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Indenyl- and Fluorenyl-Functionalized *N*-Heterocyclic Carbene Complexes of Titanium and Vanadium

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Summary: The new N-heterocyclic carbene ligands functionalized with indenyl and fluorenyl groups, 1-[ind-$(CH_2)_2$]-NHC, ***(Ind-NHC)***$^-$*, and 1-[fl-$(CH_2)_2$]-NHC,* ***(Fl-NHC)***$^-$*, where ind = 1-indenyl, fl = 9-fluorenyl, NHC = 3-DiPP-imidazol-2-ylidene, DiPP = 2,6-$\mathrm{Pr^i}_2$-C_6H_3, serve as versatile building blocks of Ti(III) and V(III) complexes.*

The use of *N*-heterocyclic carbenes (NHCs) in catalytic transition metal systems has been an active area of research over the last decade.[1] The most successful applications are in the metathesis (Ru catalyst) and C−C coupling (Pd catalyst) reactions.[2] Polydentate NHC ligands in which the NHC is linked to a neutral or anionic donor by an organic spacer are being developed, because they could offer fine-tuning of the coordination sphere of metals.[3] However, cyclopentadienyl and the alkyl-substituted or -annulated derivatives (indenyl, fluorenyl, etc.) with pendant NHC groups are not known, even though "half-sandwich" complexes of the type (Cp)M(NHC)(Ligand)$_n$ have been prepared.[4] Work on cyclopentadienyl-type ligands with pendant neutral or anionic "classical" donor groups[5] has given rise to active polymerization,[6a−c] oligomerization,[6d,e] C−H activation,[6f] and hydroamination[6g] catalysts. The role of the pendant group in these catalytic reactions is subtle and diverse. For example, it can increase complex catalyst stability by chelate formation, impose coordination rigidity by suppressing substitution or conproportionation reactions,[7] promote hemilability,[8] modify the sterics around the metal, and create chirality.

In this communication we wish to describe (i) the synthesis of the first imidazolium salts with pendant indene or fluorene groups, (ii) their deprotonation to the neutral indene- or fluorene-NHC and the anionic indenyl- and fluorenyl-NHC species, respectively, and (iii) the synthesis and structural characterization of the first Ti and V complexes with the new bidentate chelate ligands.

The new imidazolium pro-ligands (Scheme 1) are obtained in good yields by the quaternization of β-bromoethylindene[9] or β-bromoethylfluorene[10] with DiPP-imidazole.[11,12] Attempts to prepare analogous tetramethylcyclopentadienyl derivatives

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(11) Other alkyl- or aryl-imidazoles react similarly.

(12) (a) Spectroscopic data for **(IndH-NHC-H)Br**: NMR ($CDCl_3$), ^1H: δ, 10.13 (1H, s, imidazolium-H); 8.01 (1H, s, indene aromatic), 7.43−7.36 (3H, m, indene aromatic); 7.23−7.11 (5H, m, indene and DiPP aromatic); 6.99 (1H, s, backbone imidazolium); 6.48 (1H, s, backbone imidazolium); 5.10 (2H, t, $J = 6.5$ Hz, imid-$\mathrm{C}H_2\mathrm{CH_2}$-ind); 3.30 (2H, t, $J = 6.5$ Hz, imid-$\mathrm{CH_2C}H_2$-ind); 3.21 (2H, s, indenyl-$\mathrm{C}H_2$); 2.02 (2H, sept, $J = 7$ Hz, $\mathrm{(CH_3)_2C}H$); 1.06 (6H, d, $J = 7$ Hz, $(\mathrm{C}H_3)_2\mathrm{CH}$)); 0.97 (6H, d, $J = 7$ Hz, $(\mathrm{C}H_3)_2\mathrm{CH}$)). $^{13}C\{^1H\}$: δ, 144.3, 143.1, 137.8, 137.1, 130.8, 127.2, 125.4, 124.3, 124.2, 123.6, 123.0, 122.8, and 118.0 (all aromatic), 48.1 (imid-$C\mathrm{H_2CH_2}$-ind), 37.1 (imid-$\mathrm{CH_2}C\mathrm{H_2}$-ind), 27.6 $\mathrm{(CH_3)_2}C\mathrm{H}$); 27.6($\mathrm{CH_2}$), 23.1 ($(C\mathrm{H_3})_2\mathrm{CH}$). (b) Spectroscopic data for **(FlH-NHC-H)Br**: NMR, ($CDCl_3$); ^1H: δ, 10.45 (1H, s, imid-H); 7.75 (2H, d, $J = 7.5$ Hz, fluorene) 7.63 (2H, d, $J = 8.0$ Hz, fluorene); 7.46 (1H, t, $J = 8.5$ Hz, DiPP); 7.37 (2H, t, $J = 7.5$ Hz, fluorene); 7.29 (2H, d, $J = 7.5$ Hz, fluorene); 7.23 (2H, d, $J = 8.0$ Hz, DiPP); 7.16 (1H, s, backbone imidazolium); 6.90 (1H, s, backbone imidazolium); 4.46 (2H, m, imid-$\mathrm{C}H_2\mathrm{CH_2}$-fl), 4.19 (1H, t, $J = 5.0$ Hz, fluorenyl-H); 2.9 (2H, m, 2H, m, imid-$\mathrm{CH_2C}H_2$-fl); 2.15 (2H, sept, $J = 6.5$ Hz, $\mathrm{C}H\mathrm{(CH_3)_2}$); 1.19 (6H, d, $J = 6.5$ Hz, $\mathrm{CH(C}H_3)_2$); 1.19 (6H, d, $J = 6.5$ Hz, $\mathrm{CH(C}H_3)_2$). $^{13}C\{^1H\}$: δ, 145.2 (aromatic), 145.1 (aromatic), 141.0 (aromatic), 138.1 (imidazolium-CH), 131.8 (backbone imidazolium), 130.1 (aromatic), 127.7 (backbone imidazolium), 127.5 (aromatic) 124.8 (aromatic), 124.5 (aromatic), 123.6 (aromatic), 123.2 (aromatic), 120.1 (aromatic), 47.6 (imid-$C\mathrm{H_2CH_2}$-fl), 44.9 (fluorenyl-CH) 33.9 (imid-$\mathrm{CH_2}C\mathrm{H_2}$-fl), 28.5 ($C\mathrm{H(CH_3)_2}$, 24.4 ($\mathrm{CH(}C\mathrm{H_3)_2}$, 24.2 ($\mathrm{CH(}C\mathrm{H_3)_2)_2}$.

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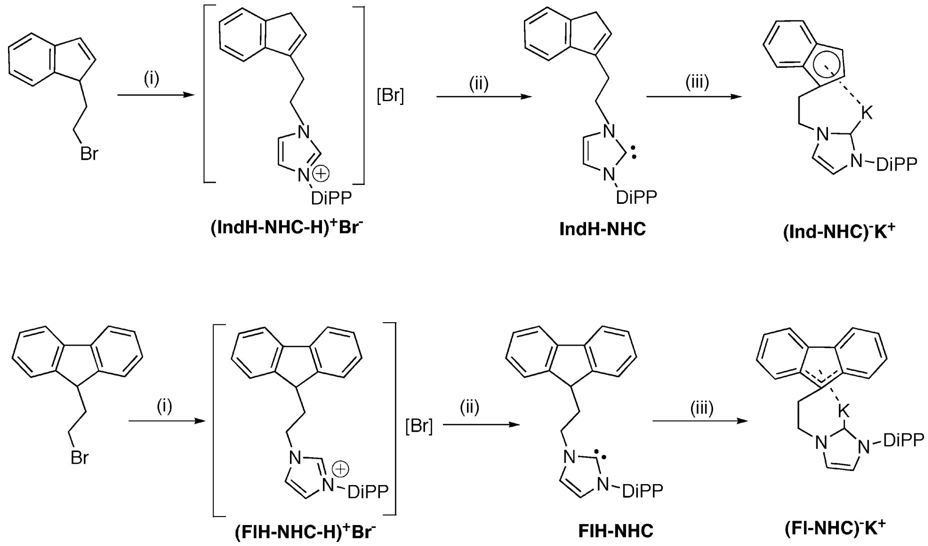
Scheme 1. Synthesis of the Functionalized Imidazolium and *N*-Heterocyclic Carbene Ligands[a]



[a] Reagents and conditions: (i) 1 equiv of DiPP-imidazole, dioxane 100° C, 24 h (50−61%); (ii) 1 equiv of $KN(SiMe_3)_2$, benzene, 12 h (55−80%); (iii) 1 equiv of $KN(SiMe_3)_2$, benzene (50%).

were hampered by the lack of synthetic methods leading to pure non-geminal-substituted β-haloethyltetramethylcyclopentadienes.[13]

Deprotonation of the bifunctional pro-ligands takes place in two steps. With 1 equiv of $KN(SiMe_3)_2$ in benzene, deprotonation leads to crude, hydrocarbon-soluble NHCs functionalized with neutral indene (**IndH-NHC**) or fluorene (**FlH-NHC**) moieties; these carbenes can be easily separated from insoluble potassium halides by filtration. Further deprotonation of the crude neutral NHCs with 1 equiv of $KN(SiMe_3)_2$ in benzene affords sparingly soluble indenide, **(Ind-NHC)$^-$K$^+$**, and fluorenide, **(Fl-NHC)$^-$K$^+$**, species, respectively, in good yields.[14] Minor amounts of the benzene-soluble spiro hydrocarbon spiro(cyclopropane-1,9′-fluorene) were isolated as side product from the deprotonation of **FlH-NHC**. The observed order of deprotonation of the C−H acidic groups in the new imidazolium salts is the opposite of that expected based on the basicity of NHCs, indenyl, and fluorenyl anions in DMSO.[15] This discrepancy may be related to the kinetic nature of the products isolated in this work and solvent effects. Heating of **IndH-NHC** or **FlH-NHC** (60 °C, THF-d_8, 8 h) results in the formation of equilibrium mixtures with the corresponding tautomers **Ind-NHC-H** and **Fl-NHC-H** (by ^{1}H NMR, see Supporting Information).

The structure of (**Fl-NHC**)$^-$**K**$^+$ was determined crystallographically.[16] It comprises polymeric "zigzag" chains with potassium atoms and bridging fluorenyl units. Two types of alternating repeat units featuring potassium atoms with different coordination spheres are observed and depicted in Figure 1a and 1b.

Assuming that the longest K−fluorene interaction can be estimated by the sum of the ionic radius of potassium and the van der Waals radius of the carbon neighbor, the coordination sphere of K in Figure 1a comprises two η^4-phenyl rings that sandwich the metal, while in Figure 1b there is one η^2- and one η^4-phenyl ring; in both types the K coordination sphere is completed by the tethered NHC group. The K−C (carbene) distances (2.896−2.911 Å) are much shorter than those observed previously (3.048 Å).[17] The crystallographic C12 carbon deviates slightly from planarity (angle sum 355−356°), while the angle between the CNC plane and the K−C vector is in the range 22−24°.

Reaction of the imidazolium salts with Ag_2O in dichloromethane[18] gives the corresponding silver carbene complexes in quantitative yields. The identity of the new complexes was established by analytical and spectroscopic (NMR and mass spectrometric) methods.[19] We have been unable to grow X-ray-quality crystals of the Ag complexes.

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(13) There are reports in the patent literature claiming the synthesis of nongeminal β-haloethyltetramethylcyclopentadienes by the reaction of tetramethylcyclopentadienyllithium with 2-chloroethyl-*p*-toluenesulfonate or 1-bromo-2-chloroethane in THF or ether, respectively. The second method, giving a mixture of nongeminal and geminal isomers (variable ratio), has been recently used for the synthesis of 1,2,3,4-tetramethylbicyclo-[2.4]hepta-1,3-diene. McConell, A. C.; Pogorzelec, P. J.; Slawin, A. M. Z.; Williams G. L.; Elliott, P. I. P.; Haynes, A.; Marr, A. C.; Cole-Hamilton, D. J. *Dalton Trans.* **2006**, 91, and references therein.

(14) **(Fl-NHC)$^-$K$^+$**. NMR (THF-d_8), ^{1}H: δ, 8.02 (2H, d, J = 8 Hz, fluorene H), 7.51 (1H, s, carbene backbone), 7.26 (3H, m, overlap. 1H carbene backbone and 2H from fluorene), 7.12 (2 H, d, J = 7 Hz, fluorene), 6.97 (3H, m, overlap; 1H from DiPP and 2H from fluorene), 6.58 (2H, m, arom. of DiPP), 4.52 (2H, m, NCH_2CH_2-Fl), 3.67 (2H, m, Fl-CH_2CH_2), 2.33 (2H, sept, J = 7 Hz, $CH(CH_3)_2$), 1.10 (6H, d, J = 7 Hz, $CH(CH_3)_2$), 0.81 (6H, d, J = 7 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$: δ, 206.9 (carbene C); 144.3, 136.2, 132.5, 126.2, 121.0, 120.5, 118.2, 117.5, 117.5, 116.7, 111.7 and 106.5 (all aromatic); 88.4 (fluorenyl C); 51.3 (Fl-CH_2CH_2N); 26.7 (Fl-CH_2CH_2-N); 25.6 ($CH(CH_3)_2$); 22.0 ($CH(CH_3)_2$); 21.10 ($CH(CH_3)_2$). **(Ind-NHC)$^-$K$^+$**. NMR (pyridine-d_5): ^{1}H, δ, 7.82 (1H, d, J = 8 Hz, indenyl); 7.72 (1H, d, J = 8 Hz, indenyl); 7.46−7.43 (1H, m, indenyl); 7.32−7.20 (4H, m, overlapping DiPP and 1H indenyl); 6.98 (2H, m, indenyl); 6.75 (1H, s, carbene backbone); 6.48 (1H, s, carbene backbone); 4.45 (2H, m, NCH_2CH_2-ind); 3.59 (2H, m, NCH_2CH_2-ind); 2.93 (2H, sept, J = 7 Hz, $CH(CH_3)_2$); 1.19 (6H, d, J = 7 Hz, $CH(CH_3)_2$); 1.14 (6H, d, J = 7 Hz, $CH(CH_3)_2$).$^{13}C\{^1H\}$: δ, 211.0 (C, carbene); 147.5 (Ar); 130.2 (Ar); 129.9 (ArH); 129.5 (Ar); 128.3 (Ar); 126.6 (Ar); 125.0 (Ar); 120.8 (ArH); 120.6 (ArH); 120.1 (ArH); 117.3 (ArH); 113.9 (ArH); 104.9 (indenyl); 93.4 (Ind-CH_2CH_2N); 55.6 (Ind-CH_2CH_2N); 32.6 ($CH(CH_3)_2$); 29.32 $CH(CH_3)_2$).

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(16) Compound **(Fl-NHC)-K$^+$** crystallized from benzene in the monoclinic space group $P2_1/n$ with a = 20.531(7) Å, b =13.027(4) Å c = 23.378(8) Å, β = 92.220(5)°. V = 6248(4) Å^3 and D_{calcd} = 1.141 Mg m^{-3} for Z = 4. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 6715 unique reflections (R_{int} = 11.36%) converged to a final R_1 = 6.62% ($I > 2(I)$) and $R_w{}^2$ = 15.2%.

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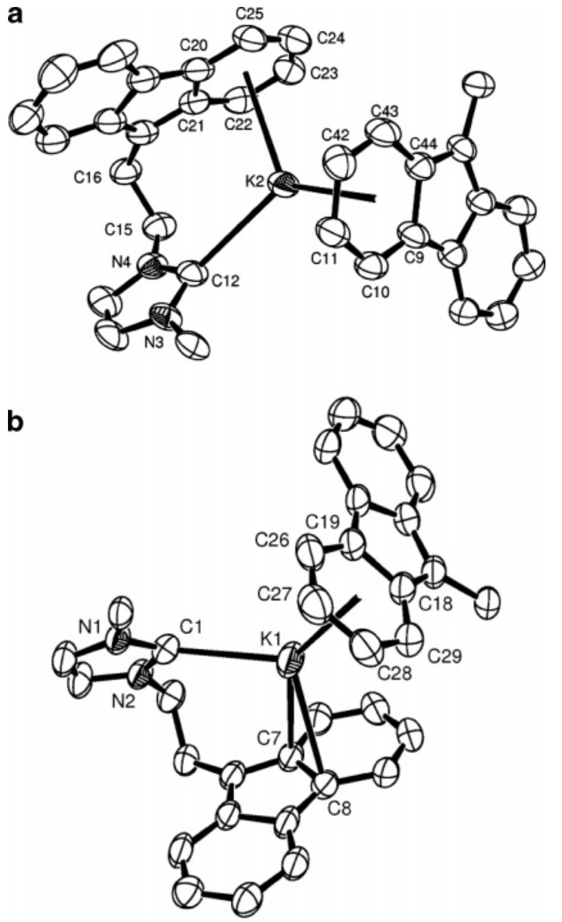
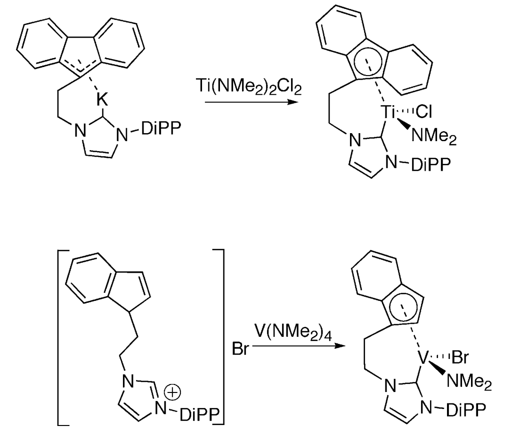


Figure 1. ORTEP representation of the coordination sphere of K in the two repeat units of the chain structure of **(Fl-NHC)$^-$K$^+$** with 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)−K(1) 2.896(5); C(7)−K(1) 2.941(5); C(8)−K(1) 3.014(5); C(48)−K(1) 3.244(5); C(12)−K(2) 2.911(5); C(20)−K(2) 3.177(5); C(21)−K(2) 3.018(5); C(22)−K(2) 3.029(5); C(23)−K(2) 3.142(5); C(24)−K(2) 3.252(5); C(25)−K(2) 3.287(5); N(2)−C(1)−K(1) 127.7(3); N(1)−C(1)−K(1) 125.1(3); N(2)−C(1)−N(1) 102.6(4); N(4)−C(12)−K(2) 123.7(3); N(3)−C(12)−K(2) 130.5(3).

The use of the new ligands in transition metal chemistry is demonstrated by the following two examples. The reaction of **(Fl-NHC)$^-$K$^+$** with Ti(NMe$_2$)$_2$Cl$_2$ in benzene gave, after filtration and crystallization, the yellow-brown, air-sensitive, crystalline paramagnetic complex **(Fl-NHC)Ti(NMe$_2$)Cl** in low yields (Scheme 2).

Scheme 2. Synthesis of Ti(III) and V(III) Complexes



The structure of the molecule was determined crystallographically (Figure 2) and comprises one tetrahedral Ti(III) center coordinated by the chelate fluorenyl-NHC (binding through the fluorenyl and the NHC), one dimethylamido group, and one chloride.[20] This is the first example of a complex of a cyclopentadienyl-type derivative with a pendant NHC.

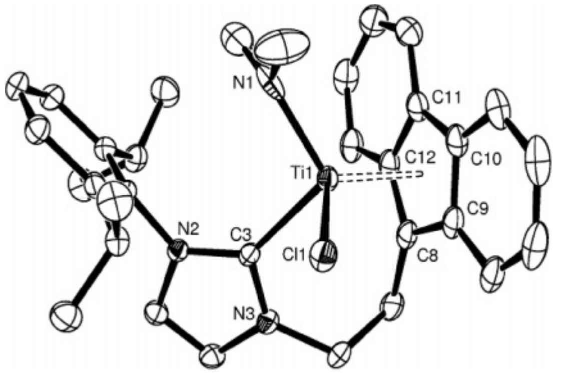


Figure 2. ORTEP representation of complex **(Fl-NHC)Ti(NMe$_2$)-Cl** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(3)−Ti(1) 2.221(2); N(1)−Ti(1) 1.984(2); C(3)−N(2) 1.372(3); C(3)−N(3) 1.365(3); N(3)−C(3)−Ti(1) 123.49(14); N(2)−C(3)−Ti(1) 133.84(14).

The Ti−C(fluorene) bond distances (Ti−C8 to C12 in the range 2.383−2.471 Å) support a symmetrically coordinated η^5-fluorenyl ring; comparable metrical data, albeit with some slip distortion, have been reported for the only other Ti(III) fluorenyl complex that has been structurally characterized.[21] The Ti−C (NHC) (2.221 Å) is in the range observed previously (2.192−2.210 Å).[22] The exact mechanism of the reduction of the metal center is not clear at present. It is plausible that the ligand acts as a reducing agent, which is supported by the isolation from the supernatant solution by fractional crystallization and crystallographic characterization of the spiro imidazolium salt shown

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(19) **Fl-NHC-Ag-Br.** NMR (CDCl$_3$): ^{1}H, δ, 7.80 (2H, m, Ar); 7.61 (2H, m, Ar); 7.40 (5H, m, Ar); 7.22 (2H, d, J = 8 Hz, Ar); 6.76 (1H, m, carbene backbone); 6.70 (1H, m, carbene backbone); 3.82 (2H, m, N-CH_2CH$_2$-Fl); 2.82 (2H, m, N-CH$_2$CH_2-Fl); 2.25 (2H, septet, J = 7 Hz, CH(CH$_3$)$_2$); 1.21 (6H, d, J = 7 Hz, CH(CH_3)$_2$), 1.08 (6H, d, J = 7 Hz, CH(CH_3)$_2$)).^{13}C-{^{1}H}: δ, 145.6, 145.0, 141.7, 130.5, 127.8, 124.3, 124.2, 123.3, 120.9, 120.2 (all aromatic), 48.2 (Fl-CH$_2$CH$_2$N) 45.1 (CH, fluorene) 34.7 (Fl-CH$_2$CH$_2$-N); 28.2 CH(CH$_3$)$_2$), 24.5 CH(CH$_3$)$_2$), 24.34 CH(CH$_3$)$_2$). MS ES$^+$: 947 [AgL$_2$]$^+$. Anal. Calcd for C$_{30}$H$_{32}$N$_2$AgBr (%): C, 59.23, H, 5.30, N, 4.60. Found: C, 59.36, H, 5.39, N, 4.50. **Ind-NHC-Ag-Br.** NMR (CDCl$_3$): ^{1}H: δ, 7.42−7.13 (7H, m, aromatic); 6.95 (1H, s, carbene backbone); 6.79 (1H, s, carbene backbone); 6.24 (1H, bs, indenyl H); 4.53 (2H, t, J = 7 Hz, bridge); 3.30 (2H, s, indenyl CH$_2$); 3.13 (2H, t, J = 7 Hz, bridge); 2.15 (2H, septet, J = 7 Hz, isopropyl CH); 1.95 (6H, d, J = 7 Hz, isopropyl CH$_3$), 0.98 (6H, d, J = 7 Hz, isopropyl CH$_3$). ^{13}C{^{1}H}: δ, 145.6, 144.7, 144.2, 139.4, 131.5, 130.5, 126.4, 125.2, 124.2 (all aromatic), 51.1 (CH$_2$, bridge); 38.0 (CH$_2$, bridge); 29.9 (CH$_2$, indenyl); 28.2 (CH, isopropyl); 24.4 (CH$_3$, isopropyl). MS ES$^+$ (m/z): 847 [AgL$_2$]$^+$. Anal. Calcd for C$_{26}$H$_{30}$N$_2$AgBr (%): C, 55.43, H, 5.42 N, 5.02. Found: C, 55.90, H, 5.34, N, 4.95.

(20) Compound **(Fl-NHC)Ti(NMe$_2$)Cl** was crystallized from benzene in the triclinic space group $P\bar{1}$ with a = 8.3495(6) Å, b = 10.7139(13) Å, c = 16.8282(19) Å, α = 73.535(9)°, β = 86.508(7)°, γ = 71.966(7)°, V = 1372.1(2) Å^3, and D_{calcd} = 1.324 Mg m^{-3} for Z = 2. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 6276 unique reflections (R_{int} = 4.11%) converged to a final R_1 = 4.84% ($I > 2(I)$) and $R_w{}^2$ = 10.81%.

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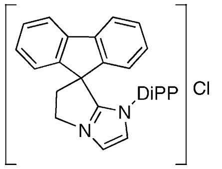
Scheme 3. Organic Side-Product Formed during the Preparation of (Fl-NHC)Ti(NMe$_2$)Cl



in Scheme 3. Attempts to further elucidate the reduction mechanism are under way.

Aminolysis of V(NMe$_2$)$_4$ by **(IndH-NHC-H)Br** in toluene is also accompanied by reduction to V(III) (Scheme 2). The red-brown crystalline product **(Ind-NHC)V(NMe$_2$)Br**, isolated in moderate yields, was shown by X-ray diffraction to have the structure shown in Figure 3.[23]

The geometry around the metal center is distorted tetrahedral; the Ind-NHC ligand is chelating through the five-membered ring of the indenyl and the NHC groups. The V−C(carbene) and V−amido bond lengths are in the range reported in the literature.[22,24] Inspection of the V−C(indenyl) distances shows a slip distortion toward C8, C9, and C10 ($\Delta = 0.114$ Å).[25] The bridgehead C atoms of the indenyl ring are strictly planar, indicating absence of strain in the chelate.

In conclusion, we have prepared the first class of imidazolium salt pro-ligands and the NHCs derived therefrom with pendant neutral or anionic indenyl and fluorenyl groups. We have also demonstrated the potential of the new ligands with some early transition metals, where a preferred chelate coordination mode is adopted. The wide scope for electronic and steric tuning, the possibility of hemilabile dynamic behavior, especially in catalytic systems, and the support of homo- or hetero-bimetallic complexes, when the ligands act as bridging, are some attractive features that are now being explored in our group. Last, the development of new water- and ionic-liquid-compatible complexes or chiral designs is another future path of development.

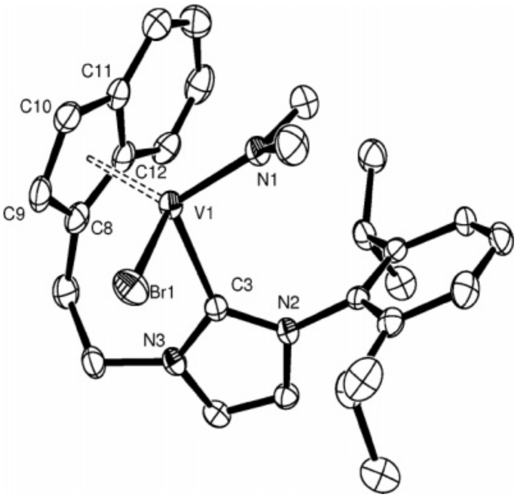


Figure 3. ORTEP representation of complex **(Ind-NHC)V(NMe$_2$)-Br** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: V(1)−N(1) 1.885(3); V(1)−C(3) 2.185(3); N(3)−C(3)1.363(4); N(2)−C(3) 1.388(4); N(3)−C(3)−N(2) 103.5(3); N(2)−C(3)−V(1) 132.0(2); N(3)−C(3)−N(2) 103.5(3).

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Supporting Information Available: Experimental methods for the preparation and characterization of the new compounds. Full details of the X-ray crystal structures, 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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(23) Compound **V(Ind-NHC)(NMe$_2$)(Br)** was crystallized from THF/toluene in the triclinic space group $P\bar{1}$ with $a = 8.208(4)$ Å, $b = 9.877(6)$ Å, $c = 17.305(10)$ Å, $\alpha = 100.63(8)°$, $\beta = 97.83(4)°$, $\gamma = 105.38(5)°$, $V = 1303.8(13)$ Å^3, and $D_{calcd} = 1.387$ Mg m^{-3} for $Z = 2$. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 5819 unique reflections ($R_{int} = 7.00\%$) converged to a final $R_1 = 5.34\%$ ($I > 2(I)$) and $R_w{}^2 = 8.75\%$.

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