); 130.4 (ArH); 128.0 (ArH); 126.2 (ArH); 125.0 (ArH); 123.8 (ArH); 123.6 (ArH); 122.7 (ArH); 118.8 (ArH); 49.0 (CH_2); 37.9 (CH_2); 28.3 (CH_2); 20.8 (CH_3); 17.2 (CH_3). MS (ES^+): 329.1 (M^+).

1-(2-Bromoethyl)-4,7-dimethylindene. 4,7-Dimethylindene (18.00 g, 125 mmol) was treated with 1 equiv of Bu^{n}Li (2.5 M in hexanes,

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50 mL, 125 mmol) in ether (500 mL) at −78 °C. After warming to room temperature and stirring for 2 h, the solution was again cooled to −78 °C and 3 equiv of dibromoethane (69.00 g, 375 mmol) was added. The solution was allowed to warm to room temperature and stirred overnight. After addition of water (200 mL) and phase separation, the organic phase was dried ($MgSO_4$). Evaporation of the volatiles under vacuum left a dark residue, which was distilled under reduced pressure (100 °C, 1 Torr) to give a light yellow-orange oil (22.90 g, 75%). The product was stored under nitrogen in the freezer. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.20 (1H, d, J = 7.5 Hz, ArH); 7.14−7.10 (3H, m, 1-H); 6.90 (1H, dd, J = 5, 3 Hz, 2-H); 3.94−3.92 (1H, m, 3-H); 3.50−3.45 (2H, m, $BrCH_2$); 2.93−2.84 (1H, m, $BrCH_2CH_2$); 2.61 (6H, s, 2 × CH_3); 2.28−2.20 (1H, m, $BrCH_2CH_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 142.2; 141.3; 134.9 128.7; 128.7; 126.7; 126.4; 125.6; 47.6; 31.3; 29.5; 17.2; 16.6. MS (EI): 250, 252 (M^+).

3-(2,6-Diisopropylphenyl)-1-[2-(3*H*-(4,7-dimethyl)inden-1-yl)-ethyl]-2*H*-imidazolium Bromide (1f). 1-(2-Bromoethyl)-4,7-dimethyl-1*H*-indene (22.60 g, 90.0 mmol) and 2,6-diisopropylphenylimidazole (21.00 g, 90.0 mmol) were dissolved in dioxane (100 mL) and heated at 110 °C for 1 week. The dioxane was removed under vacuum, and the solid residue was dissolved in dichloromethane and precipitated with ether. Azeotropic drying with toluene gave the product as an off-white powder after removal of the toluene under reduced pressure, washing the residue with petrol, and drying under vacuum (26.00 g, 61%). ^{1}H NMR ($CDCl_3$, 300 MHz): 10.34 (1H, s, imidazolium H); 7.68 (1H, s, ArH); 7.48−7.42 (1H, t, J = 6 Hz, ArH); 7.23−7.20 (3H, m, ArH); 7.00 (1H, s) 6.88 (2H, q, J = 8 Hz, ArH); 6.30 (1H, s, 2-H); 5.11 (2H, t, J = 6 Hz, CH_2); 3.47 (2H, bs, CH_2); 3.06 (2H, s, 3-H); 2.53 (3H, s, CH_3); 2.18 (3H, s, CH_3); 2.16 (2H, sept, J = 7 Hz, $CH(CH_3)_2$); 1.15 (6H, d, J = 7 Hz, $CH(CH_3)_2$); 1.04 (6H, d, J = 7 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): 145.3; 143.8; 140.9; 140.6; 138.5; 131.9; 131.8; 131.0; 130.8; 130.1; 129.8; 126.5; 124.7; 123.6; 123.2; 49.8; 36.6; 31.5; 28.7; 24.3; 24.2; 20.2 18.2. Anal. Calcd (%): C, 70.14; H, 7.36; N, 5.84. Found (%): C, 69.90; H, 7.37; N, 5.77. MS ES$^+$: 400 M^+.

1-(3-Bromopropyl)-4,7-dimethylindene. 4,7-Dimethylindene (6.50 g, 45.1 mmol) in ether (150 mL) was reacted with 1 equiv of *n*-butyllithium (2.5 M, 180 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. The solution was cooled again to −78 °C, 1,3-dibromopropane (13.8 mL, 135.3 mmol) was added dropwise, and the mixture was stirred at room temperature for 2 days. After addition of water (200 mL), isolation of the ether layer, washing with water (3 × 50 mL), drying over $MgSO_4$, removal of the volatiles under reduced pressure, and distillation of the residue under vacuum (1.2 Torr, 122 °C) gave an orange oil. Yield: ca. 41%.

^{1}H NMR ($CDCl_3$, 300 MHz): 6.91−6.79 (2H, m, Ar-H); 6.38 (1H, dd, 5.6 Hz, indenyl H-2), 3.26 (2H, dd, 6.5, 3-H); 2.32 (3H, s, CH_3-Ar); 2.31 (3H, s, CH_3-Ar); 2.25−2.05 (2H, m, bridge); 1.45−1.80 (4H, m, bridge). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): 144.5, 143.1, 138.0, 130.3, 129.7, 128.0, 127.8, 126.9, 49.3, 34.2, 29.1, 27.6, 18.8, 18.2. MS ES$^+$: 186.3 $(M - Br)^+$.

3-(2,6-Diisopropylphenyl)-1-[3-(3*H*-(4,7-dimethyl)inden-1-yl)-propyl]-2*H*-imidazolium Bromide (1g). 1-(3-Bromopropyl)-4,7-dimethylindene (0.55 g, 2.1 mmol) and 2,6-diisopropylphenylimidazole (0.58 g, 2.54 mmol) were both dissolved in 15 mL of 1,4-dioxane and refluxed for 1 week at 110 °C. After removal of the solvent under vacuum, the resulting solid was dissolved in dichloromethane (25 mL) and precipitated with ether (20 mL). The precipitate was isolated by filtration and dried azeotropically with toluene. The dried white product was washed with ether and dried under vacuum. Yield: 1.10 g, ca. 97%. ^{1}H NMR ($CDCl_3$, 300 MHz): 10.61 (1H, s, imidazole); 7.82 (1H, s, Ar-H); 7.53−7.40 (1H, m, Ar-H); 7.25−7.10 (3H, m, Ar-H and NHC backbone); 6.90−6.77 (2H, m, Ar-H); 6.22 (1H, s, backbone NHC); 4.90 (2H, t, J = 7.3 Hz, CH_2 bridge); 3.10 (2H, d, 1.9 Hz, Ind-H); 2.82 (2H, t, J = 7.0 Hz, CH_2 bridge); 2.45 (3H, s, CH_3); 2.35−2.22 [4H, m, 2 × $CH(CH_3)_2$ and CH_2 bridge]; 2.22 (3H, s, CH_3), 1.17 [6H, d, J = 6.7 Hz, $CH(CH_3)_2$]; 1.07 [6H, d, J = 6.7 Hz, $CH(CH_3)_2$]. ^{13}C-{^{1}H} NMR ($CDCl_3$, 75 MHz): 145.3, 143.9, 138.8, 131.9, 130.7, 130.1, 129.5, 129.3, 129.0, 128.2, 126.0, 124.7, 124.1, 122.6, 50.1, 36.5, 29.9, 28.8, 27.1, 24.3, 24.2, 20.0, 18.2. MS ES$^+$: 413.4 $(M - Br)^+$; $C_{29}H_{37}N_2$ requires m/z = 413.2951; found m/z = 413.2945.

General Method for the Deprotonation of the Imidazolium Salts 2a−2g. A 0.60 g amount of $KN(SiMe_3)_2$ (3 mmol) was dissolved in benzene (20 mL), and the resulting solution was added at room temperature to the imidazolium salt (3 mmol) to give a suspension. The mixture was stirred overnight. The precipitated potassium halide was removed by filtration through Celite, giving a solution of the crude neutral fluorenylethyl-, indenylethyl-, or indenylpropyl-functionalized N-heterocyclic carbene. The crude products can be isolated as air-sensitive powders by removal of benzene under reduced pressure. However, for routine work this is not necessary, and the N-heterocyclic carbene obtained as described above was further deprotonated by adding the solution to 1 equiv. of $KN(SiMe_3)_2$ in benzene at room temperature. The mixture was allowed to stir overnight. The precipitated powders were isolated by filtration on a frit, washed with benzene and petrol, and dried under vacuum. The products were extremely air-sensitive, white to beige powders. The yields were within 50−80%.

1-[2-(9-[2,7-Di-(*tert*-butyl)fluorenyl)ethyl]-3-(2,6-diisopropylphenyl)imidazol-2-ylidenepotassium (2b). This was prepared similarly from **1b** and $KN(SiMe_3)_2$. Yield: ca. 50% of deep purple, air-sensitive powder. ^{1}H NMR (THF-d_8, 300 MHz): 7.84 (2H, d, J = 8 Hz, Ar); 7.35−7.31 (2H, m, Ar); 7.29 (2H, s, Ar); 7.21−7.16 (1H, m, Ar); 7.05 (2H, d, J = 8 Hz, Ar); 6.82 (1H, d, J = 1 Hz, Ar); 6.59 (2H, dd, J = 7 ,2 Hz, imidazole backbone); 4.48 (2H, t, J = 7 Hz, CH_2-bridge); 3.63 (2H, t, J = 7 Hz, CH_2-bridge); 2.24 (2H, J = 7 Hz, $CHCH_3$); 1.40 (18H, s, ^{t}Bu); 0.96 (6H, d, J = 7 Hz, CH_3); 0.81 (6H, d J = 7 Hz, CH_3). ^{13}C{^{1}H} NMR (d_8-THF, 75 MHz): 209.2 (carbene); 144.2 (Ar); 138.8 (Ar); 136.4 (Ar); 132.9 (Ar); 126.2 (ArH); 126.1 (ArH); 120.9 (ArH); 119.7 (ArH); 116.5 (Ar); 116.4 (ArH); 106.5 (ArH); 104.7 (ArH); 88.1 (Flu); 50.1 (CH_2); 30.0 (CH_3(^{t}Bu)); 26.7 (CH_2); 25.6 (CH); 22.0 (CH_3); 21.2 (CH_3). Anal. Calcd (%): C, 79.66; H, 8.62; N, 4.89. Found (%): C, 80.02; H, 8.71; N, 4.88.

1-[2-((4,7-Dimethyl)inden-1-yl)ethyl]-3-(2,6-diisopropylphenyl)imidazol-2-ylidenepotassium (2f). The imidazolium salt **1f** (1.44 g, 3 mmol) was combined with 1 equiv of $KN(SiMe_3)_2$ (3 mmol, 0.64 g) in benzene (20 mL), and the orange suspension was stirred overnight. KBr was filtered off through Celite, and the solution of the neutral ligand was subjected to a second deprotonation with 1 equiv of $KN(SiMe_3)_2$ (3 mmol, 0.64 g) in benzene (20 mL). The red mixture was stirred overnight. The precipitate formed was isolated on a frit, washed with benzene (2 mL) and petrol (10 mL), and dried under vacuum (0.88 g, 70%). Carrying out the reaction on a larger scale results in lower yields.

^{1}H NMR (d_5-pyridine, 300 MHz): 7.33−7.09 (5H, m, Ind and DiPP-Aromat); 6.48 (2H, s, indenyl); 6.45 (1H, s, carbene backbone); 6.28 (1H, s, carbene backbone); 4.33 (2H, t, 7.2 Hz, CH_2-bridge); 3.61 (2H, t, 7.3 Hz, CH_2-bridge); 2.80 (2H, sept, J = 7.0 Hz, $CH(CH_3)_2$); 2.60 (3H, s, Me); 2.45 (3H, s, Me); 1.05 (6H, d, J = 7 Hz, $CH(CH_3)_2$); 1.00 (6H, d, J = 7.0 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (d_5-pyridine, 75 MHz): 209.4; 146.1; 138.3; 129.4; 128.1; 128.1; 123.9; 123.5; 123.4; 123.0; 122.2; 119.2; 119.1; 114.4; 112.1; 105.0; 90.0; 56.3; 32.8; 27.6; 23.9; 23.4; 21.6; 18.9. Anal. Calcd (%): C, 77.01; H, 7.62; N, 6.42. Found (%): C, 76.96; H, 7.71; N, 6.34.

1-[3-(1-[4,7-Dimethylindenyl)propyl]-3-(2,6-diisopropylphenyl)imidazol-2-ylidenepotassium (2g). Imidazolium salt **1g** (1.48 g, 3 mmol) was combined with 1 equiv. of $KN(SiMe_3)_2$ (3 mmol, 0.64 g) in benzene (20 mL), and the orange suspension was stirred

overnight. The precipitated KBr was filtered off through Celite, and the solution of the neutral ligand was subjected to a second deprotonation with another equivalent of $KN(SiMe_3)_2$ (3 mmol, 0.64 g) in benzene (20 mL). The red suspension was stirred overnight. The precipitated product was isolated on a frit washed with benzene (2 mL) and petrol (10 mL) and dried under vacuum. Yield: 0.88 g, 64%. ^{1}H NMR (d_5-pyridine, 300 MHz): 7.35−7.0 (5H, m, overlapping DiPP aromatic and indenyl); 6.88 (1H, s, indenyl); 6.48 (2H, dd, 18 Hz, carbine backbone); 6.39 (1H, d, 3.5 Hz, indenyl); 4.30 (2H, t, 6.8 Hz, CH_2-bridge); 3.40 (2H, t, 5.7 Hz, CH_2-bridge); 2.70 (3H, s, CH_3-Ind); 2.64 (2H, sept, 7.5 Hz, $CH(CH_3)_2$); 2.52 (3H, s, CH_3-Ind); 2.32 (2H, quint, 7.5 Hz, CH_2-bridge); 0.94 (6H, d, 7 Hz, $CH(CH_3)_2$); 0.88 (6H, d, 7 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (d_5-pyridine, 75 MHz): 212.5; 163.9; 146.9; 139.31; 131.27; 129.46; 129.18; 126.10; 124.93; 120.0; 118.71; 115.59; 115.34; 113.78; 108.49; 91.76; 50.51; 36.14; 28.78; 28.57; 28.48; 27.46; 24.62; 24.06; 23.88; 22.96, 20.57. Anal. Calcd (%): C, 77.30; H, 7.78; N, 6.22. Found (%): C, 77.16; H, 5.75; N, 4.38.

3-(2,6-Diisopropylphenyl)-1-[2-(1-(4,7-dimethyl)indenyl)ethyl]-imidazol-2-ylidenevanadium Dichloride (3). To a cold (−78 °C) solution of $VCl_3(THF)_3$ (0.15 g, 0.5 mmol) in THF (30 mL) was added via a cannula a precooled (−78 °C) solution of **2f** (0. 24 g, 0.5 mmol) in the same solvent (30 mL). On mixing, the reaction mixture changed color from pink to red-brown, was allowed to warm to room temperature, and was stirred for 2 h. Removal of the volatiles under reduced pressure, extraction of the solid residue with toluene (3 × 30 mL), filtration through Celite, and evaporation of toluene under reduced pressure gave the analytically pure product as a brown-red powder. The product was crystallized from toluene/petrol. Yield: 0.11 g, ca. 40%. Anal. Calcd (%): C, 64.75; H, 6.40; N, 5.39. Found (%): C, 64.62; H, 6.34; N, 5.21.

3-(2,6-Diisopropylphenyl)-1-[2-(1-(4,7-dimethyl)indenyl)ethyl]-imidazol-2-ylidenetitanium Dichloride (4). To a stirred solution of $TiCl_3(THF)_3$ (0.30 g, 0.81 mmol) in THF (30 mL) at −78 °C was added a solution of the potassium salt (**2f**) (0.33 g, 0.82 mmol) in the same solvent (30 mL). On addition the original light blue color changed to green. After stirring at −78 °C for 15 min, the reaction mixture was allowed to reach room temperature within 1 h and additionally stirred for 2 h. The solution was concentrated to half of the original volume, 10 mL of petrol was added, and the mixture was filtered through Celite. Layering of the green solution with petrol gave yellow-green plates after standing for 3−4 days at room temperature. The crystallization was completed by cooling the solution at −10 °C for 1 week. Yield: 0.18 g, ca. 50%. Anal. Calcd (%): C, 65.13; H, 6.44; N, 5.42. Found (%): C, 64.94; H, 6.32; N, 5.29.

3-(2,6-Diisopropylphenyl)-1-[2-(1-(4,7-dimethyl)indenyl)ethyl]-imidazol-2-ylidene(*tert*-butylimido)titanium Chloride (5a). To a stirred solution of $Ti(Bu^tN)Cl_2(pyridine)_3$ (0.30 g, 0.70 mmol) in THF (30 mL) at −78 °C was added dropwise via a cannula a precooled suspension of **2f** (0.29 g, 0.70 mmol) in the same solvent (30 mL). On completion of the addition the mixture was allowed to reach room temperature within 0.5 h and stirred for 1 h. Evaporation of the volatiles under reduced pressure, extraction of the yellow residue in petrol, filtration of the organic extracts through Celite, concentration, and cooling at 0 °C gave yellow crystals. Yield: 0.16 g, 45%. Anal. Calcd (%): C, 69.62; H, 7.67; N, 7.61. Found (%): C, 69.45; H, 7.55; N, 7.48. ^{1}H NMR (C_6D_6, 400 MHz): 0.95, 1.02, 1.18, 1.62 [four d, 12H, J = 6 Hz, $(CH_3)_2CH$], 1.32 [s, 9H, $(CH_3)_3N$], 1.98 and 2.55 (two s, 6H, indenyl-CH_3), 2.10 and 2.92 [two septets, J = 6 Hz, 2H, $(CH_3)_2CH$], 2.82 (d of t, 1H, CH_2-bridge), 3.22 (d of t, 1H, CH_2-bridge), 3.65 (d of t, 1H, CH_2-bridge), 4.22 (d of t, 1H, CH_2-bridge), 6.26, (d, J = 0.7 Hz, carbene backbone) 6.45 (d, J = 0.7 Hz, carbene backbone) 6.82 (d, 2H, DiPP), 6.91 (t, 1H, DiPP), 7.05, 7.15, 7.23, and 7.45 (m, 1H each, indenyl aromatic protons). ^{13}C{^{1}H} NMR (C_6D_6 100 MHz): 19.4 ($CH(CH_3)_2$); 21.5 ($CH(CH_3)_2$); 22.4 ($CH(CH_3)_2$); 22.7 ($CH(CH_3)_2$); 23.7 ($CH(CH_3)_2$); 24.3 ($CH(CH_3)_2$); 24.5 ($CH(CH_3)_2$); 25.3 (indene-CH_3); 26.0 (indene-CH_3); 28.1 28.5 (CH_2); 32.6 [$(CH_3)_3CN$]; 53.37 (CH_2); 68.4 [$(CH_3)_3CN$]; 94.0 (ArH); 109.1 (ArH); 115.6 (ArH); 120.3 (ArH); 122.3 (ArH); 122.6 (ArH); 123.7 (ArH); 123.9 (ArH); 125.3 (ArH); 125.9 (ArH); 126.1 (ArH); 129.8 (ArH); 130.05 (ArH); 132.4 (ArH); 136.8 (ArH), 144.9 (ArH), 145.8 (ArH), 196.7 (C_{NHC}).

3-(2,6-Diisopropylphenyl)-1-[2-(1-(4,7-dimethyl)indenyl)propyl]imidazol-2-ylidene(*tert*-butylimido)titanium Chloride (5b). This was prepared following a method analogous to that for **5a** from $Ti(Bu^tN)Cl_2(pyridine)_3$ (0.30 g, 0.70 mmol) and **2g** (0.32 g, 0.70 mmol). After evaporation of the volatiles under reduced pressure, extraction of the yellow-orange residue in toluene, filtration of the organic extracts through Celite, concentration, and cooling at 0 °C gave yellow-orange crystals. Yield: 0.23 g, ca. 60%. Anal. Calcd (%): C, 70.02; H, 7.84; N, 7.42. Found (%): C, 69.80; H, 7.57; N, 7.38. ^{1}H NMR (C_6D_6, 300 MHz): 0.98, 1.12, 1.28, 1.65 [four d, 12H, J = 6 Hz, $(CH_3)_2CH$], 1.38 [s, 9H, $(CH_3)_3N$], 2.43 and 2.48 (two s, 6H, indenyl-CH_3), 2.62 and 2.90, [two septets, J = 6 Hz, 2H, $(CH_3)_2CH$], 2.89 (m, 2H, CH_2-bridge), 3.22 (d of t, 1H, CH_2-bridge), 3.35 (d of d, 2H, CH_2-bridge), 5.15 (m 2H, CH_2-bridge), 6.30, (d, J = 0.7 Hz, carbene backbone) 6.45 (d, J = 0.7 Hz, carbene backbone), 6.82 (d, 2H, DiPP), 6.91 (t, 1H, DiPP), 7.05, 7.15, 7.23, and 7.45 (m, 1H each, indenyl aromatic protons). ^{13}C{^{1}H} NMR (C_6D_6 100 MHz): 21.2 ($CH(CH_3)_2$); 22.2 ($CH(CH_3)_2$); 23.1 ($CH(CH_3)_2$); 23.8 ($CH(CH_3)_2$); 24.1 ($CH(CH_3)_2$); 25.5 ($CH(CH_3)_2$); 25.9 ($CH(CH_3)_2$); 26.1 (indene-CH_3); 26.0 (indene-CH_3); 28.1 28.6 (CH_2); 32.1 [$(CH_3)_3CN$]; 53.37 (CH_2); 68.6 [$(CH_3)_3CN$]; 91.7 (ArH); 111.9 (ArH); 115.6 (ArH); 120.3 (ArH); 122.3 (ArH); 122.6 (ArH); 123.7 (ArH); 123.9 (ArH); 125.3 (ArH); 125.9 (ArH); 126.1 (ArH); 129.7 (ArH); 132.0 (ArH); 132.4 (ArH); 136.8 (ArH), 144.9 (ArH), 145.8 (ArH).

3-(2,6-Diisopropylphenyl)-1-[2-(1-(4,7-(dimethylindenyl)ethyl]-imidazol-2-ylidenezirconium Trichloride (6a). $ZrCl_4(THT)_2$ (0.50 mmol, 0.20 g) and the salt **2f** (0.5 mmol, 0.24 g) were dissolved in THF (20 mL), and the two solutions were combined at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The volatiles were removed under reduced pressure, and the residue was dissolved in toluene and filtered through Celite. The product was crystallized from toluene/petrol at −30 °C as yellow crystals (0.10 g, 66%). ^{1}H NMR (CD_2Cl_2, 300 MHz): 7.49 (1H, t, J = 8 Hz, Ar); 7.48 (1H, t, J = 8 Hz); 7.28−7.25 (2H, m, Ar); 7.11 (1H, s, Ar); 7.04 (1H, s, Ar); 6.98−6.87 (1H, s, Ar); 6.84−6.82 (1H, s, Ar); 6.58 (1H, dd, J = 6 Hz, indene-H); 4.98 (1H, t, J = 6 Hz, indene-H); 4.60 (1H, quin, J = 7 Hz, CH_2-bridge); 4.29 (1H, quin, J = 7 Hz, CH_2-bridge); 3.76−3.74 (1H, m, CH_2-bridge); 3.46 (1H, m, CH_2-bridge); 2.94 (1H, sept, J = 7 Hz, $CH(CH_3)_2$); 2.10 (1H, sept, J = 7 Hz, $CH(CH_3)_2$); 2.34 (3H, s, indene-CH_3); 2.31 (3H, s, indene-CH_3); 2.12 (6H, d, J = 7 Hz, $CH(CH_3)_2$); 1.10 (3H, d, J = 7 Hz, $CH(CH_3)_2$); 1.08 (3H, d, J = 7 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): 144.8 (Ar); 142.7 (Ar); 142.2 (Ar) 136.7 (ArH); 136.3 (Ar); 130.9 (ArH); 129.9 (ArH); 129.4 (Ar); 128.9 (ArH); 127.7 (ArH); 127.5 (ArH); 126.4 (Ar); 123.7 (ArH); 123.7 (ArH); 123.3 (ArH); 122.8 (ArH); 47.9 (CH_2); 30.8 (CH_2); 29.3 (indene-CH_3); 27.9 (indene-CH_3); 23.6 ($CH(CH_3)_2$); 23.5 ($CH(CH_3)_2$); 23.2 ($CH(CH_3)_2$); 23.1 ($CH(CH_3)_2$); 19.2 ($CH(CH_3)_2$); 17.9 ($CH(CH_3)_2$); 17.1 ($CH(CH_3)_2$). MS ES$^+$: 413.5. Anal. Calcd (%): C, 56.52; H, 5.59; N, 4.71 Found (%): C, 56.71; H, 5.42; N, 4.74.

3-(2,6-Diisopropylphenyl)-1-[3-(1-(4,7-(dimethylindenyl)propyl]imidazol-2-ylidenezirconium Trichloride (6b). $ZrCl_4(THT)_2$ (1 mmol, 0.41 g) and **2f** (1 mmol, 0.45 g) were dissolved in THF (30 mL) in separate Schlenk tubes, and the two solutions were combined at −78 °C. After stirring for 2 h at this temperature, the yellow reaction mixture was allowed to warm to room temperature and stirred overnight. The volatiles were removed under reduced pressure, and the residue was dissolved in dichloromethane and

Table 1. Crystallographic Data for the Compounds Described in the Paper

	3a	4a	5a	5b	6a	7	8
chemical formula	$C_{28}H_{33}Cl_2N_2V$	$C_{28}H_{33}Cl_2N_2Ti$	$C_{32}H_{42}ClN_3Ti$	$C_{33}H_{44}ClN_3Ti$	$C_{28}H_{33}Cl_3N_2Zr$	$C_{64}H_{88}Br_2N_4Si_2Y_2$	$C_{60}H_{64}Br_2CrN_4$
fw	519.40	516.36	552.04	566.06	595.13	1307.20	1052.97
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P21/c$	$P\bar{1}$
a/Å	16.6796(8)	16.7118(13)	10.572(3)	10.5872(2)	9.5873(5)	15.4085(2)	10.1655(18)
b/Å	10.6407(6)	10.5952(9)	20.095(5)	16.7943(4)	9.7036(6)	18.3437(2)	10.864(2)
c/Å	15.5939(6)	15.8047(10)	15.921(4)	17.7951(5)	16.7862(11)	12.82130(10)	12.940(2)
α/deg	90	90	90	90	115.110(12)	90	112.546(12)
β/deg	109.735(2)	110.096(4)°	106.194(3)	96.8550(10)	93.590(4)	108.4540(10)	98.115(15)
γ/deg	90	90	90	90	119.315(3)	90	102.188(14)
Z	4	4	4	4	2	2	1
T/K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
μ/mm^{-1}	0.605	0.548	0.526	0.382	0.729	2.914	1.870
no. of data collected	45 116	21 832	23 537	36 159	21 697	57 360	21 108
no. of unique data	5880	4638	5682	7204	4711	7891	5757
goodness of fit on F^2	1.028	1.200	1.045	1.079	1.238	1.091	1.021
R_{int}	0.2254	0.0809	0.0472	0.0550	0.0953	0.0699	0.0788
final $R(\|F\|)$ for $F_o > 2\sigma(F_o)$	0.0666	0.0843	0.0680	0.0565	0.0960	0.0656	0.0516
final $R(F^2)$ for all data	0.1867	0.1598	0.2051	0.1162	0.1947	0.1636	0.1110

filtered through Celite. The dichloromethane extracts were removed under reduced pressure, giving a yellow residue, which is the analytically pure product. Yield: 0.33 g, ca. 52%. Anal. Calcd (%): C, 57.17; H, 5.75; N, 4.59. Found (%): C, 56.92; H, 5.79; N, 4.38. ^{1}H NMR (CD_2Cl_2, 400 MHz): 7.49 (1H, t, J = 8 Hz, Ar); 7.48 (1H, t, J = 8 Hz); 7.28−7.25 (2H, m, Ar); 7.11 (1H, s, Ar); 7.04 (1H, s, Ar); 6.98−6.87 (1H, s, Ar); 6.84−6.82 (1H, s, Ar); 6.58 (1H, dd, J = 6 Hz, indene-H); 4.98 (1H, t, J = 6 Hz, indene-H); 4.60 (1H, quin, J = 7 Hz, CH_2-bridge); 4.29 (1H, quin, J = 7 Hz, CH_2-bridge); 3.76−3.74 (1H, m, CH_2-bridge); 3.46 (1H, m, CH_2-bridge); 2.94 (1H, sept, J = 7 Hz, $CH(CH_3)_2$); 2.10 (1H, sept, J = 7 Hz, $CH(CH_3)_2$); 2.34 (3H, s, indene-CH_3); 2.31 (3H, s, indene-CH_3); 2.12 (6H, d, J = 7 Hz, $CH(CH_3)_2$); 1.10 (3H, d, J = 7 Hz, $CH(CH_3)_2$); 1.08 (3H, d, J = 7 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): 144.8 (Ar); 142.7 (Ar); 142.2 (Ar) 136.7 (ArH); 136.3 (Ar); 130.9 (ArH); 129.9 (ArH); 129.4 (Ar); 128.9 (ArH); 127.7 (ArH); 127.5 (ArH); 126.4 (Ar); 123.7 (ArH); 123.7 (ArH); 123.3 (ArH); 122.8 (ArH); 47.9 (CH_2); 30.8 (CH_2); 29.3 (indene-CH_3); 27.9 (indene-CH_3); 23.6 ($CH(CH_3)_2$); 23.5 ($CH(CH_3)_2$); 23.2 ($CH(CH_3)_2$); 23.1 ($CH(CH_3)_2$); 19.2 ($CH(CH_3)_2$); 17.9 ($CH(CH_3)_2$); 17.1 ($CH(CH_3)_2$).

^{1}H NMR (C_6D_5Cl, 400 MHz): 6.52−6.34 (7H, m, Ar); 6.27 (1H, d, 3.8 Hz, Ind-H); 5.34 (1H, ddd, 9.4 Hz, Ind-H); 3.48 (1H, ddd, 7.2 Hz, CH_2-bridge); 3.36 (1H, s, CH_2-bridge); 2.70−2.60 (1H, m, $CH(CH_3)_2$); 2.37 (1H, ddd, 2.6 Hz, CH_2-bridge); 2.33 (3H, s, CH_3-Ind); 2.13 (1H, sept, 6.8, $CH(CH_3)_2$); 2.04 (3H, s, CH_3-Ind); 1.70 (1H, ddd, 4.14 Hz, CH_2-bridge); 1.39 (1H, ddd, 3.0 Hz, CH_2-bridge); 1.32 (1H, ddd, 3.0 Hz, CH_2-bridge); 1.14 (3H, d, 6.8 Hz, $CH(CH_3)_2$); 1.01 (3H, d, 6.8 Hz, $CH(CH_3)_2$); 0.83 (3H, d, 6.8 Hz, $CH(CH_3)_2$); 0.54 (3H, d, 6.8 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (C_6D_5-Cl, 100 MHz): 190.1(carbene); 145.1; 144.6; 134.5; 126.6; 125.3; 124.4; 124.0; 122.0; 120.0; 100.9; 47.5; 29.2; 28.2; 26.5; 26.3; 24.6; 24.4; 23.7; 21.9; 19.4.

3-(2,6-Diisopropylphenyl)-1-[2-(1-(4,7-dimethyl)indenyl)propyl]imidazol-2-ylidene(trimethylsilylmethyl)yttrium Bromide Dimer (7). To a solution of $Y(CH_2Si(CH_3)_3)_3(THF)_2$ (0.30 g, 0.57 mmol) in ether (20 mL) at −78 °C was added a suspension of **2f** (0.27 g, 0.57 mmol) in the same solvent (20 mL). The suspension was allowed to reach room temperature within 2 h and stirred for 20 h, when most of the solid goes into solution. Filtration through Celite, concentration under reduced pressure, and slow cooling to −35 °C gave off-white crystals. Yield: 0.08 g ca. 28%. Calculated (%): C, 58.80; H, 6.78; N, 4.29. Found (%): C, 58.02; H, 6.39; N, 4.05. ^{1}H NMR (THF-d_8, 300 MHz): −1.65 (br s, 2H, CH_2SiMe$_3$), 0.57 (s, 9H, SiMe_3), 0.90 (d, 12H, Pr^i), 1.82 (sept, 2H, Pr^i), 2.55 and 2.60 (s, 6H, indenyl CH_3), 3.55−3.85 (br multiplet, 4H, bridge), 7.25−7.80 (m, aromatics). Long accumulation times were not possible due to the appearance of a white precipitate possibly due to the dissociation of the dimer in the polar solvent.

1-[2-(9*H*-Fluoren-9-yl)ethyl]-3-(2,6-diisopropylphenyl)imidazol-2-ylidenechromium Dichloride (8). $Cr(N(SiMe_3)_2)_2(THF)_2$ (0.26 g, 0.50 mmol) and the corresponding fluorene imidazolium bromide (0.50 g, 1 mmol) were dissolved in toluene and heated to 110 °C. The resultant yellow solid was collected by filtration and crystallized from hot THF. Yield: 0.65 g, ca. 62%. Anal. Calcd (%): C, 68.44; H, 6.13; N, 5.32. Found: C, 68.45; H, 6.20; N, 5.22.

X-ray Crystallography. A summary of the crystal data, data collection, and refinement for compounds **3**, **4**, **5a**, **5b**, **6a**, **7**, and **8** is given in Table 1.

All data sets were collected on a Enraf-Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode (Mo Kα radiation) and an Oxford Cryosystems low-temperature device operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect, Scalepack, and Denzo.[27] The crystals were mounted on a glass fiber with silicon grease, from Fomblin vacuum oil. All solutions and refinements were performed using the WinGX package[28] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model. Crystal data for **5a** were collected on a Bruker SMART APEX 2 CCD diffractometer at Daresbury SRS station 9.8.[29]

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Supporting Information Available: Full details of the X-ray crystal structures of imidazolium salts **1d**, **1f**, and **1g** including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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