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New Diamide–Diamine Ligands and their Zirconium and Hafnium Dichloride and Bis(dimethylamide) Complexes

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The multigram syntheses of the protio ligands $\mathrm{(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NHSiMe_2R)_2}$ (R = Me, $\mathrm{H_2N_2NN'}$ **3**; R = $^{\mathrm{t}}$Bu, $\mathrm{H_2N_2NN^*}$ **4**) are described via reactions of the previously reported $\mathrm{(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NH_2)_2}$ (**1**). A new synthesis of **1** is reported starting from 2-aminomethylpyridine and *N*-tosylaziridine, proceeding via $\mathrm{(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NHTs)_2}$ (**2**). Reaction of $\mathrm{H_2N_2NN'}$ or $\mathrm{H_2N_2NN^*}$ with $^{\mathrm{n}}$BuLi gives good yields of the dilithiated derivatives $\mathrm{Li_2N_2NN'}$ and $\mathrm{Li_2N_2NN^*}$. Reaction of $\mathrm{H_2N_2NN'}$ or $\mathrm{H_2N_2NN^*}$ with $\mathrm{[MCl_2(CH_2SiMe_3)_2(Et_2O)_2]}$ gives the *cis*-dichloride complexes $\mathrm{[MCl_2(L)]}$ (L = $\mathrm{N_2NN'}$, M = Zr **7** or Hf **8**; L = $\mathrm{N_2NN^*}$, M = Zr **9**). The corresponding reactions of $\mathrm{H_2N_2NN'}$ or $\mathrm{H_2N_2NN^*}$ with $\mathrm{[Zr(NMe_2)_4]}$ afford the bis(dimethylamide) derivatives $\mathrm{[Zr(NMe_2)_2(L)]}$ (L = $\mathrm{N_2NN'}$ **10** or $\mathrm{N_2NN^*}$ **11**). All of these protonolysis reactions proceed smoothly and in good yields. Attempts to prepare the titanium complexes $\mathrm{[Ti(X)_2(N_2NN')]}$ (X = Cl or $\mathrm{NMe_2}$) were unsuccessful. The X-ray crystal structures of $\mathrm{(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NHTs)_2\cdot EtOH}$, $\mathrm{[ZrCl_2(N_2NN')]\cdot 0.5C_6H_6}$, $\mathrm{[Zr(NMe_2)_2(N_2NN')]}$, and $\mathrm{[Zr(NMe_2)_2(N_2NN^*)]}$ are reported.

Introduction

The bis(cyclopentadienyl) ligand set (e.g., see I in Chart 1) has been the leading dianionic environment for organotransition metal chemistry for over four decades.[1] In addition, a number of chelating cyclopentadienyl-based ligands shown in II (dianionic) and III (monoanionic) have found widespread applications.[2−5] Driven by the continuing search for new fundamental and catalytic chemistry, researchers in the past 10 years have established the importance of polydentate di- and trianionic N- and N,O-donor ligands; a few examples of N-donor systems are shown in Chart 1.[6−11]

Among the tetradentate "$\mathrm{N_4}$" donor ligands, the porphyrins (e.g., in IV) and tetraaza[14]annulenes (e.g., in V) are probably the best established *di*anionic ligands. They provide a rigid and relatively inflexible, square-base donor environment. However, there is negligible opportunity for introducing bulky or chiral substituents into the $\mathrm{N_4}$ ligand periphery to control and tune the reactivity of the metal center. The *tri*anionic triamidoamine "tren" systems (as in VI) are, on the other hand, very amenable to steric modification via changing of the N-substituents. Such ligands (and their $\mathrm{O_3N}$-donor "atrane" analogues) have been extremely useful for developing p-block, early-mid transition metal, lanthanide, and actinide chemistry.[8,9,12−14] Dianionic "$\mathrm{N_4}$" analogues of the tren systems should help advance early transition metal and lanthanide chemistry and complement the extensive studies of *tri*dentate diamide-donor systems exemplified by VII.[10,15] Indeed, it was recently reported that addition of an extra donor arm to bis(alkoxide)-donor analogues of VII can

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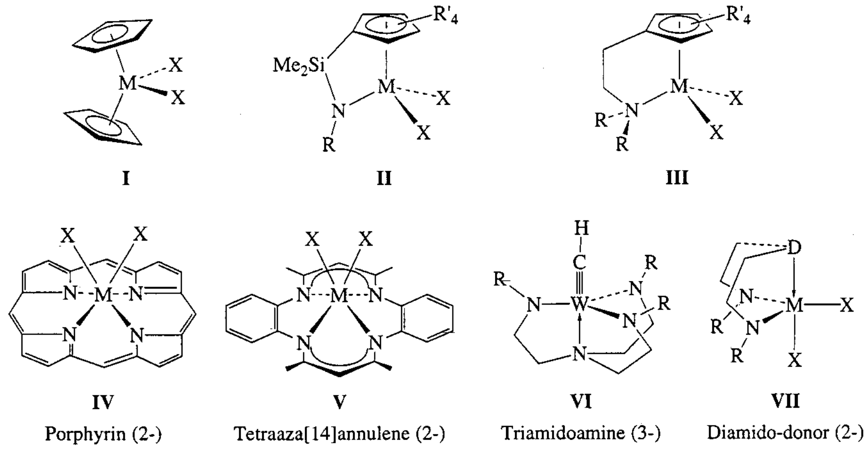
Chart 1



lead to enhanced ethylene polymerization capability.[16] In this contribution, we report the synthesis of new diamide−diamine donor protio ligands and their dilithiated derivatives, along with zirconium and hafnium dichloride and bis(dimethylamide) complexes.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or of dinitrogen. Solvents were predried over activated 4 Å molecular sieves and were refluxed over potassium (tetrahydrofuran, hexanes, benzene), sodium/potassium alloy (pentane), or calcium hydride (dichloromethane) under a dinitrogen atmosphere and collected by distillation. Deuterated solvents were dried over potassium (C_6D_6) or calcium hydride ($CDCl_3$) distilled under reduced pressure and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300 or Varian Unity Plus 500 spectrometer. ^1H and ^{13}C assignments were confirmed when necessary with the use of DEPT-135, DEPT-90, and two-dimensional $^1H-^1H$ and $^{13}C-^1H$ correlation NMR experiments. All spectra were referenced internally to residual protio solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in hertz.

Infrared spectra were prepared as Nujol mulls between CsBr plates or CH_2Cl_2 solutions in a NaCl cell and were recorded on a Perkin-Elmer 1710 FTIR spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the mass spectroscopy services of the University of Oxford's Dyson Perrin's Laboratory. Combustion elemental analyses were carried out by the analytical services of the University of Oxford's Inorganic Chemistry Laboratory and Mikroanalytisches Labor Pascher, Germany.

Literature Preparations. The compounds $[MCl_2(CH_2SiMe_3)_2(Et_2O)]_2$ (M = Zr, Hf) were prepared according to established methods.[17] Tosyl aziridine was prepared by a slightly modified version of the published methods in which $CHCl_3-EtOH$, 1:4, was used to crystallize ditosylated ethanolamine rather than CCl_4.[18] Other reagents were obtained from commercial sources and dried and/or distilled before use according to standard procedures.

$(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NHTs)_2$ (2). To a slurry of tosyl aziridine (431.5 g, 1.26 mol) in EtOH (2.5 L) was added 2-aminomethyl pyridine (52.7 g, 0.487 mol). The reaction mixture was stirred for 24 h at 35 °C after which time the volatile parts of the resulting brown mixture were removed under reduced pressure yielding a thick brown oil. The oil was dissolved in the minimum quantity of warm CH_2Cl_2 (∼250 mL) to which 4 volumetric equiv of EtOH (∼1 L) was added. The clear, dark brown solution was stored at 4 °C overnight, whereupon $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NHTs)_2$ (**2**) crystallized as a light brown solid. The product was isolated and dried in vacuo. Yield: 166 g (68%). Colorless single crystals suitable for X-ray diffraction were grown by slow evaporation of a concentrated solution of **2** in CH_2Cl_2-EtOH (1:4 v/v).

^1H NMR data (300.1 MHz, 298 K, $CDCl_3$): 8.60 (1 H, d, $^3J = 4.9$ Hz, 6-C_5H_4N), 7.65 (4 H, d, $^3J = 8.1$ Hz, *o*-C_6H_4), 7.58 (1 H, m, 4-C_5H_4N), 7.20 (4 H, d, $^3J = 8.1$ Hz, *m*-C_6H_4), 7.19 (1 H, m, 5-C_5H_4N), 7.07 (1 H, d, $^3J = 7.7$ Hz, 3-C_5H_4N), 6.87 (2 H, br t, SO_2NH), 3.52 (2 H, s, $C_5H_4NCH_2$), 2.82 (4 H, m, NCH_2CH_2NS), 2.51 (4 H, m, NCH_2CH_2NS), 2.34 (6 H, s, Me). $^{13}C\{^1H\}$ NMR data (75.5 MHz, 298 K, $CDCl_3$): 158.2 (2-C_5H_4N), 149.2 (6-C_5H_4N), 142.8 (CSO or CMe_3), 137.1 (CSO or CMe_3), 137.0 (4-C_5H_4N), 129.5 (*m*-C_6H_4), 126.9 (*o*-C_6H_4), 123.0 (3-C_5H_4N), 122.6 (5-C_5H_4N), 58.5 ($C_5H_4NCH_2$), 53.9 (NCH_2CH_2NS), 40.8 (NCH_2CH_2NS), 21.3 (Me). IR data (NaCl cell, CH_2Cl_2): 3278 (m, NH), 3050 (m), 2852 (m), 1595 (s), 1446 (m), 1400 (m), 1320 (s, SO_2), 1234 (w), 1161 (s, SO_2), 1093 (s), 1019 (w), 949 (m), 818 (s, $SiMe_3$), 758 (s), 660 (s), 552 (s), 472 (w) cm^{-1}. EI mass spectrum: $m/z = 502$ $[M]^+$ 100%, $m/z = 349$ $[M - Ts]^+$ 3%, $m/z = 318$ $[M - CH_2NHTs]^+$ 45%. Found (Calcd for $C_{24}H_{30}N_4O_4S_2$): C, 57.5 (57.4); H, 6.0 (6.0); N, 11.4 (11.2)%.

$(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NH_2)_2$ (1). A slurry of $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NHTs)_2$ (**2**) (22.5 g, 44.9 mmol) partially dissolved in H_2SO_4 (18 M, 250 mL) was heated under a nitrogen atmosphere at 90 °C for 48 h. With constant cooling in an ice bath, the cooled mixture was diluted with slow addition of distilled water (500 mL) and subsequently basified to pH 14 with a saturated NaOH solution. The water was removed under reduced pressure, and the remaining oil extracted into CH_2Cl_2 to give a yellow solution. The solution was dried over Na_2SO_4 and filtered, and the volatiles were removed

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under reduced pressure to yield crude $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NH_2)_2$ (**1**) as a brown oil. The crude sample was vacuum distilled (5×10^{-3} mbar, 180 °C) yielding a spectroscopically pure sample of **1** as a yellow oil in good yield. Yield: 7.27 g (83%). The NMR data for **1** prepared this way are identical to those reported previously.[19]

H_2N_2NN' (3). To a solution of $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NH_2)_2$ (**1**) (5.40 g, 27.8 mmol) and Et_3N (15.6 mL, 112.0 mmol) in THF (200 mL) cooled to 0 °C was added dropwise a solution of $ClSiMe_3$ (7.1 mL, 56.4 mmol) in THF (40 mL) resulting in the immediate formation of a white precipitate. The reaction mixture was allowed to warm to room temperature and stirred for a further 2.5 h. The yellow solution was filtered, and the volatiles were removed under reduced pressure yielding a yellow oil. The oil was extracted into pentane and filtered, and the volatiles were removed once again under reduced pressure giving a spectroscopically pure sample of H_2N_2NN' (**3**) as a pale yellow oil. Attempts to distill the product under reduced pressure led to partial decomposition. Yield: 7.1 g (75%).

^1H NMR data (300.1 MHz, 298 K, $CDCl_3$): 8.50 (1 H, d, $^3J = 4.8$ Hz, 6-C_5H_4N), 7.62 (1 H, dd, $^3J = 7.8, 7.5$ Hz, 4-C_5H_4N), 7.43 (1 H, d, $^3J = 7.8$ Hz, 3-C_5H_4N), 7.13 (1 H, dd, $^3J = 7.5, 4.8$ Hz, 5-C_5H_4N), 3.74 (2 H, s, $C_5H_4NC\mathit{H}_2$), 2.77 (4 H, br m, $NCH_2C\mathit{H}_2NSi$), 2.51 (4 H, t, $NC\mathit{H}_2CH_2NSi$), 0.75 (2 H, br s, NH), 0.01 (18 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR data (75.5 MHz, 298 K, $CDCl_3$): 160.5 (2-C_5H_4N), 148.9 (6-C_5H_4N), 136.2 (4-C_5H_4N), 122.9 (3-C_5H_4N), 121.8 (5-C_5H_4N), 61.0 ($C_5H_4N\mathit{C}H_2$), 58.5 ($N\mathit{C}H_2CH_2NSi$), 39.6 ($NCH_2\mathit{C}H_2NSi$), −0.1 ($SiMe_3$). IR data (NaCl cell, CH_2Cl_2): 3300 (m), 2951 (s), 287 (m), 1590 (m), 1575 (w), 1429 (m), 1399 (m), 1248 (s), 1118 (s), 1040 (m), 933 (m), 836 (s), 753 (m), 682 (w), 670 (w), 655 (w) cm^{-1}. EI mass spectrum: $m/z = 338$ $[M]^+$ 13%, $m/z = 323$ $[M - Me]^+$ 16%, $m/z = 192$ $[M - 2SiMe_3]^+$ 22%. Found (Calcd for $C_{16}H_{34}N_4Si_2$): C, 56.2 (56.8); H, 9.6 (10.1); N, 16.7 (16.5)%.

$H_2N_2NN^*$ (4). To a yellow solution of $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NH_2)_2$ (3.40 g, 17.5 mmol) and Et_3N (9.8 mL, 69.8 mmol) in THF (100 mL) cooled to 0 °C was added dropwise a solution of $ClSiMe_2{}^tBu$ (5.30 g, 35.0 mmol) in THF (30 mL). A white precipitate formed immediately. The reaction mixture was allowed to warm to room temperature and stirred for a further 4 h. The resulting yellow solution was filtered away from the white solid, and the volatiles were removed under reduced pressure yielding a yellow oil. The oil was extracted into pentane and filtered, and the volatiles were removed under reduced pressure yielding $H_2N_2NN^*$ (**4**) as a pale yellow oil. Yield: 6.90 g (93%).

^1H NMR data (300.1 MHz, 298 K, $CDCl_3$): 8.41 (1 H, d, $^3J = 5.5$ Hz, 6-C_5H_4N), 7.42 (1 H, dd, $^3J = 7.8, 7.5$ Hz, 4-C_5H_4N), 7.37 (1 H, d, $^3J = 7.3$ Hz, 3-C_5H_4N), 7.04 (1 H, dd, $^3J = 7.5, 4.8$ Hz, 5-C_5H_4N), 3.63 (2 H, s, $C_5H_4NC\mathit{H}_2$), 2.71 (4 H, m, $NCH_2C\mathit{H}_2NSi$), 2.40 (4 H, m, $NC\mathit{H}_2CH_2NSi$), 0.72 (18 H, s, ^tBu), 0.63 (2 H, br s, NH), −0.17 (12 H, s, $SiMe_2$). $^{13}C\{^1H\}$ NMR data (75.5 MHz, 298 K, $CDCl_3$): 160.6 (2-C_5H_4N), 148.9 (6-C_5H_4N), 136.2 (4-C_5H_4N), 122.9 (3-C_5H_4N), 121.8 (5-C_5H_4N), 61.1 ($C_5H_4N\mathit{C}H_2$), 58.7 ($N\mathit{C}H_2CH_2NSi$), 40.3 ($NCH_2\mathit{C}H_2NSi$), 26.5 ($C\mathit{Me}_3$), 18.3 ($\mathit{C}Me_3$), −5.0 ($SiMe_2$). IR data (KBr plates, Nujol): 3382 (m), 3068 (w), 3010 (w), 2927 (s), 2883 (s), 1590 (m), 1571 (w), 1434 (m), 1402 (m), 1253 (s), 1116 (s), 1048 (m), 938 (m), 829 (s), 809 (s), 770 (s), 679 (w), 659 (m), 614 (w), 572 (w) cm^{-1}. Found (Calcd for $C_{22}H_{46}N_4Si_2$): C, 62.5 (62.2); H, 10.6 (11.0); N, 13.3 (13.3)%.

Li_2N_2NN' (5). To a solution of H_2N_2NN' (**3**) (7.09 g, 20.9 mmol) in pentane (160 mL), cooled to −78 °C, was added dropwise a 2.5 M solution of ^nBuLi in hexanes (18.4 mL, 46.0 mmol). The mixture was allowed to warm to room temperature and stirred for a further 4 h after which time the resulting red solution was filtered away from the white solid which had formed. This was washed with pentane (3 × 20 mL) and dried in vacuo yielding Li_2N_2NN' (**5**) as a white solid. Yield: 4.20 g (57%).

^1H NMR data (300.1 MHz, 298 K, C_6D_6): 8.27 (1 H, br s, 6-C_5H_4N), 6.88 (1 H, br apparent t, 4-C_5H_4N), 6.50 (1 H, br m, 5-C_5H_4N), 6.47 (1 H, br s, 3-C_5H_4N), 3.39 (2 H, br m, $NCH_2C\mathit{H}_2NSi$), 3.37 (2 H, br m, $C_5H_4NC\mathit{H}_2$), 3.29 (2 H, br m, $NCH_2C\mathit{H}_2NSi$), 2.75 (2 H, br m, $NC\mathit{H}_2CH_2NSi$), 2.34 (2 H, br m, $NC\mathit{H}_2CH_2NSi$), 0.32 (18 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR data (75.5 MHz, 298 K, C_6D_6): 160.7 (2-C_5H_4N), 149.3 (6-C_5H_4N), 137.1 (4-C_5H_4N), 122.6 (3-C_5H_4N), 122.5 (5-C_5H_4N), 58.7 ($N\mathit{C}H_2CH_2NSi$), 58.5 ($C_5H_4N\mathit{C}H_2$), 45.0 ($NCH_2\mathit{C}H_2NSi$), 2.9 ($Si(CH_3)_3$). IR data (KBr plates, Nujol): 1600 (s), 1571 (m), 1305 (w), 1247 (m), 1151 (w), 1083 (m), 1007 (w), 939 (w), 832 (m), 670 (w), 583 (w), 461 (w) cm^{-1}. EI mass spectrum: $m/z = 338$ $[M - Li - Me]^+$ 5%. Found (Calcd for $C_{16}H_{32}Li_2N_4Si_2$): C, 54.3 (54.8); H, 9.3 (9.2); N, 15.4 (16.0)%.

$Li_2N_2NN^*$ (6). To a pale yellow solution of $H_2N_2NN^*$ (1.23 g, 2.91 mmol) in pentane (30 mL) cooled to −78 °C was added dropwise a 2.5 M solution of ^nBuLi in hexanes (2.35 mL, 5.88 mmol). The mixture was allowed to warm to room temperature and stirred for a further 2 h. The orange solution was filtered away from a white solid which was then washed with pentane. The solid was dried in vacuo to give $Li_2N_2NN^*$ (**6**) as a pale orange solid. Yield: 0.86 g (68%).

^1H NMR data (300.1 MHz, 298 K, C_6D_6): 8.27 (1 H, d, $^3J = 4.8$ Hz, 6-C_5H_4N), 6.84 (1 H, dd, $^3J = 7.7$ Hz, 7.7 Hz, 4-C_5H_4N), 6.50 (1 H, dd, $^3J = 4.8$ Hz, 7.3 Hz, 5-C_5H_4N), 6.43 (1 H, d, $^3J = 7.7$ Hz, 3-C_5H_4N), 3.38 (2 H, s, $C_5H_4NC\mathit{H}_2$), 3.23 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 3.10 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 2.38 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 2.21 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 1.08 (18 H, s, ^tBu), 0.20 (6 H, s, $SiMe_2$), 0.02 (6 H, s, $SiMe_2$). $^{13}C\{H\}$ NMR data (75.7 MHz, 298 K, C_6D_6): 161.1 (2-C_5H_4N), 149.5 (6-C_5H_4N), 137.0 (4-C_5H_4N), 122.4 (3-C_5H_4N), 122.2 (5-C_5H_4N), 59.1 ($C_5H_4N\mathit{C}H_2$), 58.1 ($NCH_2\mathit{C}H_2NSi$), 46.7 ($N\mathit{C}H_2CH_2NSi$), 28.3 ($C\mathit{Me}_3$), 21.0 ($\mathit{C}Me_3$), −2.8 ($SiMe_2$). IR data (KBr plates, Nujol): 1590 (m), 1259 (s), 1096 (s), 1019 (s), 827 (s), 802 (s), 659 (w), 465 (w), 450 (w) cm^{-1}. Found (Calcd for $C_{22}H_{44}Li_2N_4Si_2$): C, 60.7 (60.8); H, 10.0 (10.3); N, 12.8 (12.9).

$[ZrCl_2(N_2NN')]$ (7). To a yellow solution of $[ZrCl_2(CH_2SiMe_3)_2(Et_2O)_2]$ (2.60 g, 5.36 mmol) in benzene (30 mL) was added dropwise a solution of H_2N_2NN' (**3**) (1.81 g, 5.36 mmol) in benzene (25 mL). The mixture was stirred for 16 h at room temperature giving an opaque yellow mixture. This was filtered and the remaining yellow residue washed with benzene (2 × 40 mL). The volatiles were removed under reduced pressure yielding $[ZrCl_2(N_2NN')]$ (**7**) as a yellow solid. Yield: 2.49 g (93%). Colorless single crystals of **7** were grown from a saturated benzene solution left standing at room temperature in a vibration-free environment for 72 h.

^1H NMR data (500.0 MHz, 298 K, C_6D_6): 9.00 (1 H, d, $^3J = 5.5$ Hz, 6-C_5H_4N), 6.94 (1 H, dd, $^3J = 7.5, 7.5$ Hz, 4-C_5H_4N), 6.59 (1 H, d, $^3J = 7.5$ Hz, 3-C_5H_4N), 6.45 (1 H, dd, $^3J = 5.5, 7.5$ Hz, 5-C_5H_4N), 3.72 (2 H, s, $C_5H_4NC\mathit{H}_2$), 3.43 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 2.99 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 2.80 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 2.54 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 0.42 (18 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR data (125.7 MHz, 298 K, C_6D_6): 157.2 (2-C_5H_4N), 148.6 (6-C_5H_4N), 138.1 (4-C_5H_4N), 122.5 (5-C_5H_4N), 121.1 (3-C_5H_4N), 62.2 ($N\mathit{C}H_2CH_2NSi$), 61.5 ($C_5H_4N\mathit{C}H_2$), 49.5 ($NCH_2\mathit{C}H_2NSi$), 0.5 ($SiMe_3$). IR data (CsBr plates, Nujol): 1608 (m), 1572 (w), 1307

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(w), 1246 (s), 1158 (w), 1074 (m), 1018 (m), 937 (m), 907 (s), 839 (s), 784 (m), 750 (m), 727 (m), 682 (m), 647 (w), 581 (w) cm^{-1}. Found (Calcd for $C_{16}H_{32}Cl_2N_4Si_2Zr$): C, 38.7 (38.5); H, 6.8 (6.5); N, 11.2 (11.2)%.

[$HfCl_2(N_2NN)$] (8). To a colorless solution of [$HfCl_2(CH_2SiMe_3)_2(Et_2O)_2$] (2.46 g, 4.29 mmol) in benzene (25 mL) was added a solution of H_2N_2NN' (**3**) (1.45 g, 4.29 mmol) in benzene (25 mL). The solution was stirred for 16 h producing an opaque white mixture which, when the volatiles were removed under reduced pressure, yielded a very thick sticky oil. The product was triturated with Et_2O giving a white solid which when dried in vacuo yielded [$HfCl_2(N_2NN)$] (**8**). Yield: 2.35 g (91%).

^1H NMR data (500.0 MHz, 298 K, C_6D_6): 8.80 (1 H, d, $^3J = 5.0$ Hz, 6-C_5H_4N), 6.84 (1 H, dd, $^3J = 7.5$, 8.0 Hz, 4-C_5H_4N), 6.43 (1 H, d, $^3J = 8.0$ Hz, 3-C_5H_4N), 6.38 (1 H, dd, $^3J = 8.0$, 5.0 Hz, 5-C_5H_4N), 3.71 (2 H, s, $C_5H_4NC\mathit{H}_2$), 3.47 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 2.96 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 2.60 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 2.53 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 0.39 (18 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR data (125.7 MHz, 298 K, C_6D_6): 158.3 (2-C_5H_4N), 148.5 (6-C_5H_4N), 138.9 (4-C_5H_4N), 123.8 (5-C_5H_4N), 122.0 (3-C_5H_4N), 64.8 ($N\mathit{C}H_2CH_2NSi$), 64.4 ($C_5H_4N\mathit{C}H_2$), 49.0 ($NCH_2\mathit{C}H_2NSi$), 1.7 ($SiMe_3$). IR data (CsBr plates, Nujol): 1727 (w), 1610 (w), 1294 (w), 1243 (m), 1073 (m), 1016 (m), 929 (s), 859 (s), 788 (w), 748 (w), 648 (w) cm^{-1}. EI mass spectrum: $m/z = 551$ $[M - Cl]^+$ 20%, $m/z = 513$ $[M - SiMe_3]^+$ 54%. Found (Calcd for $C_{16}H_{32}Cl_2HfN_4Si_2$): C, 32.5 (32.8); H, 5.3 (5.5); N, 9.0 (9.6)%.

[$ZrCl_2(N_2NN^*)$] (9). To a yellow solution of [$ZrCl_2(CH_2SiMe_3)_2(Et_2O)_2$] (1.88 g, 3.87 mmol) in benzene (20 mL) was added dropwise a solution of $H_2N_2NN^*$ (1.63 g, 3.86 mmol) also in benzene (20 mL). The mixture was stirred for 16 h at room temperature to give an opaque dark yellow suspension. This was filtered, and the remaining yellow residues were washed with benzene (2 × 20 mL). The volatile components of the combined filtrates were removed under reduced pressure to give [$ZrCl_2(N_2NN^*)$] (**9**) as a yellow solid. Yield: 2.08 g (92%).

^1H NMR data (300.1 MHz, 298 K, C_6D_6): 9.02 (1 H, d, $^3J = 5.5$ Hz, 6-C_5H_4N), 6.72 (1 H, dd, $^3J = 7.7$ Hz, 7.7 Hz, 4-C_5H_4N), 6.33 (1 H, dd, $^3J = 6.3$ Hz, 5.5 Hz, 5-C_5H_4N), 6.26 (1 H, d, $^3J = 8.0$ Hz, 3-C_5H_4N), 3.48 (2 H, s, $C_5H_4NC\mathit{H}_2$), 3.55 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 3.07 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 2.65 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 2.42 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 1.06 (18 H, s, ^tBu), 0.61 (6 H, s, $SiMe_2$), 0.41 (6 H, s, $SiMe_2$). $^{13}C\{^1H\}$ NMR data (75.5 MHz, 298 K, C_6D_6): 158.0 (2-C_5H_4N), 150.0 (6-C_5H_4N), 138.7 (4-C_5H_4N), 123.4 (5-C_5H_4N), 121.5 (3-C_5H_4N), 63.4 ($C_5H_4N\mathit{C}H_2$), 63.3 ($N\mathit{C}H_2CH_2NSi$), 51.1 ($NCH_2\mathit{C}H_2NSi$), 28.2 ($C\mathit{Me}_3$), 21.5 ($\mathit{C}Me_3$), −2.1 ($SiMe_2$). IR data (KBr plates, Nujol): 1637 (w), 1510 (m), 1420 (s), 1396 (s), 1223 (s), 1199 (w), 1121 (s), 1081 (m), 1047 (s), 998 (m), 869 (m), 826 (w), 880 (m), 766 (s), 722 (m), 711 (s), 656 (m), 615 (m) cm^{-1}. EI mass spectrum: $m/z = 525$ $[M - {}^tBu]^+$ 100%, $m/z = 467$ $[M - SiMe_2 - {}^tBu]^+$ 5%. Found (Calcd for $C_{22}H_{44}Cl_2N_4Si_2Zr$): C, 44.9 (45.3); H, 7.6 (7.6); N, 8.9 (9.6)%.

[$Zr(NMe_2)_2(N_2NN')$] (10). To a colorless solution of [$Zr(NMe_2)_4$] (174 mg, 0.65 mmol) in benzene (20 mL) was added H_2N_2NN' (**3**) (220 mg, 0.65 mmol) in benzene (10 mL). The mixture was stirred at room temperature for 16 h after which time the volatiles were removed under reduced pressure to give crude [$Zr(NMe_2)_2(N_2NN')$] (**10**) as an orange solid. This was extracted into pentane (30 mL) and the resulting orange solution filtered, concentrated to 5 mL, and cooled to −30 °C yielding **10** as single orange crystals suitable for X-ray diffraction. Yield: 0.185 g (55%).

^1H NMR data (500.0 MHz, 298 K, C_6D_6): 8.67 (1 H, d, $^3J = 4.5$ Hz, 6-C_5H_4N), 6.80 (1 H, dd, $^3J = 7.0$, 8.0 Hz, 4-C_5H_4N), 6.47 (1 H, dd, $^3J = 4.5$, 8.0 Hz, 5-C_5H_4N), 6.29 (1 H, d, $^3J = 7.0$ Hz, 3-C_5H_4N), 3.50 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 3.48 (6 H, s, NMe_2), 3.26 (2 H, s, $C_5H_4NC\mathit{H}_2$), 3.22 (6 H, s, NMe_2), 3.05 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 2.91 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 2.14 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 0.19 (18 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR data (125.7 MHz, 298 K, C_6D_6): 158.1 (2-C_5H_4N), 150.4 (6-C_5H_4N), 137.2 (4-C_5H_4N), 122.4 (5-C_5H_4N), 122.2 (3-C_5H_4N), 59.0 ($N\mathit{C}H_2CH_2NSi$), 58.7 ($C_5H_4N\mathit{C}H_2$), 49.2 (NMe_2), 47.0 ($NCH_2\mathit{C}H_2NSi$), 46.1 (NMe_2), 1.5 ($SiMe_3$). IR data (CsBr plates, Nujol): 2760 (s), 2750 (s), 1606 (m), 1573 (w), 1349 (w), 1334 (w), 1307 (w), 1253 (s), 1240 (s), 1155 (w), 1144 (w), 1130 (m), 1083 (m), 1067 (m), 1054 (m), 1041 (m), 1012 (w), 997 (w), 963 (m), 946 (m), 916 (m), 905, (m), 833 (m), 801 (m), 776 (w), 758 (w), 745 (w), 732 (w), 678 (w), 666 (w), 630 (w), 584 (w), 559 (w), 535 (w), 490 (w) cm^{-1}. EI mass spectrum: $m/z = 514$ $[M]^+$ 42%, $m/z = 470$ $[M - NMe_2]^+$ 100%, $m/z = 426$ $[M - 2\ NMe_2]^+$ 67%. Found (Calcd for $C_{20}H_{44}N_6Si_2Zr$): C, 46.2 (46.6); H, 8.4 (8.6); N, 15.6 (16.3)%.

[$Zr(NMe_2)_2(N_2NN^*)$] (11). To a solution of [$Zr(NMe_2)_4$] (0.309 g, 1.16 mmol) in benzene (20 mL) was added dropwise $H_2N_2NN^*$ (0.496 g, 1.17 mmol) in benzene (10 mL). After stirring at room temperature for 16 h, the volatiles were removed under reduced pressure to give an orange-red solid. This was extracted into pentane, filtered, concentrated to 5 mL, and cooled to −80 °C yielding [$Zr(NMe_2)_2(N_2NN^*)$] (**11**) as an orange solid. Yield: 0.449 g (65%). Diffraction-quality, pale orange crystals of [$Zr(NMe_2)_2(N_2NN^*)$] were grown from a saturated hexane solution at room temperature.

^1H NMR data (300.1 MHz, 298 K, C_6D_6): 8.75 (1 H, d, $^3J = 5.5$ Hz, 6-C_5H_4N), 6.81 (1 H, dd, $^3J = 7.7$ Hz, 7.7 Hz, 4-C_5H_4N), 6.49 (1 H, dd, $^3J = 6.2$ Hz, 6.6 Hz, 5-C_5H_4N), 6.29 (1 H, d, $^3J = 8.0$ Hz, 3-C_5H_4N), 3.54 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 3.45 (6 H, s, NMe_2), 3.41 (2 H, s, $C_5H_4NC\mathit{H}_2$), 3.24 (2 H, s, NMe_2), 3.22 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 2.98 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 2.29 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 0.93 (18 H, s, ^tBu), 0.29 (6 H, s, $SiMe_2$), 0.12 (6 H, s, $SiMe_2$). $^{13}C\{H\}$ NMR data (75 MHz, 298 K, C_6D_6): 158.7 (2-C_5H_4N), 150.0 (6-C_5H_4N), 137.4 (4-C_5H_4N), 122.3 (5-C_5H_4N), 121.7 (3-C_5H_4N), 60.3 ($NCH_2\mathit{C}H_2NSi$), 59.7 ($C_5H_4N\mathit{C}H_2$), 49.0 (NMe_2), 48.6 ($N\mathit{C}H_2CH_2NSi$), 45.9 (NMe_2), 28.5 ($C\mathit{Me}_3$), 21.4 ($\mathit{C}Me_3$), −2.7 ($SiMe_2$), −3.6 ($SiMe_2$). IR data (KBr plates, Nujol): 2725 (w), 1671 (w), 1591 (w), 1399 (m), 1357 (m), 1343 (w), 1315 (w), 1227 (w), 1147 (w), 1123 (w), 1111 (w), 1063 (w), 864 (w), 667 (w), 521 (w), 434 (w), 404 (w) cm^{-1}. EI mass spectrum: $m/z = 598$ $[M]^+$ 2%, $m/z = 554$ $[M - NMe_2]^+$ 100%, $m/z = 510$ $[M - 2NMe_2]^+$ 13%. Found (Calcd for $C_{26}H_{56}N_6Si_2Zr$): C, 51.8 (52.0); H, 9.8 (9.4); N, 13.7 (14.0).

Crystal Structure Determinations of (2-NC_5H_4)CH_2N(CH_2CH_2NHTs)$_2$·EtOH (2·EtOH), [$ZrCl_2(N_2NN')$]·0.5C_6H_6 (7·0.5C_6H_6), [$Zr(NMe_2)_2(N_2NN')$] (10), and [$Zr(NMe_2)_2(N_2NN^*)$] (11). Crystal data collection and processing parameters are given in Table 1. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to an Enraf-Nonius DIP2000 image plate or (for **11**) a Kappa-CCD diffractometer equipped with an Oxford Cryosystems low temperature device.[20] Data were collected at low temperature using Mo Kα radiation; equivalent reflections were merged, and the images were processed with the DENZO and SCALEPACK programs.[21] Corrections for Lorentz polarization effects and absorption were performed, and the structures were solved by direct methods using SIR92.[22] Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were placed geometrically

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Table 1. X-ray Data Collection and Processing Parameters for $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NHTs)_2\cdot EtOH$ (**2**·EtOH), $[ZrCl_2(N_2NN')]\cdot 0.5C_6H_6$ (**7**·$0.5C_6H_6$), $[Zr(NMe_2)_2(N_2NN')]$ (**10**), and $[Zr(NMe_2)_2(N_2NN^*)]$ (**11**)

	2·EtOH	**7**	**10**	**11**
empirical formula	$C_{24}H_{30}N_4S_2O_4\cdot C_2H_6O$	$C_{16}H_{32}Cl_2N_4Si_2Zr\cdot 0.5(C_6H_6)$	$C_{20}H_{44}N_6Si_2Zr$	$C_{26}H_{56}N_6Si_2Zr$
fw	548.72	537.81	516.01	600.17
temp/K	175	150	175	150
wavelength/Å	0.71069	0.71069	0.71069	0.71069
space group	$P2_1/c$	$P2_1/n$	$P1$	$P2_1/c$
a/Å	16.9180(5)	8.4280(1)	9.6100(5)	19.2974(5)
b/Å	13.6490(5)	14.3380(4)	11.8690(4)	10.7630(2)
c/Å	25.9760(6)	21.5020(6)	12.5800(7)	17.4036(3)
α/deg	90	90	80.982(3)	90
β/deg	105.271(2)	93.295(2)	76.264(3)	113.1174(9)
γ/deg	90	90	8.220(3)	90
V/Å^3	5786.0	2594.0	1376.6	3324.4
Z	8	4	2	4
d(calcd)/Mg·m^{-3}	1.26	1.38	1.24	1.20
abs coeff/mm^{-1}	0.21	0.73	0.49	0.42
R indices R_1, R_w[a] [$I > 3\sigma(I)$]	0.0386, 0.0469	0.0278, 0.0269	0.0327, 0.0356	0.0829, 0.0930

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \sqrt{\{\Sigma w(|F_o| - |F_c|)^2/\Sigma(w|F_o|^2)\}}$.

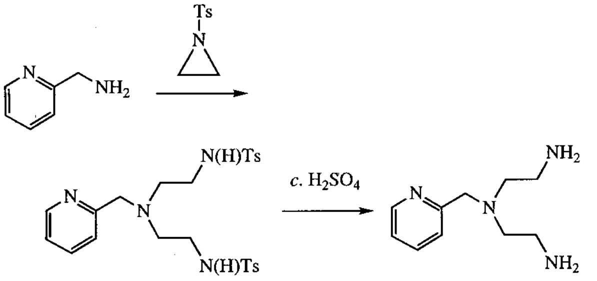
unless stated otherwise. Extinction corrections were applied as required.[23] Crystallographic calculations were performed using SIR92[22] and CRYSTALS.[24]

For **2**·EtOH, there are two molecules of $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NHTs)_2\cdot EtOH$ in the asymmetric unit. Carbon-bound H atoms were placed geometrically and refined in a riding model. Hydrogen atoms bound to N and O were located from Fourier maps and positionally refined with isotropic displacement parameters. For **10**, examination of normalized structure factors and subsequent structure solution, full-matrix refinement, and refined Flack parameter[25] suggested that the space group is $P1$ with $Z = 2$. There is no apparent relationship between the two independent molecules in the unit cell; no unusual correlations were found between the parameters refined for the two independent molecules. Loose similarity and (in the case of the pyridyl moieties) planarity restraints were applied to the distances, angles, and displacement parameters of the pyridyl and $SiMe_3$ moieties of the N_2NN' ligands and to two of the NMe_2 groups [those containing N(5) and N(105)]. For **11**, one of the $SiMe_2{}^tBu$ groups is disordered. A satisfactory anisotropic model could not be developed, and so, this group was refined in the isotropic approximation subject to similarity restraints applied to the Si−Me and C−C distances.

A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for **2**·EtOH, **7**·$0.5C_6H_6$, **10**, and **11** have been deposited at the Cambridge Crystallographic Data Center.

Results and Discussion

Synthesis of the New Protio Ligands and Their Lithiated Derivatives. Fenton and co-workers were the first to describe the synthesis of the parent tetra-amine $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NH_2)_2$ (**1**).[19] They report that reaction of the phthalimide-protected diethylenetriamine $HN(CH_2CH_2N\{1,2\text{-}C_6H_4(CO)_2\})_2$ and 2-chloromethylpyridine affords $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2N\{1,2\text{-}C_6H_4(CO)_2\})_2$ which was then deprotected to give **1**. Unfortunately, we could not find conditions suitable for the reproducible multigram synthesis of **1** and therefore sought an alternative synthesis. Initial efforts attempted to emulate Fenton's route but started from Cloke's readily prepared[26] bis(trimethylsilyl)diethylenetriamine derivative $HN(CH_2CH_2NHSiMe_3)_2$ and 2-chloromethylpyridine with the aim of directly accessing the protio ligand $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NHSiMe_3)_2$ (**3**, hereafter H_2N_2NN'). However, despite exploring numerous combinations of solvent and base in this reaction, we met with little success and eventually turned to the approach summarized in eq 1.



2 **1** (1)

The yield-optimized, multigram synthesis of the di-N-tosylated amine $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NHTs)_2$ (**2**, Ts = $OSO_2\text{-}4\text{-}C_6H_4CF_3$) is conveniently achieved by reaction of commerically available 2-aminomethylpyridine with 2 equiv of N-tosylaziridine[18] as a slurry in EtOH at 35 °C over 48 h. Careful control of the temperature is needed to avoid the ring-opening polymerization of the aziridine, but otherwise, subsequent recrystallization and drying routinely affords **2** in 60%−70% yield in quantities typically in excess of 150 g. Full characterizing data for **2** are listed in the Experimental Section and support the structure illustrated in eq 1. Diffraction-quality crystals of $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NHTs)_2\cdot EtOH$ (**2**·EtOH) were grown by slow evaporation of a saturated EtOH−CH_2Cl_2 (4:1 v/v) solution. The crystals contain two crystallographically indepedent molecules of $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NHTs)_2\cdot EtOH$ in the asymmetric unit, and a view of one of them is given in Figure 1. Hydrogen atoms attached to nitrogen and oxygen were located from Fourier maps and positionally refined. Selected bond lengths

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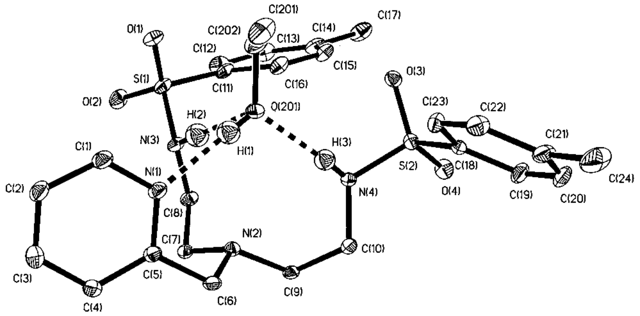


Figure 1. One of the crystallographically independent molecules of (2-$NC_5H_4)CH_2N(CH_2CH_2NHTs)_2$·EtOH (**2**·EtOH). Hydrogen atoms bound to carbon are omitted for clarity. Displacement ellipsoids are drawn at the 25% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for One of the Crystallographically Independent Molecules of (2-$NC_5H_4)CH_2N(CH_2CH_2NHTs)_2$·EtOH (**2**·EtOH); Corresponding Values for the Other Molecule Are Given in Brackets

Distances					
N(1)−H(1)	1.96(3)	[1.92(3)]	C(201)−C(202)	1.402(4)	[1.412(3)]
N(3)−H(2)	0.86(3)	[0.82(4)]	C(202)−O(201)	1.450(4)	[1.491(4)]
N(4)−H(3)	0.80(3)	[0.76(3)]	O(201)−H(1)	0.81(3)	[0.86(3)]
N(3)−S(1)	1.605(2)	[1.608(2)]	O(201)−H(2)	2.19(3)	[1.98(4)]
N(4)−S(2)	1.599(2)	[1.608(2)]	O(201)−H(3)	2.00(3)	[2.32(3)]
S(1)−O(1)	1.431(2)	[1.427(2)]	S(2)−O(3)	1.438(2)	[1.431(2)]
S(1)−O(2)	1.425(2)	[1.432(2)]	S(2)−O(4)	1.423(2)	[1.427(2)]

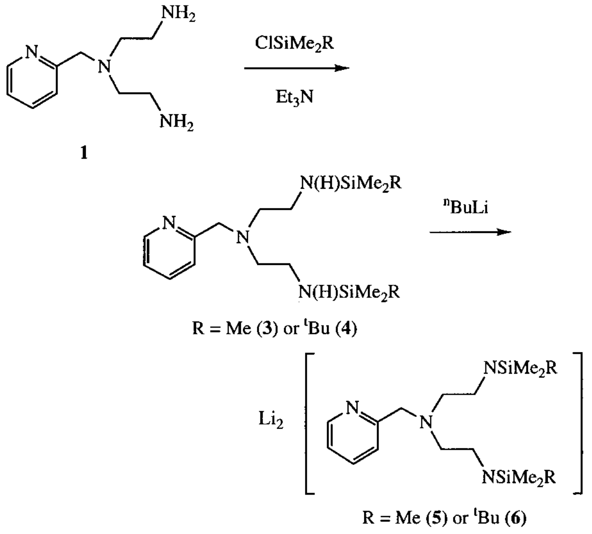
Angles		
C(1)−N(1)−C(5)	118.8(2)	[118.1(2)]
C(1)−N(1)−H(1)	114.9(10)	[115.1(11)]
C(5)−N(1)−H(1)	124.1(10)	[126.0(11)]
C(6)−N(2)−C(7)	112.0(2)	[110.1(2)]
C(6)−N(2)−C(9)	111.4(2)	[112.2(2)]
C(7)−N(2)−C(9)	110.2(2)	[110.1(2)]
C(8)−N(3)−S(1)	119.9(2)	[121.4(2)]
C(8)−N(3)−H(2)	119(3)	[116(3)]
S(1)−N(3)−H(2)	109(3)	[112(3)]
C(10)−N(4)−S(2)	121.3(2)	[119.5(2)]
C(10)−N(4)−H(3)	116(2)	[115(3)]
S(2)−N(4)−H(3)	108(2)	[111(3)]
N(1)−H(1)−O(201)	171(3)	[166(3)]
N(3)−H(2)−O(201)	179(3)	[179(4)]
N(4)−H(3)−O(201)	173(3)	[174(4)]
H(1)−O(201)−C(202)	114(3)	[107(3)]
H(2)−O(201)−C(202)	116.1(10)	[131.3(12)]
H(3)−O(201)−C(202)	126.9(9)	[117.1(9)]
H(2)−O(201)−H(3)	88.7(13)	[86(2)]
H(2)−O(201)−H(1)	84(2)	[84.9(14)]
H(3)−O(201)−H(1)	114(3)	[119(3)]

and angles for both molecules are listed in Table 2 and are not substantially dissimilar; discussion will concentrate on those for the molecule illustrated.

Figure 1 confirms the connectivity for **2** illustrated in eq 1. The bond lengths and angles within the (2-$NC_5H_4)CH_2N(CH_2CH_2NHTs)_2$ molecule itself are unexceptional with regard to typical ranges.[27] Of interest is the incorporation of an EtOH molecule of crystallization held in place through three near-linear hydrogen bonds. Two are donated by the amino nitrogens N(3) and N(4), and the other is from the hydroxyl group of EtOH and accepted by the pyridyl nitrogen N(1). The angles subtended at O(201) span the range 84(2)°−126.9(9)°, but clearly, the geometry is approximately tetrahedral as would be expected on the basis of the use of sp^3 hybrid orbitals. There is no interaction between the tertiary nitrogen N(2) and the EtOH, but in most other respects, the "coordination mode" of **2** to EtOH anticipates that between the bis(*N*-trialkylsilyl) homologues N_2NN' and N_2NN^* ligands and metal centers as described later.

Deprotection of the tosylated tetra-amine is most easily achieved using relatively harsh conditions whereby **2** is heated at 90 °C in 18 M H_2SO_4 for 48 h followed by cautious basification and extraction into dichloromethane. The compound (2-$NC_5H_4)CH_2N(CH_2CH_2NH_2)_2$ (**1**) is obtained as a yellow oil that is >95% pure by ^1H NMR spectroscopy. The oil can be distilled carefully at Schlenk line vacuum using a Kugelrohr apparatus at 180 °C to give pure **1** in very good yield (83%) in 5−10 g quantities. The spectroscopic properties of **1** prepared via this route are identical to those described previously by Fenton.[19]

Equation 2 summarizes the synthesis of protio ligands (2-$NC_5H_4)CH_2N(CH_2CH_2NHSiMe_2R)_2$ [R = Me **3** (H_2N_2NN') or ^tBu **4** ($H_2N_2NN^*$)] and their lithiated derivatives Li_2N_2NN' (**5**) and $Li_2N_2NN^*$ (**6**). Thus, reaction of **1** with $ClSiMe_2R$ (R = Me or ^tBu) in the presence of an excess of Et_3N at 0 °C in THF gave **3** (75%) or **4** (93%) in good yields after separation from the triethylammonium chloride side products. Attempts to distill either compound at high vacuum lead to partial decomposition. However, the products obtained after initial extraction are sufficiently clean to be used without additional purification. The characterizing data for both protio ligands are entirely consistent with the proposed structures. As shown later, the protio ligands themselves can be used directly in reaction with transition metal complexes, but it is clearly advantageous (in principle) to have in hand lithiated derivatives, too, for use via salt elimination reactions.



(2)

Compounds **3** and **4** were readily lithiated by the dropwise addition of ^nBuLi in hexanes to a cold (−78 °C) pentane solution of the protio ligands followed by stirring at room temperature for 2−4 h. Separation of the red or orange supernatant from the white solids so-formed gave Li_2N_2NN' (**5**) or $Li_2N_2NN^*$ (**6**) in ~60%−70% yield. Stirring the lithiated ligands in the reaction mixture for significantly

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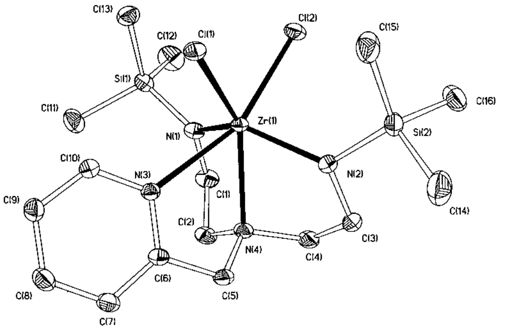


Figure 2. Molecular structure of $[ZrCl_2(N_2NN')]$ (**7**). Hydrogen atoms and benzene molecule of crystallization omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level.

longer periods than 2−4 h, or adding the ^nBuLi at temperatures higher than −78 °C, leads to reduced yields. The lithiated species **5** and **6** are air- and moisture-sensitive white powders that dissolve easily in nonchlorinated aromatic solvents or ethers. While the structures shown in eq 2 for **5** and **6** are indicative of the general stoichiometry of these complexes, it is possible that in the solid state these lithiated amides exist as bi- or polynuclear aggregates.[28−30] However, we have not yet been able to obtain diffraction-quality crystals in order to explore these possibilities.

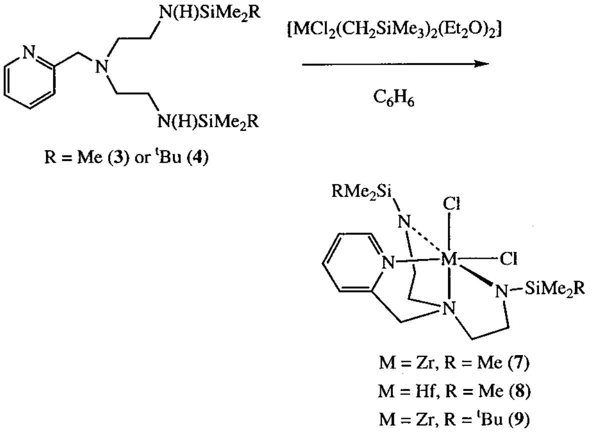
Synthesis of the Zirconium and Hafnium Dichloride and Bis(dimethylamide) Derivatives. We first attempted to prepare group 4 dichloride complexes of the diamide−diamine ligands from the lithiated derivatives Li_2N_2NN' (**5**) or $Li_2N_2NN^*$ (**6**) and the corresponding MCl_4 or $MCl_4(THF)_2$ (M = Ti or Zr) under a variety of conditions with varying temperature, solvents, and rates and methods of addition. In all of these cases, we obtained ill-defined mixtures in which there was some evidence of $ClSiMe_3$ being produced, arising presumably from degradation of the silylamine functionalities of the ligands themselves. Therefore, the remainder of this contribution focuses on the synthesis of zirconium and hafnium dichloride and bis(dimethylamide) complexes of N_2NN' and N_2NN^*, but starting instead from the protio ligands H_2N_2NN' (**3**) and $H_2N_2NN^*$ (**4**). However, the lithiated analogues **5** and **6** are nevertheless useful precursors to monochloride complexes of Sc and Y[31] and imido complexes of titanium and the heavier group 5 elements.[32]

The syntheses of the zirconium and hafnium *cis*-dichloride complexes $[MCl_2(N_2NN')]$ (M = Zr **7** or Hf **8**) and $[ZrCl_2(N_2NN^*)]$ (**9**) are summarized in eq 3. Thus, reaction of the protio ligand H_2N_2NN' with $[MCl_2(CH_2SiMe_3)_2(Et_2O)_2]$ (M = Zr or Hf)[17] in benzene afforded $[MCl_2(N_2NN')]$ as yellow or pale white solids in isolated yields of greater than 90%. A similar reaction gave $[ZrCl_2(N_2NN^*)]$ (**9**), again in greater than 90% yield. While the reaction of $[MCl_2(CH_2SiMe_3)_2(Et_2O)_2]$ with lithiated ligands to form dialkyl[33] or dibenzyl[34] complexes has been reported previously, the use of these complexes with protio ligands to form the corresponding dichloride derivatives apparently has not.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[ZrCl_2(N_2NN')]$ (**7**)

Distances			
Zr(1)−Cl(1)	2.4760(4)	Zr(1)−N(2)	2.085(2)
Zr(1)−Cl(2)	2.5077(5)	Zr(1)−N(3)	2.446(1)
Zr(1)−N(1)	2.070(2)	Zr(1)−N(4)	2.414(1)

Angles			
Cl(1)−Zr(1)−Cl(2)	87.31(2)	Cl(2)−Zr(1)−N(4)	131.09(4)
Cl(1)−Zr(1)−N(1)	120.17(4)	N(1)−Zr(1)−N(4)	72.93(6)
Cl(2)−Zr(1)−N(1)	89.25(4)	N(2)−Zr(1)−N(4)	71.74(5)
Cl(1)−Zr(1)−N(2)	107.40(4)	N(3)−Zr(1)−N(4)	66.74(5)
Cl(2)−Zr(1)−N(2)	90.58(4)	Zr(1)−N(1)−C(1)	119.8(1)
N(1)−Zr(1)−N(2)	132.35(6)	Zr(1)−N(1)−Si(1)	126.93(8)
Cl(1)−Zr(1)−N(3)	77.19(3)	C(1)−N(1)−Si(1)	113.2(1)
Cl(2)−Zr(1)−N(3)	159.21(3)	Zr(1)−N(2)−C(3)	122.8(1)
N(1)−Zr(1)−N(3)	86.73(5)	Zr(1)−N(2)−Si(2)	126.69(8)
N(2)−Zr(1)−N(3)	107.13(5)	C(3)−N(2)−Si(2)	109.2(1)
Cl(1)−Zr(1)−N(4)	141.14(4)		



(3)

The three new compounds **7**−**9** are soluble in aromatic or halogenated solvents, and also in THF, but insoluble in pentane or hexanes. Diffraction-quality crystals of $[ZrCl_2(N_2NN')]\cdot0.5(C_6H_6)$ ($\mathbf{7}\cdot0.5C_6H_6$) were grown from a saturated benzene solution, and the molecular structure of the zirconium complex is shown in Figure 2; selected bond lengths and angles are listed in Table 3.

Molecules of **7** possess six-coordinate metal centers bound to both the amide [N(1) and N(2)] and amine N(4) and pyridyl N(3) donors of N_2NN'. The remaining coordination sites are occupied by mutually cis chloride ligands. Although six-coordinate, the geometry is significantly far from octahedral, presumably because of the constraining nature of the N_2NN' ligand itself. Nevertheless, the metal−ligand distances are all within typical ranges for zirconium[27] with the pyridyl nitrogen being quite firmly bound despite the Cl(1)−Zr−N(3) angle of 77.19(3) Å. The Zr−Cl distances of 2.4760(4) and 2.5077(5) Å differ only slightly, the latter being for the chloride trans to pyridyl. The molecules have approximately C_s symmetry with the molecular mirror plane

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passing through the atoms Zr(1), Cl(1), Cl(2), N(3), and N(4). The pyridyl ring atoms' plane is displaced slightly (by 37°) to one side of the molecular mirror plane probably because of ligand geometric constraints, but possibly also to minimize nonbonded interactions between Cl(1) and the *ortho* hydrogen of the pyridyl ring [i.e., the H bonded to C(10)].

The sums of the angles subtended at the amide nitrogens N(1) and N(2) are 359.9° and 358.7°, respectively, indicating that they are sp^2 hybridized and, in principle, capable of π-donating to the metal center which thus has a maximum possible valence electron count of 16. However, as in other examples of transition metal complexes with strong π-donor ligands,[35] the actual extent of π-donation from the ligand lone pairs can be less than that formally permitted by apparent hybridization alone. In the case of the complexes [$MCl_2(N_2NN')$] and [$ZrCl_2(N_2NN^*)$], it is likely that the actual electron count at the metal is, in fact, best considered as 14 rather than 16. This is because the structure of **7** shows that the amide nitrogen 2p orbitals accommodating the lone pairs [assumed to be orthogonal to the trigonal planes formed by atoms N(1), Si(1), C(1), Zr(1) and N(2), Si(2), C(3), Zr(1)] are coplanar and approximately trans to each other. In this case, the two filled 2p(π) donor orbitals must compete for one zirconium 4d(π) acceptor orbital, and the result of this three-orbital four-electron interaction would be the formation of three metal−nitrogen π-orbitals of the types bonding (holding 2 electrons), nonbonding (nitrogen-based holding 2 electrons, not donated therefore to Zr), and antibonding (unoccupied).

The ^{1}H and ^{13}C NMR spectra of [$MCl_2(N_2NN')$] (**7**, **8**) and [$ZrCl_2(N_2NN^*)$] (**9**) are consistent with the solid-state structure of **7**. The two $CH_2CH_2SiMe_2R$ "arms" of the ligands are equivalent, consistent with C_s symmetry on the NMR time scale. The ortho hydrogens of the pyridyl groups appear in the range ~9.0−8.8 ppm in benzene-d_6, significantly downfield from the corresponding positions for the protio ligands H_2N_2NN' and $H_2N_2NN^*$ (~8.5 ppm) in the same solvent, and therefore indicate that the pyridyl moieties are coordinated in solution. The four diastereotopic methylene hydrogens of the $CH_2CH_2NSiMe_2R$ "arms" give rise to four mutually coupled multiplets; the $SiMe_3$ group hydrogens in [$MCl_2(N_2NN')$] appear as a singlet, whereas the $SiMe_2{}^tBu$ group in [$MCl_2(N_2NN^*)$] gives rise to two singlets for the inequivalent methyl groups each of relative intensity 6 H (with respect to the pyridyl *ortho* hydrogen) and a further singlet of intensity 18 H for the ^{t}Bu groups.

Transamination reactions of [$Zr(NMe_2)_4$] to form zirconium bis(dimethylamide) complexes of diamide ligands are well established.[36] The analogous reactions of H_2N_2NN' or $H_2N_2NN^*$ with [$Zr(NMe_2)_4$] proceed smoothly with elimination of $HNMe_2$ (observed by NMR) to form the complexes [$Zr(NMe_2)_2(N_2NN')$] (**10**) and [$Zr(NMe_2)_2(N_2NN^*)$] (**11**) as shown in eq 4. The new compounds were isolated in 55%−65% yields as air- and moisture-sensitive orange crystalline solids. The bis(dimethylamide) complexes have considerably better solubility in alkane solvents than the corresponding dichlorides as would be expected.

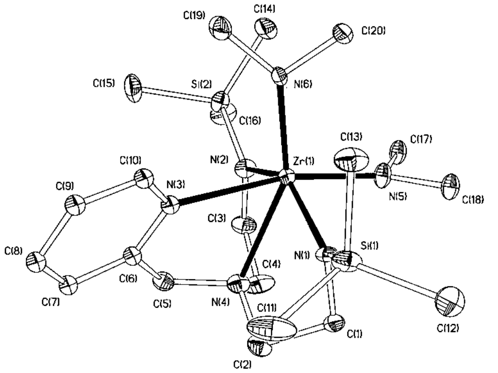


Figure 3. One of the crystallographically independent molecules of [Zr-(NMe_2)$_2$(N_2NN')] (**10**). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 25% probability level.

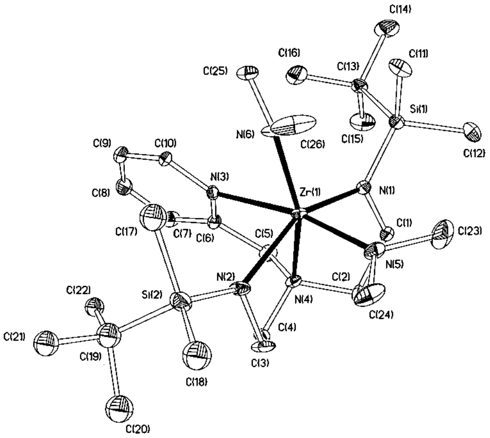
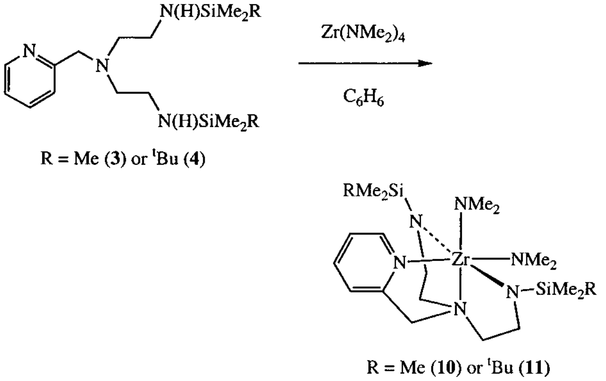


Figure 4. Molecular structure of [$Zr(NMe_2)_2(N_2NN^*)$] (**11**). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 25% probability level.



(4)

Diffraction-quality crystals of both **10** and **11** were grown from alkane solutions, and the molecular structures are shown in Figures 3 and 4; selected bond lengths and angles are given in Tables 4 and 5. Crystals of **10** contain two independent [$Zr(NMe_2)_2(N_2NN')$] molecules in the asymmetric unit. There are no significant differences between them, and discussion refers to the molecule illustrated in Figure 3.

The overall geometries of [$Zr(NMe_2)_2(N_2NN')$] and [Zr-(NMe_2)$_2$(N_2NN^*)] are analogous to that of the dichloride

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for One of the Crystallographically Independent Molecules of $[\mathrm{Zr(NMe_2)_2(N_2NN')}]$ (**10**); Corresponding Values for the Other Molecule Are Given in Brackets

Distances

Zr(1)−N(1)	2.15(5)	[2.18(5)]	Zr(1)−N(6)	2.12(4)	[2.04(5)]
Zr(1)−N(2)	2.16(4)	[2.13(5)]	N(1)−C(1)	1.50(7)	[1.44(8)]
Zr(1)−N(3)	2.51(4)	[2.58(4)]	N(1)−Si(1)	1.73(5)	[1.68(6)]
Zr(1)−N(4)	2.42(6)	[2.46(5)]	N(2)−C(3)	1.47(7)	[1.45(8)]
Zr(1)−N(5)	2.03(6)	[2.14(5)]	N(2)−Si(2)	1.71(5)	[1.76(5)]

Angles

N(1)−Zr(1)−N(2)	142(2)	[142(2)]
N(1)−Zr(1)−N(3)	80(2)	[81(2)]
N(2)−Zr(1)−N(3)	97(2)	[95(2)]
N(1)−Zr(1)−N(4)	74(2)	[74(2)]
N(2)−Zr(1)−N(4)	71(2)	[712)]
N(3)−Zr(1)−N(4)	67.5(14)	[65.9(13)]
N(1)−Zr(1)−N(5)	87(2)	[90(2)]
N(2)−Zr(1)−N(5)	91(2)	[90(2)]
N(3)−Zr(1)−N(5)	167(2)	[170.6(13)]
N(4)−Zr(1)−N(5)	105(2)	[109(2)]
N(1)−Zr(1)−N(6)	112(2)	[1122)]
N(2)−Zr(1)−N(6)	106(2)	[105(2)]
N(3)−Zr(1)−N(6)	86(2)	[84(2)]
N(4)−Zr(1)−N(6)	152(2)	[149(2)]
N(5)−Zr(1)−N(6)	103(2)	[102(2)]
Zr(1)−N(1)−C(1)	109(3)	[110(4)]
Zr(1)−N(1)−Si(1)	136(3)	[137(3)]
C(1)−N(1)−Si(1)	115(4)	[113(4)]
Zr(1)−N(2)−C(3)	117(4)	[121(4)]
Zr(1)−N(2)−Si(2)	128(3)	[129(3)]
C(3)−N(2)−Si(2)	116(4)	[110(4)]

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[\mathrm{Zr(NMe_2)_2(N_2NN^*)}]$ (**11**)

Distances

Zr(1)−N(1)	2.17(1)	Zr(1)−N(6)	2.09(1)
Zr(1)−N(2)	2.14(1)	N(1)−Si(1)	1.72(1)
Zr(1)−N(3)	2.52(1)	N(1)−C(1)	1.47(2)
Zr(1)−N(4)	2.45(1)	N(2)−Si(2)	1.69(1)
Zr(1)−N(5)	2.11(1)	N(2)−C(3)	1.52(2)

Angles

N(1)−Zr(1)−N(2)	144.2(4)	N(2)−Zr(1)−N(6)	108.6(5)
N(1)−Zr(1)−N(3)	93.4(4)	N(3)−Zr(1)−N(6)	86.7(4)
N(2)−Zr(1)−N(3)	82.5(4)	N(4)−Zr(1)−N(6)	154.0(4)
N(1)−Zr(1)−N(4)	71.2(4)	N(5)−Zr(1)−N(6)	102.6(5)
N(2)−Zr(1)−N(4)	74.3(4)	Zr(1)−N(1)−Si(1)	131.7(6)
N(3)−Zr(1)−N(4)	67.8(4)	Zr(1)−N(1)−C(1)	117.1(8)
N(1)−Zr(1)−N(5)	89.4(5)	Si(1)−N(1)−C(1)	110.8(9)
N(2)−Zr(1)−N(5)	89.1(6)	Zr(1)−N(2)−Si(2)	135.7(7)
N(3)−Zr(1)−N(5)	169.1(4)	Zr(1)−N(2)−C(3)	109.0(9)
N(4)−Zr(1)−N(5)	103.3(5)	Si(2)−N(2)−C(3)	114.0(9)
N(1)−Zr(1)−N(6)	106.6(5)		

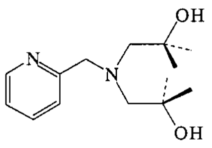
$[\mathrm{ZrCl_2(N_2NN')}]$ (**10**) and feature κ^4-bound diamide−diamine ligands and mutually *cis*-coordinated $\mathrm{NMe_2}$ ligands. The zirconium−nitrogen bond lengths associated with the $\mathrm{Zr(N_2NN')}$ and $\mathrm{Zr(N_2NN^*)}$ moieties are experimentally identical for the two structures. In both compounds, all of these bond lengths are longer that the corresponding ones in $[\mathrm{ZrCl_2(N_2NN')}]$, reflecting the more crowded nature of the bis(dimethylamide) homologues and the better electron-donating ability of $\mathrm{NMe_2}$ in comparison to that of chloride. As for **7**, the zirconium−ligand distances in **10** and **11** are within acceptable ranges.

Both of the bis(dimethylamide) compounds possess approximately C_s symmetry with the mirror plane passing through atoms Zr(1), N(3), N(4), N(5), and N(6). As in **7**, the pyridyl rings are bent slightly out of the approximate mirror plane and away from the closest $\mathrm{NMe_2}$ methyl group (that with C(19) in **10** and C(25) in **11**), presumably for similar reasons to those proposed for **7**. The methyl groups of the $\mathrm{NMe_2}$ ligand containing N(6) are also slightly twisted out of the approximate mirror plane (so as to move C(19) and C(25) away from the pyridyl group). This is reflected in the values of the dihedral angles: N(5)−Zr(1)−N(6)−C(20) = 19.2° for **10** and N(5)−Zr(1)−N(6)−C(26) = 20.6° for **11** (if the $\mathrm{NMe_2}$ carbons were in the mirror plane, these angles would be 0°). The bulky ^{t}Bu groups of the $\mathrm{N_2NN^*}$ ligand in **11** are oriented away from the $\mathrm{NMe_2}$ groups and "back" toward the most open part of the ligand periphery. There is no apparent effect of these bulky groups on the molecular structure.

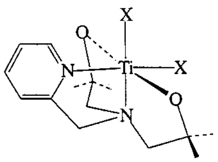
All of the amide nitrogens in both complexes have sums of angles subtended at nitrogen that suggest sp^2 hybridization for these atoms. Notwithstanding the obvious deviations from octahedral geometry at zirconium, and the small twisting out of the mirror plane of the $\mathrm{NMe_2}$ group cis to pyridyl, the lone pairs of the $\mathrm{NMe_2}$ ligands appear to be approximately orthogonal to each other so as to minimize mutual competition for the available 4d(π) acceptor orbitals at zirconium. The lone pairs of the $\mathrm{N_2NN'}$ and $\mathrm{N_2NN^*}$ amide nitrogens are again effectively coplanar and mutually trans and, therefore, in competition with each other for a single 4d(π) metal acceptor orbital. The orientation of the $\mathrm{NMe_2}$ ligand lone pairs appears to minimize competition with the $\mathrm{N_2NN'}$ and $\mathrm{N_2NN^*}$ amide nitrogen lone pairs. Therefore, we propose that $[\mathrm{Zr(NMe_2)_2(N_2NN^*)}]$ formally possesses an 18 valence electron count, with both of the $\mathrm{NMe_2}$ ligands donating in full their nitrogen π-lone pairs, while the $\mathrm{N_2NN'}$ and $\mathrm{N_2NN^*}$ amide nitrogens can only donate one lone pair between them, the other residing in a ligand-based orbital as in the dichloride $[\mathrm{ZrCl_2(N_2NN')}]$ (**7**). However, despite these apparent differences in zirconium−nitrogen bonding, the Zr−$\mathrm{N_{amide}}$ distances in the two bis(dimethylamide) complexes **10** and **11** are not (with experimental error) significantly different, although there is an apparent tendency for the Zr−$\mathrm{NMe_2}$ distances to be slightly shorter. Of course, this could also (or alternatively) reflect any diamide−diamine ligand geometric constraints, the different substituents at nitrogen, and/or the fact that the $\mathrm{NMe_2}$ ligands are trans only to amine donors whereas the $\mathrm{N_2NN'}$ and $\mathrm{N_2NN^*}$ amide nitrogens are approximately trans to each other (i.e., to better σ-donors than neutral amine-type donors).

The ^{1}H and ^{13}C NMR spectra of $[\mathrm{Zr(NMe_2)_2(N_2NN')}]$ (**10**) and $[\mathrm{Zr(NMe_2)_2(N_2NN^*)}]$ (**11**) are similar to those of corresponding dichlorides and are consistent with molecular C_s symmetry on the NMR time scale. The pyridyl group ortho hydrogen resonances appear at ~8.7 ppm, which is again downfield of the positions for the protio ligands in benzene-d_6, and indicate that this group is coordinated in solution. The $\mathrm{NMe_2}$ groups appear as two singlets (relative intensity 6 H each). This is not expected from the X-ray structures in which the methyls of the $\mathrm{NMe_2}$ ligands cis to the pyridyl groups are in chemically different environments, and so, in principle, one would expect the see three $\mathrm{NMe_2}$ signals in the ratio 3 H/3 H/6 H. Cooling a sample of **10** in toluene-d_8 to −90 °C gave no change in the appearance of the^{1}H NMR spectrum, and so, we conclude that rotation about the Zr−NMe_2 bonds is fast on the NMR time scale in these complexes (as is usually the case with NMe_2 ligands).

We have attempted to prepare the titanium complexes $[TiCl_2(N_2NN')]$ and $[Ti(NMe_2)_2(N_2NN)]$ via similar routes to those used for the zirconium congeners **7** and **10**. However, reaction of H_2N_2NN' with $[TiCl_2(NMe_2)_2]$ gave intractable products rather than the desired $[TiCl_2(N_2NN')]$ (although the expected side product $NHMe_2$ was observed in an NMR tube scale experiment). Prolonged heating of H_2N_2NN' with $[Ti(NMe_2)_4]$ in benzene failed to produce any new products at all. We believe that the coordination pocket of the N_2NN' ligand might be too crowded to accommodate six-coordinate first row metal complexes. We have been able to prepare in other studies several five-coordinate complexes of the type $[M(X)(N_2NN')]$ (M = Sc, X = Cl or CH_2SiMe_3;[31] M = Ti, X = N^tBu or NAr[32]). Furthermore, using the less sterically demanding bis(alkoxide)−diamine analogue of N_2NN', namely $(2\text{-}NC_5H_4)CH_2N\{CH_2C(Me)_2O\}_2$ (abbreviated as O_2NN'), we have been able to make the six-coordinate dichloride and bis(dimethylamide) complexes $[TiX_2(O_2NN')]$ (X = Cl or NMe_2) shown.[37]



H_2O_2NN'



X = Cl or NMe_2

Conclusions

We have reported the multigram scale syntheses of the protio ligands H_2N_2NN' and $H_2N_2NN^*$, along with the dilithiated homologues Li_2N_2NN' and $Li_2N_2NN^*$. Zirconium and hafnium dichloride derivatives of the type $[MX_2(L)]$ (M = Zr or Hf; X = Cl or NMe_2; L = N_2NN' or N_2NN^*) have been prepared and all show that the N_2NN' and N_2NN^* ligands provide a well-defined coordination environment for these larger metals. Attempted synthesis of titanium dichloride or bis(dimethylamide) complexes of N_2NN' were unsuccessful. Studies of the organometallic and reaction chemistry of early transition metal complexes of the N_2NN' and N_2NN^* ligand systems, their *N*-aryl substituted homologues, as well as their applications in lanthanide and actinide chemistry, are underway and will be reported in due course.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NHTs)_2\cdot EtOH$ (**2**·EtOH), $[ZrCl_2(N_2NN')]\cdot 0.5C_6H_6$ (**7**·$0.5C_6\mathbf{H_6}$), $[Zr(NMe_2)_2(N_2NN')]$ (**10**), and $[Zr(NMe_2)_2(N_2NN^*)]$ (**11**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) Cowhig, D. A.; Skinner, M. E. G.; Toupance, T.; Mountford, P. Unpublished results.