Communications

A New Chelating Anilido-Imine Donor Related to β-Diketiminato Ligands for Stabilization of Organoyttrium Cations

Paul G. Hayes, Gregory C. Welch, David J. H. Emslie, Cassandra L. Noack, Warren E. Piers,*,[1] and Masood Parvez

Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4

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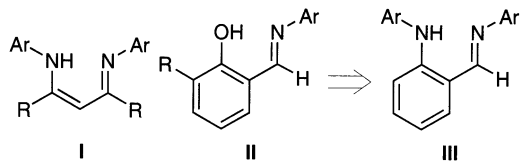
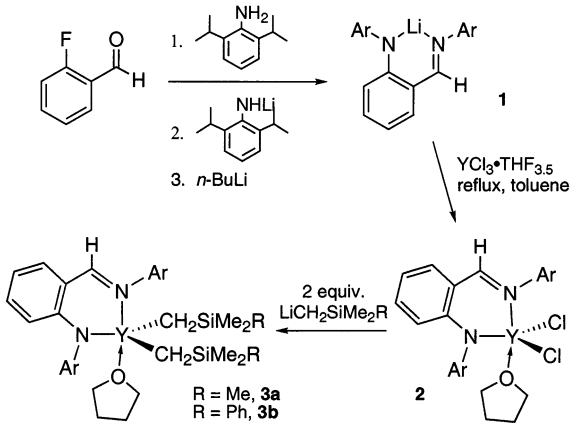
Summary: A bulky anilido-imine donor that marries the attributes of the β-diketiminato and salicylaldiminato ligand frameworks has been prepared and used to stabilize bis-alkyl yttrium derivatives, which act as precursors to cationic organoyttrium complexes.

The rise of the β-diketiminato, or "nacnac", donor framework (**I**) to the "A-list" of ancillary ligands has been dramatic, with recent applications in bioinorganic, main group, and transition metal chemistry[2] Despite their wide applicability, examples of organoyttrium compounds stabilized by the nacnac ligands are not known, and although we have extensively developed organoscandium nacnac chemistry,[3] attempts to prepare analogous yttrium derivatives have thus far been unsuccessful.



On the other hand, organoyttrium derivatives using the salicylaldiminato ligand family **II** can be prepared, but thermally stable LYR_2 complexes were not available even with bulky examples[4] since they are prone to ligand distribution processes.[5] Given the recent interest in non-cyclopentadienyl ligand environments for group 3 metals,[6] we envisioned a ligand that combines the steric and electronic features of the nacnac and salicylaldiminato donor frameworks to prepare bis-alkyl yttrium derivatives. Herein we report the synthesis of the new monoanionic, bulky anilido-imine ligand family **III**[7] and its deployment as an ancillary for organoyttrium compounds. As a variant on the enormously popular nacnac ligand family, these new ligands could find applications in many areas of inorganic chemistry.

Scheme 1



The anilido-aldimine ligand **1** was straightforwardly prepared in two steps from commercially available starting materials as shown in Scheme 1. Imine formation occurs smoothly at room temperature using 2,6-diisopropylaniline and *ortho*-fluoro benzaldehyde. The anilido donor portion of the ligand was installed via a nucleophilic aromatic displacement of fluoride using LiN(H)Ar. Although both reagents are reasonably sterically bulky, the reaction is high yielding and no doubt aided by the electron-withdrawing nature of the neighboring imine group.[8] The resulting proteo ligand **1** can

(1) Phone: 403-220-5746. Fax: 403-289-9488. E-mail: wpiers@ucalgary.ca. S. Robert Blair Professor of Chemistry 2000−2005. E. W. R. Steacie Memorial Fellow, 2001−2003.

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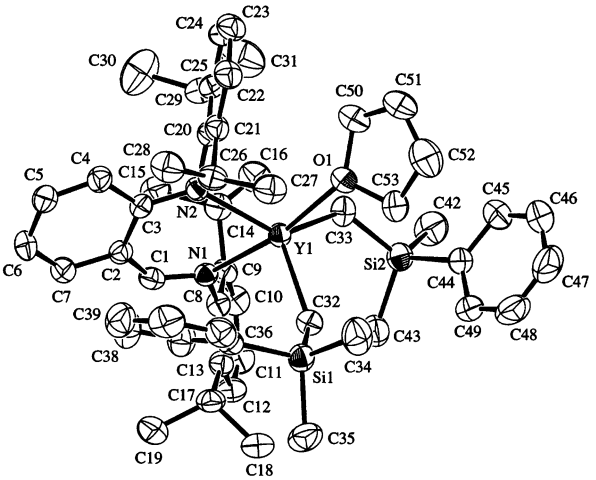
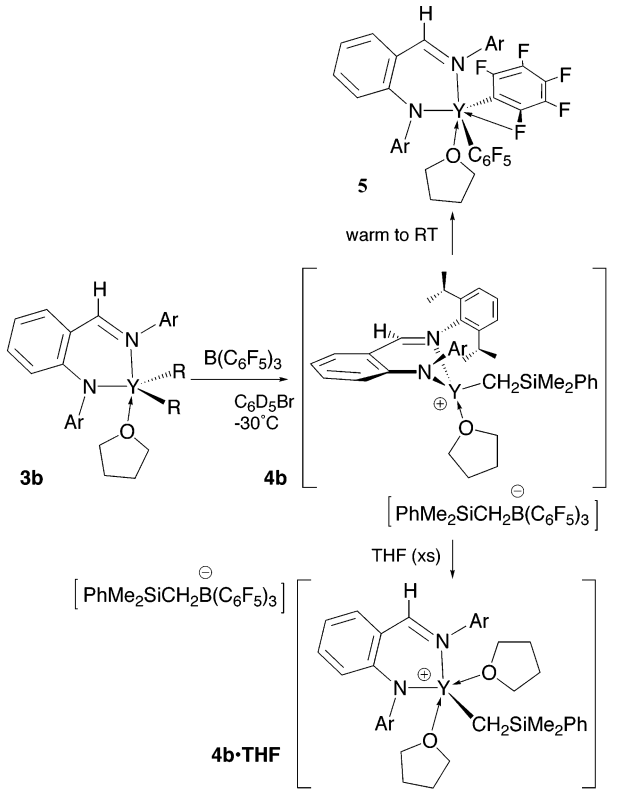


Figure 1. Molecular structure of **3b**. Selected bond distances (Å): Y(1)−N(1), 2.454(3); Y(1)−N(2), 2.324(3); Y(1)−O(1), 2.376(3); Y(1)−C(32), 2.381(4); Y(1)−C(33), 2.419(4). Selected bond angles (deg): N(1)−Y(1)−N(2), 75.85(9); N(1)−Y(1)−O(1), 169.47(9); N(2)−Y(1)−O(1), 97.25(9); C(32)−Y(1)−C(33), 108.90(13); N(2)−Y(1)−C(32), 121.86(12); N(2)−Y(1)−C(33), 128.99(12).

be lithiated with *n*-BuLi to give a lithium salt as a mono THF adduct. This salt serves as a convenient reagent for ligand installation upon reaction with $YCl_3{\cdot}THF_{3.5}$; refluxing these two partners in toluene for 4 days gives excellent yields of the dichloride **2** as indicated in Scheme 1. The compound retains 1 equiv of THF, as determined by ^{1}H NMR spectroscopy; attempts to remove the THF by heating these solids under vacuum led only to decomposition. Diagnostic ligand resonances in the ^{1}H NMR spectrum include those for the aldimine proton at 8.2 ppm and four upfield shifted multiplets between 5.8 and 7.0 ppm for the aromatic protons of the backbone. The asymmetry of the ligand and restricted rotation about the N−C_{aryl} bonds give rise to four separate doublets for the isopropyl methyl groups.

Alkylation of dichloride **2** using $LiCH_2SiMe_2R$ gives the bis-alkyl compounds **3** (R = Me, **3a**; R = Ph,[5b] **3b**), in which the THF ligand is retained. The X-ray structure of **3b** has been determined, and an ORTEP diagram is shown in Figure 1.[9] The yttrium center exhibits distorted trigonal bipyramidal geometry, in which the imine nitrogen N(1) and the THF ligand occupy the axial sites. This geometry implies that the two alkyl groups are equivalent, although upon cooling, the uncharacteristically broad signal for the Y−CH_2 groups splits into an AB quartet when restricted mobility of the alkyl groups renders the C−H moieties diastereotopic, while the ^{13}C resonance remains a broad singlet with unresolved Y−C coupling. Since all attempts to remove THF failed, and reactions of these compounds with strong

Scheme 2



Lewis acids (vide infra) lead to alkide abstraction, it appears that the THF ligand is not dissociatively labile.

The yttrium atom lies 0.819(5) Å out of the C_3N_2 ligand plane, which is consistent with what is observed in related five-coordinate organoscandium compounds incorporating a bulky nacnac ligand. Unlike the nacnac ligands, the donor framework in the anilido-imine ligand is more localized and the two nitrogens bond to yttrium with markedly different bond lengths (Y(1)−N(1) = 2.454(3) Å; Y(1)−N(2) = 2.324(3) Å). The steric effect of the N-aryl groups is also unbalanced, as demonstrated by the different values for the angles C(1)−N(1)−C(8) (111.5(3)°) and C(15)−N(2)−C(20) (115.1(3)°).

While the presence of THF is not ultimately desirable, it does appear to fortify bis-alkyl compounds **3** against a metalation process involving the C−H bonds of the aryl isopropyl methyl groups, which is a factor in nacnac organoscandium chemistry.[3c] Furthermore, upon reaction of **3b** with $B(C_6F_5)_3$, abstraction of one CH_2SiMe_2-Ph group occurs exclusively, forming ion pair **4b** with no observation of $THF{\cdot}B(C_6F_5)_3$ (Scheme 2). At low temperature, ^{1}H and ^{19}F NMR spectroscopy indicates that **4b** exists as three isomers, as indicated by three separate aldimine hydrogen resonances, and three sets of *ortho*, *meta*, and *para* fluorine signals. The $\Delta\delta_{m,p}$ values in the ^{19}F NMR spectrum[10] are 2.6, 2.6, and 3.4 ppm, indicating that the anion is not contacting the cation through the abstracted carbon atom. Due to the instability of **4b** toward $-C_6F_5$ back-transfer (see below) and the complexity of the low-temperature NMR spectra, we are not sure if the isomers are geometric in nature or are distinguished by different modes of ion−ion contact.[11]

(9) Crystal data for **3b**: $C_{53}H_{73}N_2OSi_2Y$, MW = 899.22, monoclinic, $P2_1/n$, a = 10.8537(3) Å, b = 18.7713(7) Å, c = 24.9649(9) Å, β = 91.444(2)°, V = 5084.7(3) Å^3, Z = 4, ρ_{calc} = 1.175 g cm^{-3}, Mo Kα radiation, λ = 0.71073 Å, T = 173(2) K, 14 631 measured reflections, 8495 unique, 5919 reflections with $I_{net} > 2.0\sigma(I_{net})$, μ = 1.23 mm^{-1}, min./max. transmission = 0.748 and 0.818, R1 ($I>2\sigma$) = 0.053, wR2 0.098, GoF = 1.06, no. of parameters = 535, final difference map within +0.28 and −0.33 e Å^3. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-201288. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

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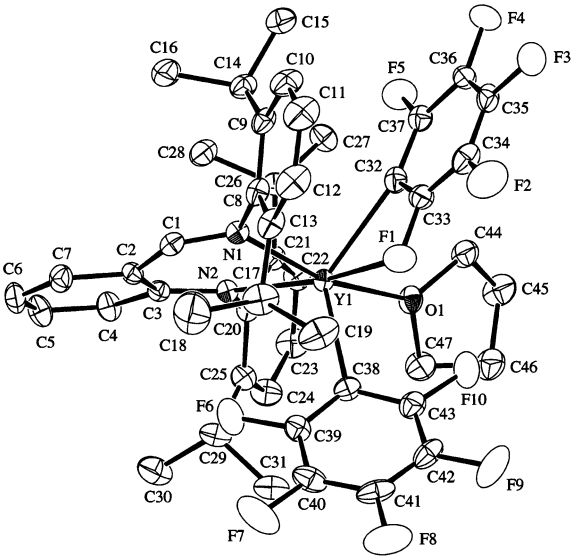

Figure 2. Molecular structure of **5**. Selected bond distances (Å): Y(1)−N(1), 2.421(2); Y(1)−N(2), 2.262(2); Y(1)−O(1), 2.337(2); Y(1)−C(32), 2.492(3); Y(1)−C(38), 2.460(3); Y(1)−F(1), 2.786(2). Selected bond angles (deg): N(1)−Y(1)−N(2), 77.52(8); N(1)−Y(1)−O(1), 166.54(8); N(2)−Y(1)−O(1), 103.61(8); C(32)−Y(1)−C(38), 118.18(10); C(33)−C(32)−Y(1), 102.8(2); C(37)−C(32)−Y(1), 144.7(2).

The stability of **4b** is strongly dependent on the temperature and the presence or absence of excess THF. For example, if **3b** is activated in C_6D_5Br at −30 °C, ion pair **4b** is only persistent at temperatures lower than −20 °C; above these temperatures, facile $-C_6F_5$ transfer processes occur, ultimately yielding bis-pentafluorophenyl derivative **5** and unidentified boron-containing products. Compound **5** was isolated in low yield and identified by X-ray crystallography[12] and features a distinct Y−F (Y(1)−F(1) = 2.786(2) Å) interaction involving one of the *ortho* F atoms in the solid state as shown in Figure 2. Apart from this feature, neutral compound **5** is in other ways structurally similar to the dialkyl starting complex **3b**.

While prone to C_6F_5 back-transfer as described above, if **4b** is generated at low temperature and immediately treated with an excess of THF, the resulting ion pair is stable indefinitely even at temperatures as high as 60 °C. The ^{19}F and ^1H NMR spectra simplify dramatically,[13] indicating that the metal is stabilized by two THF donors, symmetrizing the structure. Compound **4b**·THF can be isolated from these solutions in 87% yield as an analytically pure yellow solid and stored indefinitely under an inert atmosphere.

Cationic organoyttrium compounds are rare species due to their high reactivity, and few are stable enough to characterize even in solution;[14] the remarkable stability of **4b**·THF offers the opportunity to explore the chemistry of these elusive species. This has been made possible by the development of a new ligand family, related structurally to the important nacnac family of ligands. The anilido-imine is sterically similar to the most efficacious nacnac ligands, but the more localized donor structure provides the opportunity to probe electronic modifications which have been shown to have profound effects on the reactivity of nacnac complexes.[15] The potential of this new ligand environment for use in other areas is high, given the wide applicability of the nacnac ligand framework.[2]

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Supporting Information Available: Full experimental details for the synthesis of all new compounds, plus spectroscopic and other characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) For example, it is possible that the phenyl substituent from the abstracted CH_2SiMe_2Ph group might be interacting in an η^6 bonding mode with the cationic center (see ref 3a).

(12) Crystal data for **5**: $C_{47}H_{47}F_{10}N_2OY$, MW = 934.78, triclinic, $P\bar{1}$, a = 10.272(2) Å, b = 11.673(3) Å, c = 19.348(4) Å, α = 84.118(14)°, β = 82.302(14)°, γ = 74.364(15)°, V = 2208.6(8) Å^3, Z = 2, ρ_{calc} = 1.406 g cm^{-3}, Mo Kα radiation, λ = 0.71073 Å, T = 173(2) K, 35 807 measured reflections, 9949 unique, μ = 1.400 mm^{-1}, min./max. transmission = 0.7211 and 0.7867, R1($I>2\sigma$) = 0.0496, wR2 0.0898, GoF = 1.112, no. of parameters = 550, final difference map within +0.543 and −0.506 e Å^3. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-206037. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

(13) Selected NMR data for **4b**·THF (C_7D_8, 270 K). ^1H NMR: δ 7.92 (s, C*H*=NAr), 1.48 (br s, BC*H*$_2$SiMe$_2$Ph), 0.46 (s, BCH$_2$Si*Me*$_2$Ph), 0.15, 0.13 (s, Y−CH$_2$Si*Me*$_2$Ph), −0.13 (d, $^2J_{H-Y}$ = 3.6 Hz, Y−C*H*$_2$SiMe$_2$Ph). $^{13}C\{^1H\}$ NMR: δ 174.03 (*C*H=NAr), 44.56 (d, $^1J_{C-Y}$ = 53.6 Hz, Y−*C*H$_2$SiMe$_2$Ph), 8.83 (br, B*C*H$_2$SiMe$_2$Ph), 2.53, 2.49 (Y−CH$_2$Si*Me*$_2$Ph), −0.35 (BCH$_2$Si*Me*$_2$Ph). ^{19}F NMR: −130.7 (d, $^3J_{F-F}$ = 21 Hz, *ortho*-F), −163.9 (t, $^3J_{F-F}$ = 21 Hz, *para*-F), −166.4 (t, $^3J_{F-F}$ = 21 Hz, *meta*-F). ^{11}B NMR: δ −14.2. Anal. Calcd for $C_{75}H_{81}N_2O_2Si_2BF_{20}Y$: C, 57.50; H, 5.50; N, 1.89. Found: C, 57.01; H, 5.60; N, 1.84. Full spectroscopic details can be found in the Supporting Information.

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