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Zirconium Complexes of Diamine−Bis(phenolate) Ligands: Synthesis, Structures, and Solution Dynamics

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A family of new organometallic and coordination compounds supported by the diamine−bis(phenolate) ligands $O_2NN'^{Me}$ and $O_2NN'^{tBu}$ are reported [$H_2O_2NN'^{R} = (2\text{-}C_5H_4N)CH_2N(CH_2\text{-}2\text{-}HO\text{-}3,5\text{-}C_6H_2R_2)_2$, where R = Me (**1a**) or ^tBu (**1b**)]. Reaction of $H_2O_2NN'^{R}$ with sodium hydride in THF gives the corresponding sodium salts $Na_2O_2NN'^{R}$ (R = Me (**2a**) or ^tBu (**2b**)). Reaction of $H_2O_2NN'^{R}$ with $Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2$ gives the *cis*-dichloride derivatives $ZrCl_2(O_2NN'^{R})$ (R = Me (**3a**) or ^tBu (**3b**)), which exist as two isomers (possessing either C_1 (major) or C_s symmetry) in dynamic equilibrium with each other in solution. The compound **3b** can also be prepared from $Na_2O_2NN'^{tBu}$ and $ZrCl_4(THF)_2$, but reaction of $Na_2O_2NN'^{Me}$ with either $ZrCl_4$ in benzene or $ZrCl_4(THF)_2$ in THF gives mixtures of **3a** and the eight-coordinate bis(diamine−bis(phenolate)) complex $Zr(O_2NN'^{Me})_2$ (**4a**). The latter can also be prepared from 2 equiv of $H_2O_2NN'^{Me}$ and $Zr(CH_2SiMe_3)_4$. Treatment of $Zr(NMe_2)_4$ with $H_2O_2NN'^{tBu}$ leads to the bis(dimethylamide) derivative $Zr(NMe_2)_2(O_2NN'^{tBu})$ (**5b**). Similar protonolysis reactions between ZrR'_4 (R′ = CH_2SiMe_3, CH_2CMe_3, or CH_2Ph) give the corresponding organometallic alkyl or benzyl compounds $ZrR'_2(O_2NN'^{R})$ [R′ = CH_2SiMe_3 (**8a**, **8b**), CH_2CMe_3 (**9a**, **9b**), or CH_2Ph (**10a**, **10b**); R = Me (suffix **a**) or ^tBu (suffix **b**)]. The dichloride complexes $ZrCl_2(O_2NN'^{R})$ (**3a**, **3b**) are also precursors to new organometallic derivatives, and treatment with LiR′ (R′ = Me or CH_2SiMe_3) or R′MgCl (R′ = CH_2Ph or C_3H_5) yields $ZrR'_2(O_2NN'^{R})$ [R′ = Me (**6a**, **6b**), η^3-C_3H_5 (**7b**), CH_2SiMe_3 (**8a**, **8b**), CH_2Ph (**10a**, **10b**)]. The thermally unstable bis(η^3-allyl) complex **7b** is highly fluxional in solution. Reaction of the dibenzyl compound **10a** or **10b** with $B(C_6F_5)_3$ in the presence of THF gives the cationic complexes $[Zr(CH_2Ph)(THF)(O_2NN'^{R})]^+$ as the $[PhCH_2B(C_6F_5)_3]^-$ salts (**11a**, **11b**). The X-ray crystal structures of the compounds **3a**, **3b**, **4a**, **5b**, **6a**, **6b**, and **10a** are described.

Introduction

Following on from the historical dominance of metallocene and other cyclopentadienyl-based complexes in the development of group 4 organometallic chemistry[1] have been intense recent efforts to expand the repertoire of new dianionic supporting ligand sets. Many new systems have been described over the past 10 years in particular[2−9] in the drive for both fundamental new chemistry and potential applications in, for example, polymerization catalysis.[10] Of particular relevance to the new chemistry reported in this contribution are the recent developments in group 4 organometallic and catalytic chemistry with dianionic $\{N_2O_2\}$ donor ligand sets from the groups of Floriani,[11,12] Jordan,[13−16] Scott,[17,18] Coates,[19] Fujita,[20,21] Kol and Goldberg,[22−24] and others.[25]

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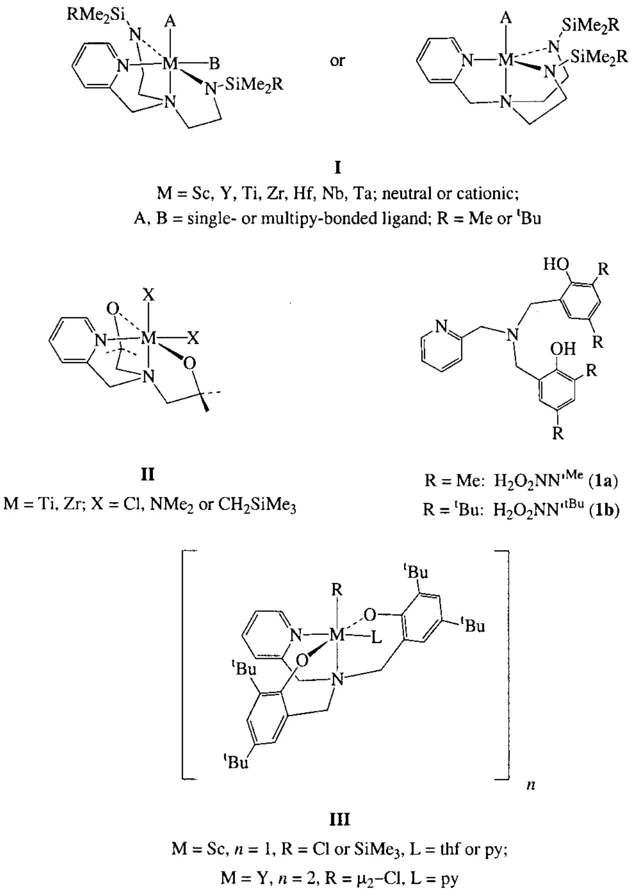
Chart 1



I

M = Sc, Y, Ti, Zr, Hf, Nb, Ta; neutral or cationic;
A, B = single- or multipy-bonded ligand; R = Me or ᵗBu

II

M = Ti, Zr; X = Cl, NMe$_2$ or CH$_2$SiMe$_3$

R = Me: H$_2$O$_2$NN$'^{Me}$ (**1a**)
R = ᵗBu: H$_2$O$_2$NN$'^{tBu}$ (**1b**)

III

M = Sc, *n* = 1, R = Cl or SiMe$_3$, L = thf or py;
M = Y, *n* = 2, R = μ$_2$–Cl, L = py

In our group we have been developing new diamine–bis(amide) ligands of the type (2-C$_5$H$_4$N)CH$_2$N(CH$_2$CH$_2$NSiMe$_2$R)$_2$ (abbreviated as N$_2$NN′, where R = Me or ᵗBu).[26] These dianionic, tetradentate ligands proved to be useful supporting environments for early transition metal, six- and five-coordinate complexes of the general type M(A)(B)(N$_2$NN′) and M(A)(N$_2$NN′) (**I**, Chart 1). We have developed in parallel studies the diamine–bis(alkoxide) ligand (2-C$_5$H$_4$N)CH$_2$N(CH$_2$CMe$_2$O)$_2$ and have reported some new titanium and zirconium coordination and organometallic complexes of the type **II** in Chart 1.[26,27] Recently we have extended these studies to include complexes of the diamine–bis(phenoxide) ligands O$_2$NN$'^{Me}$ and O$_2$NN$'^{tBu}$ [H$_2$O$_2$NN$'^{R}$ = (2-C$_5$H$_4$N)CH$_2$N(CH$_2$-2-HO-3,5-C$_6$H$_2$R$_2$)$_2$, where R = Me (**1a**) or ᵗBu (**1b**);[28] see Chart 1]. The more sterically demanding ligand O$_2$NN$'^{tBu}$ supports new scandium and yttrium coordination and organometallic complexes of the type **III** in Chart 1.[27,29] We were also interested to extend these ligands to other transition metals. Here we describe new organometallic and coordination chemistry of zirconium supported by diamine–bis(phenolate) ligands. The new compounds include *cis*-dichloride, bis(dimethylamide), dimethyl, bis(η^3-allyl), bis(trimethylsilylmethyl), bis(neopentyl), and dibenzyl derivatives.

Experimental Section

General Methods and Instrumentation. All manipulations of air- and/or moisture-sensitive compounds were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or dinitrogen. Solvents used with air- and/or moisture-sensitive compounds were predried over activated 4 Å molecular sieves and were refluxed over potassium (THF, hexane, or benzene), sodium (toluene), sodium/potassium alloy (pentane), sodium dispersion/benzophenone (diethyl ether), or calcium hydride (dichloromethane) under a dinitrogen atmosphere and collected by distillation. Deuterated solvents for air- and/or moisture-sensitive compounds were dried over potassium (C$_6$D$_6$) or calcium hydride (CD$_2$Cl$_2$ and C$_5$D$_5$N), distilled under reduced pressure, and stored under dinitrogen in ampules fitted with J. Young Teflon valves. NMR samples of air- and/or moisture-sensitive compounds were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. All other solvents and reagents were used as received from commercial suppliers.

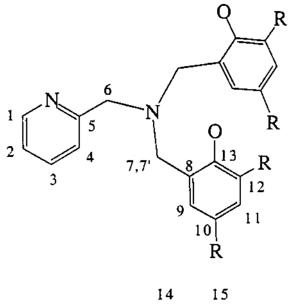
^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Varian Venus 300 or Varian Unity Plus 500 spectrometers. ^{1}H and ^{13}C assignments were confirmed when necessary with the use of one-dimensional NOE experiments and of two-dimensional ^{1}H–^{1}H COSY, ^{1}H–^{1}H NOESY, ^{13}C–^{1}H HSQC, and HMBC NMR experiments. All spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to trimethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ (ppm); coupling constants, in hertz.

Infrared spectra were prepared as Nujol mulls between KBr plates and were recorded on a Perkin-Elmer 1710 FTIR spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}), “vs” stands for very strong, “s” for strong, “m” for medium, “w” for weak, and “vw” for very weak.

Mass spectra were recorded on an AEI MS 902 or Micomass Autospec 500 mass spectrometer. Elemental analyses were carried out by the analytical services of the University of Oxford’s Inorganic Chemistry Laboratory.

Literature Preparations. The compounds H$_2$O$_2$NN$'^{tBu}$ (**1b**),[28] ZrCl$_4$(THF)$_2$,[30] Zr(CH$_2$SiMe$_3$)$_2$Cl$_2$(Et$_2$O)$_2$,[31] Zr(CH$_2$SiMe$_3$)$_4$,[32] Zr(CH$_2$CMe$_3$)$_4$,[33] and Zr(CH$_2$Ph)$_4$[34,35] were prepared according to previously reported procedures.

Syntheses. To clarify the NMR chemical shift assignments, diagrams showing a concise atom-labeling scheme accompany each new type of ligand or complex.



14 15
For R = Me: *o*-Me, *p*-Me
For R = *t*-Bu: *o*-CMe$_3$, *p*-CMe$_3$
14 15 16 17

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_N_-(2-Pyridylmethyl)-_N_,_N_-bis(2′-hydroxy-3′,5′-dimethylbenzyl)amine ($H_2O_2NN'^{Me}$, 1a). 2-Aminomethylpyridine (2.70 g, 24.9 mmol), 2,4-dimethylphenol (6.10 g, 49.9 mmol), and paraformaldehyde (1.50 g, 49.9 mmol) were dissolved in absolute ethanol (50 mL) in a thick-walled ampule equipped with a Rotaflo valve. The mixture was stirred at 110 °C for 3 days. The volatiles were subsequently removed under reduced pressure to leave an orange oil. This oil was triturated with 30 mL of absolute ethanol to yield a white powder, which was isolated by filtration and drying. Yield: 4.80 g (51%).

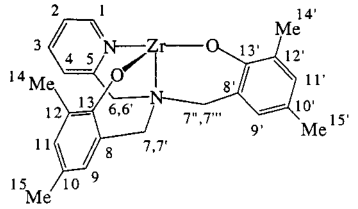
^{1}H NMR (300.18 MHz, $CDCl_3$, 293 K): δ 10.42 (s, 2H, OH), 8.69 (d, $^3J_{H1-H2} = 5.8$ Hz, 1H, H_1), 7.68 (ddd, $^3J_{H3-H4} = 8.2$ Hz, $^3J_{H3-H2} = 7.0$ Hz, $^4J_{H3-H1} = 1.8$ Hz, 1H, H_3), 6.26 (dd, $^3J_{H2-H1} = 5.8$ Hz, $^3J_{H2-H3} = 7.0$ Hz, 1H, H_2), 7.10 (d, $^3J_{H4-H3'} = 8.2$ Hz, 1H, H_4), 6.90 (d, $^4J_{H11-H9} = 1.2$ Hz, 2H, H_{11}), 6.74 (d, $^4J_{H9-H11} = 1.2$ Hz, 2H, H_9), 3.82 (s, 2H, H_6), 3.74 (s, 4H, H_7), 2.28 (s, 3H, H_{14}), 2.21 (s, 3H, H_{15}). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 293 K): δ 156.1 (C_5), 153.1 (C_{13}), 148.2 (C_1), 137.4 (C_3), 131.1 (C_{11}), 128.4 (C_9), 127.4 (C_{12}), 125.4 (C_{10}), 123.6 (C_4), 122.4 (C_2), 120.7 (C_8), 56.4 (C_7), 55.4 (C_6), 20.3 (C_{15}), 16.2 (C_{14}). MS-EI (*m*/*z*): 377 (50%) $[MH]^+$, 243 (70%) $[MH - CH_2(C_6H_2(CH_3)_2O)]^+$. Anal. Found (Calcd for $C_{24}H_{28}N_2O_2$): C 76.55 (76.56), H 7.40 (7.50), N 7.52 (7.44).

_N_-(2-Pyridylmethyl)-_N_,_N_-bis(2′-oxo-3′,5′-dimethylbenzylsodium)amine ($Na_2O_2NN'^{Me}$, 2a). A solution of $H_2O_2NN'^{Me}$ (1.51 g, 4 mmol) in THF (20 mL) was added dropwise to a NaH suspension (0.388 g, 16.1 mmol) in THF (20 mL) at −80 °C. Upon progressive return to room temperature, a gas was evolved and the stirring at room temperature was continued for 2 h. The mixture was then filtered and the solvent was removed under reduce pressure to give a bright white powder after drying overnight under vacuum at 90 °C. Yield: 1.51 g (88%). The THF content was determined by careful integration of the ^{1}H NMR spectrum.

^{1}H NMR (300.18 MHz, C_5D_5N, 293 K): δ 8.16 (d, $^3J_{H1-H2} = 4.7$ Hz, 1H, H_1), 7.42 (dd, $^3J_{H3-H4} = 8.2$ Hz, $^3J_{H3-H2} = 7.6$ Hz, 1H, H_3), 7.10 (d, $^3J_{H4-H3} = 8.2$ Hz, 1H, H_4), 7.08 (br s, 2H, H_{11}), 6.87 (br s, 2H, H_9), 6.74 (dd, $^3J_{H2-H3'} = 7.6$ Hz, $^3J_{H2-H1} = 4.7$ Hz, 1H, H_2), 3.82 (vbr s, 4H, $H_{6\ \mathrm{or}\ 7,7'}$), 2.90 (vbr s, 2H, H_7 or 7′), 2.38 (s, 3H, H_{14}), 2.34 (s, 3H, H_{15}). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_5D_5N, 293 K): δ 166.9 (C_{13}), 161.0 (C_5), 150.5 (C_1), 137.7 (C_3), 133.0 (C_9), 132.3 (C_{11}), 126.1 (C_{12}), 125.3 (C_4), 122.5 (C_2), 119.4 (C_{10}), 62.5 (C_6), 61.2 (vbr,C_7), 20.1 (C_{15}), 19.8 (C_{14}) (C_8 not observed). IR (Nujol mull) ν (cm^{-1}) 1608 (m), 1596 (m), 1570 (m), 1554 (m), 1312 (s), 1274 (m), 1212 (w), 1162 (m), 1114 (s), 1050 (w), 1002 (w), 988 (w), 978 (w), 952 (w), 912 (w), 860 (m), 792 (s), 770 (w), 756 (m), 692 (w), 668 (w), 638 (w), 620 (w), 594 (w), 574 (w), 506 (w), 480 (s). Anal. Found (Calcd for $C_{24}H_{26}N_2O_2Na_2\cdot(THF)_{0.125}$): C 67.25 (67.12), H 5.99 (6.10), N 6.27 (6.52), Na 10.05 (10.70).

_N_-(2-Pyridylmethyl)-_N_,_N_-bis(2′-oxo-3′,5′-_tert_-butylbenzylsodium)amine ($Na_2O_2NN'^{tBu}$, 2b). 2b was produced by a procedure analogous with that for $Na_2O_2NN'^{Me}$, with $H_2O_2NN'^{tBu}$ (1.5 g, 2.75 mmol) and sodium hydride (0.265 g, 11.2 mmol). After drying, a white powder was obtained. Yield: 1.3 g (80%).

^{1}H NMR (300.18 MHz, C_5D_5N, 293 K): δ 7.61 (d, $^3J_{H1-H2} = 4.5$ Hz, 1H, H_1), 7.37 (ddd, $^3J_{H3-H4} = 7.7$ Hz, $^3J_{H3-H2} = 7.4$ Hz, $^4J_{H3-H1} = 1.9$ Hz, 1H, H_3), 7.32 (d, $^4J_{H11-H9} = 2.7$ Hz, 2H, H_{11}), 7.19 (d, $^3J_{H4-H3'} = 7.7$ Hz, 1H, H_4), 6.98 (d, $^4J_{H9-H11} = 2.7$ Hz, 2H, H_9), 6.63 (dd, $^3J_{H2-H1} = 4.5$ Hz, $^3J_{H2-H3} = 7.4$ Hz, 1H, H_2), 4.71 (br s, 2H, $H_{7or7'}$), 4.14 (s, 2H, H_6), 3.39 (br s, 2H, $H_{7or7'}$), 1.63 (s, 18H, H_{15}), 1.33 (s, 18H, H_{17}). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_5D_5N, 293 K): δ 168.9 (C_{13}), 162.2 (C_5), 149.1 (C_1), 137.0 (C_3), 136.7 (C_{12}), 126.95 and 126.9 (C_8 and C_9), 123.5 (C_4), 123.0 (C_{11}), 121.6 (C_2), 66.1 ($C_{7or7'}$), 62.8 (C_6), 36.1 (C_{14}), 34.3 (C_{16}), 32.9 (C_{17}), 30.7 (C_{15}). IR (Nujol mull) ν (cm^{-1}) 1598 (s), 1572 (m), 1414 (w), 1361 (w), 1317 (s), 1233 (m), 1201 (m), 1160 (m), 1133 (vw), 1117 (w), 1090 (m), 1054 (w), 1005 (m), 987 (w), 932 (w), 907 (w), 864 (m), 829 (s), 794 (m), 750 (s), 735 (s), 683 (w), 660 (vw), 641 (m), 623 (w), 567 (w), 543 (w), 514 (m). Anal. Found (Calcd for $C_{36}H_{50}N_2O_2Na_2$): C 72.68 (73.44), H 8.36 (8.56), N 4.69 (4.76), Na 7.38 (7.81).



Only one half of the molecule has been illustrated. The other ligand atoms are generated by the molecular C_2 axis.

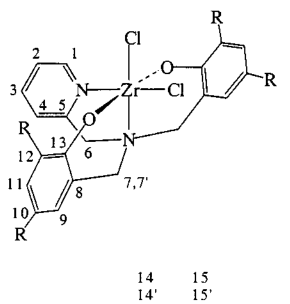
$Zr(O_2NN'^{Me})_2$ (4a). Method A. A suspension of $ZrCl_4$ (0.13 g, 0.56 mmol) and $Na_2O_2NN'^{Me}$ (0.46 g, 1.16 mmol) in benzene (40 mL) was stirred overnight at room temperature. After filtration, the colorless solution obtained was concentrated under reduced pressure. The crude product was extracted with dichloromethane (20 mL), and the solution was allowed to stand for 2 h. After evaporation of the solvent, the powder obtained was recrystallized from toluene at −80 °C to give a white powder after drying. Yield: 0.20 g (42%).

Method B. A solution of $H_2O_2NN'^{Me}$ (0.5 g, 1.33 mmol) in benzene (15 mL) was added dropwise to $Zr(CH_2SiMe_3)_4$ (0.302 g, 0.685 mmol) in benzene (15 mL) with cooling using an ice/water bath. The mixture was then heated at 60 °C for 2 h. After return to room temperature, the volatiles were removed under reduced pressure. The same purification steps as in method A gave a white powder. Yield: 0.25 g (44%). Crystals suitable for X-ray diffraction study were grown by slow evaporation of a benzene solution.

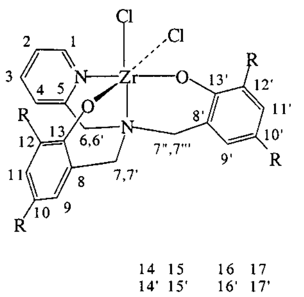
^{1}H NMR (499.99 MHz, CD_2Cl_2, 293 K): δ 9.75 (d, $^3J_{H1-H2} = 5.7$ Hz, 1H, H_1), 7.43 (ddd, $^3J_{H3-H4} = 7.8$ Hz, $^3J_{H3-H2} = 7.5$ Hz, $^4J_{H3-H1} = 1.7$ Hz, 1H, H_3), 7.02 (dd, $^3J_{H2-H1} = 5.7$ Hz, $^3J_{H2-H3} = 7.5$ Hz, 1H, H_2), 6.81 (d, $^3J_{H4-H3} = 7.8$ Hz, 1H, H_4), 6.72 (d, $^4J_{H11'-H9'} = 2.2$ Hz, 1H, $H_{11'}$), 6.64 (d, $^4J_{H9'-H11'} = 2.2$ Hz, 1H, $H_{9'}$), 6.51 (d, $^4J_{H9-H11} = 2.2$ Hz, 1H, H_9), 6.36 (d, $^4J_{H11-H9} = 2.2$ Hz, 1H, H_{11}), 4.84 (d, $^2J_{H6-H6'} = 15.0$ Hz, 1H, $H_{6or6'}$), 4.75 (d, $^2J_{H7''-H7'''} = 12.8$ Hz, 1H, $H_{7''or7'''}$), 3.91 (d, $^2J_{H7-H7'} = 12.2$ Hz, 1H, $H_{7or7'}$), 3.61 (d, $^2J_{H6-H6'} = 15.0$ Hz, 1H, $H_{6or6'}$), 3.10 (d, $^2J_{H7''-H7'''} = 12.8$ Hz, 1H, $H_{7''or7'''}$), 2.57 (d, $^2J_{H7-H7'} = 12.2$ Hz, 1H, $H_{7or7'}$), 2.15 (s, 3H, H_{14}), 2.12 (s, 3H, $H_{15'}$), 2.03 (s, 3H, H_{15}), 1.42 (s, 3H, $H_{14'}$). $^{13}C\{^1H\}$ NMR (125.74 MHz, CD_2Cl_2, 293 K): δ 160.8 ($C_{13'}$), 158.2 (C_{13}), 157.2 (C_5), 148.4 (C_1), 137.1 (C_3), 131.4 ($C_{11'}$), 131.1 (C_{11}), 127.9 (C_9), 127,8 ($C_{9'}$), 125.1 ($C_{12'}$), 125.0 ($C_{10'}$), 124.9 (C_8), 124.8 and 124.75 (C_{10} and C_{12}), 124.2 ($C_{8'}$), 121.8 (C_2), 120.8 (C_4), 65.9 (C_6), 64.1 ($C_{7''}$), 60.3 (C_7), 20.5 ($C_{15'}$), 20.3 (C_{15}), 18.4 (C_{14}), 16.6 ($C_{14'}$). IR (Nujol mull) ν (cm^{-1}): 1606 (m), 1574 (w), 1418 (w), 1344 (w), 1324 (w), 1292 (m), 1222 (w), 1076 (w), 1054 (m), 990 (w), 960 (m), 859 (m), 826 (m), 810 (s), 756 (m), 730 (m), 696 (m), 640(w), 632 (w), 594 (w), 532 (m), 504 (m). MS-EI (*m*/*z*): 838 (20%) $[M]^+$, 746 (100%) $[M - CH_2C_5H_4N]^+$, 703 (70%) $[M - CH_2(C_6H_2(CH_3)_2O)]^+$, 612 (100%) $[M - CH_2C_5H_4N - CH_2(C_6H_2(CH_3)_2O)]^+$. Anal. Found (Calcd for $C_{48}H_{52}N_4O_4Zr\cdot(C_6H_6)_{0.25}$): C 69.06 (69.15), H 6.35 (6.27), N 6.37 (6.51).

$ZrCl_2(O_2NN'^{Me})$ (3a). A solution of $H_2O_2NN'^{Me}$ (1.17 g, 3.1 mmol) in benzene (25 mL) was added dropwise to $ZrCl_2(CH_2SiMe_3)_2\cdot(Et_2O)_2$ (1.5 g, 3.1 mmol) in benzene (30 mL) with cooling using an ice/water bath. The mixture was allowed to warm to room temperature and stirred overnight. A strong white precipitate progressively appeared. The supernatant was removed, and the resulting powder was washed twice with 50 mL of pentane. After drying in a vacuum, the crude product was extracted into 80 mL of dichloromethane. Filtration and evaporation of the solvent gave a white powder. Yield: 1.15 g (69%). The NMR data at 213 K are consistent with the presence of two isomers of C_1 and C_s symmetry in the ratio

95:5%, respectively. Slow evaporation of a THF solution provided suitable crystals of the C_1 symmetry isomer for X-ray diffraction study.



For R = Me: *o*-Me, *p*-Me



For R = *t*-Bu: *o*-CMe$_3$, *p*-CMe$_3$

^{1}H NMR (499.99 MHz, CD$_2$Cl$_2$, 213 K): C_1 symmetry isomer: δ 8.76 (d, $^3J_{\mathrm{H1-H2}}$ = 5.2 Hz, 1H, H$_1$), 7.63 (ddd, $^3J_{\mathrm{H3-H4}}$ = $^3J_{\mathrm{H3-H2}}$ = 7.8 Hz, $^4J_{\mathrm{H3-H1}}$ = 1.7 Hz, 1H, H$_3$), 7.21 (dd, $^3J_{\mathrm{H2-H1}}$ = 5.2 Hz, $^3J_{\mathrm{H2-H3}}$ = 7.8 Hz, 1H, H$_2$), 7.00 (d, $^3J_{\mathrm{H4-H3}}$ = 7.8 Hz, 1H, H$_4$), 6.99 (s, 1H, H$_{11'}$), 6.90 (s, 1H, H$_{9'}$), 6.60 (s, 1H, H$_9$), 6.49 (d, 1H, H$_{11}$), 4.97 (d, $^2J_{\mathrm{H7''-H7'''}}$ = 13.4 Hz, 1H, H$_{7''\mathrm{or}7'''}$), 4.62 (d, $^2J_{\mathrm{H6-H6'}}$ = 15.4 Hz, 1H, H$_{6\mathrm{or}6'}$), 3.82 (d, $^2J_{\mathrm{H6-H6'}}$ = 15.4 Hz, 1H, H$_{6\mathrm{or}6'}$), 3.82 (d, $^2J_{\mathrm{H7-H7'}}$ = 12.9 Hz, 1H, H$_{7\mathrm{or}7'}$), 3.55 (d, $^2J_{\mathrm{H7''-H7'''}}$ = 13.4 Hz, 1H, H$_{7\mathrm{or}7'}$), 2.97 (d, $^2J_{\mathrm{H7-H7'}}$ = 12.9 Hz, 1H, H$_{7\mathrm{or}7'}$), 2.24 (s, 3H, H$_{14'}$), 2.23 (s, 3H, H$_{15'}$), 2.00 (s, 3H, H$_{15}$), 1.84 (s, 3H, H$_{14}$). C_s symmetry isomer: δ 8.82 (d, $^3J_{\mathrm{H1-H2}}$ = 5.8 Hz, 1H, H$_1$), 7.48 (ddd, $^3J_{\mathrm{H3-H4}}$ = 8.3 Hz, $^3J_{\mathrm{H3-H2}}$ = 7.4 Hz, $^4J_{\mathrm{H3-H1}}$ = 1.7 Hz, 1H, H$_3$), 7.11 (dd, $^3J_{\mathrm{H2-H1}}$ = 5.8 Hz, $^3J_{\mathrm{H2-H3}}$ = 7.4 Hz, 1H, H$_2$), 6.82 (s, 2H, H$_{11}$), 6.75 (s, 2H, H$_9$), 6.57 (d, $^3J_{\mathrm{H4-H3}}$ = 8.3 Hz, 1H, H$_4$), 4.74 (d, $^2J_{\mathrm{H7-H7'}}$ = 13.4 Hz, 2H, H$_{7\mathrm{or}7'}$), 3.78 (s, 2H, H$_6$), 3.53 (d, $^2J_{\mathrm{H7-H7'}}$ = 13.4 Hz, 2H, H$_{7\mathrm{or}7'}$), 2.15 (s, 6H, H$_{14}$), 1.96 (s, 6H, H$_{15}$). ^{13}C{^{1}H} NMR (125.74 MHz, CD$_2$Cl$_2$, 233 K): C_1 symmetry isomer: δ 156.0 (C$_{13}$), 155.6 (C$_5$), 153.9 (C$_{13'}$), 146.0 (C$_1$), 140.0 (C$_3$), 131.6 (C$_{11'}$), 131.4 (C$_{11}$), 129.9 (C$_{10'}$), 128.6 (C$_{10}$), 127.8 (C$_{9'}$), 127.1 (C$_9$), 125.4 (C$_{12'}$), 124.4 (C$_{12}$), 123.3 (C$_2$), 123.0 (C$_8$), 122.7 (C$_{8'}$), 122.2 (C$_4$), 64.1 (C$_6$), 63.4 (C$_{7''}$), 60.0 (C$_7$), 20.4 (C$_{15'}$), 20.1 (C$_{15}$), 15.9(C$_{14'}$), 15.3 (C$_{14}$). IR (Nujol mull) ν (cm^{-1}): 1612 (m), 1570 (vw), 1346 (vw), 1326 (w), 1296 (w), 1244 (s), 1220 (m), 1162 (m), 1078 (w), 1058 (w), 1026 (w), 968 (vw), 960 (vw), 946 (w), 860 (s), 828 (s), 758 (m), 694 (vw), 648 (w), 632 (vw), 600 (m), 554 (m). MS-EI (*m*/*z*): 536 (85%) [M]$^+$, 498 (100%) [M − Cl]$^+$, 401 (100%) [M − CH$_2$(C$_6$H$_2$(CH$_3$)$_2$O)]$^+$. Anal. Found (Calcd for C$_{24}$H$_{26}$Cl$_2$N$_2$O$_2$Zr): C 53.43 (53.72), H 4.99 (4.88), N 4.97 (5.22).

ZrCl$_2$(O$_2$NN′$^{\mathrm{tBu}}$) (3b). Method A. 3b was formed by a procedure analogous with that for ZrCl$_2$(O$_2$NN′$^{\mathrm{Me}}$), with H$_2$O$_2$-NN′$^{\mathrm{tBu}}$ (1.65 g, 3.03 mmol) and ZrCl$_2$(CH$_2$SiMe$_3$)$_2$(Et$_2$O)$_2$ (1.45 g, 3.02 mmol) in benzene (50 mL). After stirring at room temperature overnight, the supernatant was removed and the resulting powder was washed twice with 60 mL of pentane. After drying in a vacuum, the crude product was extracted into 60 mL of dichloromethane. Filtration and evaporation of the solvent gave a white powder. Yield: 1.35 g (63%).

Method B. A solution of Na$_2$O$_2$NN′$^{\mathrm{tBu}}$ (0.50 g, 0.84 mmol) in THF (20 mL) was added dropwise to ZrCl$_4$(THF)$_2$ (0.32 g, 0.84 mmol) in THF (20 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for a further 4 h. After filtration and evaporation of the solvent, the white solids obtained were extracted into CH$_2$Cl$_2$ (25 mL). The resulting solution was filtered, layered with 20 mL of hexane, and allowed to stand for 2 h at room temperature to provide colorless plates. Yield: 0.30 g (50%).

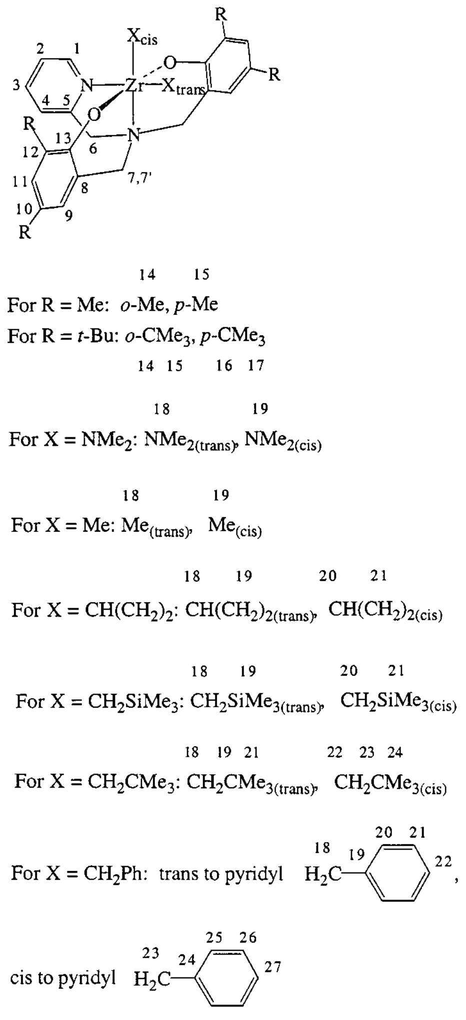
The NMR data at 213 K are consistent with the presence of two isomers of C_1 and C_s symmetry in the ratio 65:35%, respectively. This ratio has hampered the assignment of the phenyl ring and *tert*-butyl protons and, also, of the ^{13}C spectrum.

^{1}H NMR (499.99 MHz, CD$_2$Cl$_2$, 213 K): δ 8.73 (C_s, d, $^3J_{\mathrm{H1-H2}}$ = 5.2 Hz, 1H, H$_1$), 8.59 (C_1, d, $^3J_{\mathrm{H1-H2}}$ = 5.4 Hz, 1H, H$_1$), 7.60 (C_1, ddd, $^3J_{\mathrm{H3-H4}}$ = 7.9 Hz, $^3J_{\mathrm{H3-H2}}$ = 7.6 Hz, $^4J_{\mathrm{H3-H1}}$ = 1.5 Hz, 1H, H$_3$), 7.47 (C_s, ddd, $^3J_{\mathrm{H3-H4}}$ = 8.0 Hz, $^3J_{\mathrm{H3-H2}}$ = 7.4 Hz, $^4J_{\mathrm{H3-H1}}$ = 1.7 Hz, 1H, H$_3$), 7.26 (C_1, d, 1H), 7.16 (C_1, dd, $^3J_{\mathrm{H2-H1}}$ = 5.5 Hz, $^3J_{\mathrm{H2-H3}}$ = 7.6 Hz, 1H, H$_2$), 7.09 (C_s, dd, $^3J_{\mathrm{H2-H1}}$ = 5.6 Hz, $^3J_{\mathrm{H2-H3}}$ = 7.4 Hz, 1H, H$_2$), 7.08−7.05 (m, 3H), 7.03 (d, 1H), 6.78 (m, 2H), 6.61 (C_s, d, $^3J_{\mathrm{H4-H3}}$ = 8.0 Hz, 1H, H$_4$), 5.02 (C_1, d, $^2J_{\mathrm{H7''-H7'''}}$ = 13.5 Hz, 1H, H$_{7''\mathrm{or}7'''}$), 4.76 (C_s, d, $^2J_{\mathrm{H7-H7'}}$ = 14.0 Hz, 2H, H$_{7\mathrm{or}7'}$), 4.73 (C_1, d, $^2J_{\mathrm{H6-H6'}}$ = 15.5 Hz, 1H, H$_{6\mathrm{or}6'}$), 3.94 (C_1, d, $^2J_{\mathrm{H6-H6'}}$ = 15.5 Hz, 1H, H$_{6\mathrm{or}6'}$), 3.93 (C_s, s, 4H, H$_6$), 3.74 (C_1, d, $^2J_{\mathrm{H7-H7'}}$ = 13.1 Hz, 1H, H$_{7\mathrm{or}7'}$), 3.60 (C_s, d, $^2J_{\mathrm{H7-H7'}}$ = 14.0 Hz, 2H, H$_{7\mathrm{or}7'}$), 3.57 (C_1, d, $^2J_{\mathrm{H7''-H7'''}}$ = 13.5 Hz, 1H, H$_{7\mathrm{or}7'}$), 3.00 (C_1, d, $^2J_{\mathrm{H7-H7'}}$ = 13.1 Hz, 1H, H$_{7\mathrm{or}7'}$), 1.41 (s, 9H), 1.20 (s, 18H), 1.18 (s, 9H), 1.16 (s, 9H), 1.02 (s, 9H). ^{13}C{^{1}H} NMR (75.48 MHz, CD$_2$Cl$_2$, 223 K): δ 157.5, 156.7, 156.1, 155.0, 150.7 (C_s, C$_1$), 147.3 (C_1, C$_1$), 143.1, 142.3, 141.7, 140.4 (C_s and C_1, C$_3$), 136.2, 135.7, 134.9, 125.5, 125.1, 124.6, 124.5, 124.2, 124.0, 123.9, 123.5, 123.4, 122.6, 121.4 (C_s, C$_4$), 64.8 (C_1, C$_6$), 64.4 (C_s, C$_7$), 64.0 (C_1, C$_{7''}$), 60.8 (C_1, C$_7$), 58.8 (C_s, C$_6$), 35.5, 35.3, 35.0, 34.9, 34.8, 34.5, 31.9, 31.8, 29.9. IR (Nujol mull): ν (cm^{-1}) 1606 (m), 1568 (vw), 1418 (w), 1362 (m), 1240 (m), 1202 (m), 1170 (m), 1128 (m), 1058 (w), 974 (w), 914 (w), 880 (w), 862 (m), 846 (m), 760 (s), 674 (w), 648 (w), 600 (w), 564 (m), 554 (m), 506 (w). MS-EI (*m*/*z*): 704 (M$^+$, 100%), 668 (MH$^+$ − Cl, 50%). Anal. Found (Calcd for C$_{36}$H$_{50}$Cl$_2$N$_2$O$_2$Zr): C 61.12 (61.34), H 7.12 (7.15), N 3.80 (3.97).

Zr(NMe$_2$)$_2$(O$_2$NN′$^{\mathrm{tBu}}$) (5b). A solution of H$_2$O$_2$NN′$^{\mathrm{tBu}}$ (0.30 g, 0.55 mmol) in benzene (20 mL) was added dropwise to Zr(NMe$_2$)$_4$ (0.15 g, 0.56 mmol) in benzene (20 mL) with cooling using an ice/water bath. The mixture was allowed to warm to room temperature and stirred for a further 2 h. The volatiles were then removed under reduced pressure. The crude product was washed with pentane (20 mL) to yield a white powder after drying. Yield: 0.24 g (80%). Crystals suitable for X-ray diffraction study were grown by slow evaporation of a benzene solution.

^{1}H NMR (300.18 MHz, C$_6$D$_6$, 293 K): δ 8.29 (d, $^3J_{\mathrm{H1-H2}}$ = 5.3 Hz, 1H, H$_1$), 7.33 (d, $^4J_{\mathrm{H11-H9}}$ = 3 Hz, 2H, H$_{11}$), 6.91 (d, $^4J_{\mathrm{H9-H11}}$ = 3 Hz, 2H, H$_9$), 6.41 (ddd, $^3J_{\mathrm{H3-H4}}$ = 7.6 Hz, $^3J_{\mathrm{H3-H2}}$ = 7.6 Hz, $^4J_{\mathrm{H3-H1}}$ = 1.8 Hz, 1H, H$_3$), 6.17 (dd, $^3J_{\mathrm{H2-H1}}$ = 5.3 Hz, $^3J_{\mathrm{H2-H3}}$ = 7.6 Hz, 1H, H$_2$), 5.68 (d, $^3J_{\mathrm{H4-H3}}$ = 7.6 Hz, 1H, H$_4$), 4.44 (d, $^2J_{\mathrm{H7-H7'}}$ = 12.3 Hz, 2H, H$_{7\mathrm{or}7'}$), 3.63 (s, 6H, H$_{19\mathrm{or}18}$), 3.34 (s, 6H, H$_{18\mathrm{or}19}$), 3.16 (s, 2H, H$_6$), 2.90 (d, $^2J_{\mathrm{H7-H7'}}$ = 12.3 Hz, 2H, H$_{7\mathrm{or}7'}$), 1.60 (s, 18H, H$_{15}$), 1.37 (s, 18H, H$_{17}$). ^{13}C{^{1}H} NMR (75.48 MHz, C$_6$D$_6$, 293 K): δ 159.2 (C$_{13}$), 158.4 (C$_5$), 149.7 (C$_1$), 138.9 (C$_{10}$), 137.2 (C$_3$), 136.6 (C$_{12}$), 125.1 (C$_9$), 124.7 (C$_8$), 123.8 (C$_{11}$), 121.5 (C$_2$), 120.9 (C$_4$), 64.1 (C$_7$), 57.5 (C$_6$), 45.9 (C$_{18\mathrm{or}19}$), 44.7 (C$_{19\mathrm{or}18}$), 35.3 (C$_{14}$), 34.2 (C$_{16}$), 32.1 (C$_{17}$), 30.1 (C$_{15}$). IR (Nujol mull): ν (cm^{-1}) 1605 (m), 1414 (w), 1272 (s), 1240 (m), 1205 (w), 1170 (w), 1148 (w), 1137 (w), 1061 (w), 976 (w), 960 (m), 942 (m), 876 (m), 840 (m), 760 (m), 641(w), 631 (w), 544 (m). MS-EI (*m*/*z*) 720 (100%) [M]$^+$. Anal. Found (Calcd for C$_{40}$H$_{62}$N$_4$O$_2$Zr): 66.53; H, 8.65; N, 7.76. Found: C 66.18 (66.53), H 8.74 (8.65), N 7.37 (7.76).

ZrMe$_2$(O$_2$NN′$^{\mathrm{Me}}$) (6a). Method A. A solution of MeLi 1.55 M in ether (0.75 mL, 1.16 mmol) was added dropwise to a suspension of ZrCl$_2$(O$_2$NN′$^{\mathrm{Me}}$) (0.30 g, 0.56 mmol) in benzene (25 mL) with cooling using an ice/water bath. The mixture was



allowed to warm to room temperature and stirred for a further 2 h. The volatiles were then removed under reduced pressure. The crude product was extracted into ether (10 mL). The resulting solution was filtered and evaporated to dryness to give a white powder. This was washed twice with 10 mL of hexane, leading to a white powder after drying. Yield: 0.15 g (54%). Crystals suitable for X-ray diffraction study were grown by slow evaporation of an ether solution.

Method B. A solution of MeMgBr 1.4 M in toluene/THF (3:1 v/v, 0.68 mL, 0.95 mmol) was added dropwise to a solution of $ZrCl_2(O_2NN'^{Me})$ (0.25 g, 0.47 mmol) in THF (25 mL) at −78 °C. The mixture was allowed to return to room temperature and stirred for a further 2 h. Dry 1,4-dioxane (0.250 mL, 2.75 mmol) was added via microsyringe, and the mixture was stirred for 20 min. After evaporation of the solvent, the solids were extracted into ether (30 mL). The resulting solution was filtered and concentrated to 5 mL, and 20 mL of pentane was added to give a white powder. Yield: 0.07 g (30%).

^{1}H NMR (499.99 MHz, C_6D_6, 293 K): δ 8.18 (d, $^3J_{H1-H2}$ = 5.4 Hz, 1H, H_1), 6.71 (s, 2H, H_{11}), 6.50 (s, 2H, H_9), 6.30 (ddd, $^3J_{H3-H4}$ = 7.8 Hz, $^3J_{H3-H2}$ = 7.6 Hz, $^4J_{H3-H1}$ = 0.9 Hz, 1H, H_3), 6.01 (dd, $^3J_{H2-H1}$ = 5.4 Hz, $^3J_{H2-H3}$ = 7.6 Hz, 1H, H_2), 5.54 (d, $^3J_{H4-H3}$ = 7.8 Hz, 1H, H_4), 4.11 (d, $^2J_{H7-H7'}$ = 12.9 Hz, 2H, $H_{7or7'}$), 2.97 (s, 2H, H_6), 2.66 (d, $^2J_{H7-H7'}$ = 12.9 Hz, 2H, $H_{7or7'}$), 2.26 (s, 6H, H_{14}), 2.15 (s, 6H, H_{15}), 1.11 (s, 3H, H_{19}), 0.85 (s, 3H, H_{18}). ^{13}C{^{1}H} NMR (125.74 MHz, C_6D_6, 293 K): δ 158.7 (C_{13}), 158.3 (C_5), 148.1 (C_1), 137.2 (C_3), 132.0 (C_{11}), 128.2 (C_9), 126.5 (C_{10}), 125.8 (C_{12}), 123.6 (C_8), 121.8 (C_2), 120.4 (C_4), 62.7 (C_7), 58.2 (C_6), 38.6 (C_{19}), 38.2 (C_{18}), 20.6 (C_{15}), 16.1 (C_{14}). IR (Nujol mull): ν (cm^{-1}) 1604 (m), 1568 (vw), 1320 (w), 1308 (m), 1262 (s), 1218 (vw), 1158 (m), 1054 (w), 958 (w), 854 (m), 826 (s), 752 (m), 642 (w), 624 (w), 590 (m), 554 (m), 510 (w). MS-EI (*m/z*): 495 (100%) $[MH]^+$. HRMS-EI: Found (Calcd) 494.1049 [494.1511]. Anal. Found (Calcd for $C_{26}H_{32}N_2O_2Zr$): C 60.88 (62.99), H 6.80 (6.50), N 5.32 (5.60). (Despite repeated attempts a satisfactory %C analysis could not be obtained for the crystallographically characterized compound.)

$ZrMe_2(O_2NN'^{tBu})$ (6b). Method A. 6b was formed by a procedure analogous with that for $ZrMe_2(O_2NN'^{Me})$, with MeLi (0.55 mL, 0.86 mmol) and $ZrCl_2(O_2NN'^{tBu})$ (0.30 g, 0.43 mmol) in benzene (20 mL). The volatiles were then removed under reduced pressure. The crude product was extracted into ether (10 mL). The resulting solution was filtered, layered with 10 mL of hexane, and cooled to −30 °C to yield a white powder after drying. Yield: 0.12 g (42%). Crystals suitable for X-ray diffraction study were grown by slow evaporation of an ether solution.

Method B. 6b was formed by a procedure analogous with that for $ZrMe_2(O_2NN'^{Me})$, with MeMgBr (0.52 mL, 0.73 mmol) and $ZrCl_2(O_2NN'^{tBu})$ (0.25 g, 0.35 mmol) in THF (30 mL). After addition of 1,4-dioxane (0.2 mL, 2.3 mmol) and solvent evaporation, the solids were extracted into benzene (30 mL). The resulting solution was filtered and concentrated to 2 mL, and addition of 30 mL of pentane yielded a white powder. Yield: 0.08 g (35%).

^{1}H NMR (499.99 MHz, C_6D_6, 293 K): δ 8.19 (d, $^3J_{H1-H2}$ = 5.6 Hz, 1H, H_1), 7.36 (d, $^4J_{H11-H9}$ = 2.6 Hz, 2H, H_{11}), 6.86 (d, $^4J_{H9-H11}$ = 2.6 Hz, 2H, H_9), 6.32 (ddd, $^3J_{H3-H4}$ = 8.0 Hz, $^3J_{H3-H2}$ = 7.6 Hz, $^4J_{H3-H1}$ = 1.7 Hz, 1H, H_3), 6.05 (dd, $^3J_{H2-H1}$ = 5.6 Hz, $^3J_{H2-H3}$ = 7.6 Hz, 1H, H_2), 5.56 (d, $^3J_{H4-H3}$ = 8.0 Hz, 1H, H_4), 4.07 (d, $^2J_{H7-H7'}$ = 12.9 Hz, 2H, $H_{7or7'}$), 2.97 (s, 2H, H_6), 2.65 (d, $^2J_{H7-H7'}$ = 12.9 Hz, 2H, $H_{7or7'}$), 1.62 (s, 18H, H_{15}), 1.34 (s, 18H, H_{17}), 1.16 (s, 3H, H_{19}), 0.88 (s, 3H, H_{18}). ^{13}C{^{1}H} NMR (75.48 MHz, C_6D_6, 293 K): δ 159.2 (C_{13}), 158.7 (C_5), 149.4 (C_1), 140.1 (C_{10}), 137.2 (C_3), 136.5 (C_{12}), 125.0 (C_9), 124.7 (C_8), 124.3 (C_{11}), 121.6 (C_2), 120.4 (C_4), 63.3 (C_7), 57.7 (C_6), 41.1 (C_{19}), 37.6 (C_{18}), 35.4 (C_{14}), 34.3 (C_{16}), 32.0 (C_{17}), 30.1 (C_{15}). IR (Nujol mull): ν (cm^{-1}) 1602 (m), 1566 (w), 1420 (w), 1360 (m), 1268 (s), 1238 (m), 1202 (m), 1168 (m), 1128 (m), 1094 (w), 1054 (w), 1012 (w), 974 (m), 914 (m), 882 (m), 872 (w), 842 (s), 808 (m), 772 (w), 750 (s), 726 (s), 688 (w), 644(w), 630 (w), 614 (vw), 606 (w), 564 (vw), 548 (m), 510 (w). MS-EI (*m/z*): 649 (50%) $[M - CH_3]^+$. Anal. Found (Calcd for $C_{38}H_{56}N_2O_2Zr$): C, 66.50 (68.78), H 8.52 (8.50), N 4.05 (4.22), (Despite repeated attempts a satisfactory %C analysis could not be obtained for the crystallographically characterized compound.)

$Zr(\eta^3\text{-}C_3H_5)_2(O_2NN'^{tBu})$ (7b). A 1.73 M solution of C_3H_5MgCl in THF (0.5 mL, 0.42 mmol) was added dropwise to a suspension of $ZrCl_2(O_2NN'^{tBu})$ (0.292 g, 0.42 mmol) in benzene (20 mL) with cooling using an ice/water bath. The mixture was allowed to warm to room temperature and stirred for a further 2 h with exclusion of light. The volatiles were then removed under reduced pressure. Yield: 0.13 g (42%). The instability in solution of this compound has prevented us from obtaining a good microanalysis.

^{1}H NMR (499.99 MHz, C_6D_6, 293 K): δ 8.90 (d, $^3J_{H1-H2}$ = 5.6 Hz, 1H, H_1), 7.23 (d, $^4J_{H11-H9}$ = 2.4 Hz, 2H, H_{11}), 7.09 (apparent quintet, apparent $^3J_{H20-H21}$ = 11 Hz, 1H, H_{20}), 6.79 (d, $^4J_{H9-H11}$ = 2.4 Hz, 2H, H_9), 6.43 (ddd, $^3J_{H3-H4}$ = 7.8 Hz, $^3J_{H3-H2}$ = 7.6 Hz, $^4J_{H3-H1}$ = 1.7 Hz, 1H, H_3), 6.25 (apparent quintet, apparent $^3J_{H18-H19}$ = 12.4 Hz, 1H, H_{18}), 6.21 (dd, $^3J_{H2-H1}$ = 5.6 Hz, $^3J_{H2-H3}$ = 7.6 Hz, 1H, H_2), 5.79 (d, $^3J_{H4-H3}$ = 7.8 Hz, 1H, H_4), 4.51 (d, $^2J_{H7-H7'}$ = 13.2 Hz, 2H, $H_{7or7'}$), 3.83 (br s, 4H, H_{21}), 3.71 (d, $^2J_{H19-H18}$ = 13.2 Hz, 4H, H_{19}), 3.17 (s, 2H, H_6), 2.76 (d, $^2J_{H7-H7'}$ = 13.2 Hz, 2H, $H_{7or7'}$), 1.35 (s, 18H, H_{15}), 1.31 (s, 18H, H_{17}). ^{13}C{^{1}H} NMR (75.48 MHz, C_6D_6, 293 K): δ 158.5 (C_5), 158.3 (C_{13}), 150.3 (C_1), 145.8 (C_{20}), 141.2 (C_{18}), 140.0 (C_{10}), 137.2 (C_3), 136.3 (C_{12}), 125.1 (C_9), 124.6 (C_8), 123.8 (C_{11}), 122.0 (C_2), 121.2 (C_4), 81.3 (C_{19}), 79.2 (vb, C_{21}), 66.2 (C_7), 60.9 (C_6), 35.1 (C_{14}), 34.2 (C_{16}), 32.0 (C_{17}), 30.2 (C_{15}). IR (Nujol mull): ν (cm^{-1}) 1603 (w), 1599 (m), 1537 (w), 1572 (w), 1413 (w), 1320 (s), 1283 (w), 1263 (s), 1240 (m), 1204 (w), 1169 (m), 1132 (w), 1100 (w), 1018 (w), 974 (w), 914 (w), 870 (w), 840 (s), 807 (m), 760 (m), 751 (m), 723 (m), 675 (w), 646 (w), 634 (vw), 595 (w), 547 (s), 504 (w).

$Zr(CH_2SiMe_3)_2(O_2NN'^{Me})$ (8a). Method A. A solution of $H_2O_2NN'^{Me}$ (0.34 g, 0.91 mmol) in benzene (20 mL) was added dropwise to $Zr(CH_2SiMe_3)_4$ (0.40 g, 0.91 mmol) in benzene (20 mL) with cooling using an ice/water bath. The mixture was allowed to warm to room temperature and stirred for a further 2 h. The volatiles were subsequently removed under reduced pressure, and the resulting solids were extracted into 80 mL of dry pentane. The orange solution was filtered, concentrated to 60 mL, and cooled to −30 °C to give a yellowish crystalline solid. Yield: 0.36 g (62%).

Method B (NMR tube scale). At room temperature, a solution of $LiCH_2SiMe_3$ (5.3 mg, 55.6 μmol) in C_6D_6 (1 mL) was added to $ZrCl_2(O_2NN'^{Me})$ (14.9 mg, 27.8 μmol). The latter progressively dissolved, and a slightly cloudy solution was obtained after 5 min. After filtration, the ^1H NMR spectrum indicated the formation of pure **8a**.

^1H NMR (300.18 MHz, C_6D_6, 293 K): δ 8.30 (d, $^3J_{H1-H2}$ = 5.5 Hz, 1H, H_1), 6.71 (d, $^4J_{H11-H9}$ = 1.5 Hz, 2H, H_{11}), 6.50 (d, $^4J_{H9-H11}$ = 1.5 Hz, 2H, H_9), 6.34 (ddd, $^3J_{H3-H4}$ = 8.0 Hz, $^3J_{H3-H2}$ = 7.5 Hz, $^4J_{H3-H1}$ = 1.8 Hz, 1H, H_3), 6.10 (dd, $^3J_{H2-H1}$ = 5.5 Hz, $^3J_{H2-H3}$ = 7.5 Hz, 1H, H_2), 5.57 (d, $^3J_{H4-H3}$ = 8.0 Hz, 1H, H_4), 4.21 (d, $^2J_{H7-H7'}$ = 13.2 Hz, 2H, $H_{7or7'}$), 3.00 (s, 2H, H_6), 2.73 (d, $^2J_{H7-H7'}$ = 13.2 Hz, 2H, $H_{7or7'}$), 2.33 (s, 6H, H_{14}), 2.17 (s, 6H, H_{15}), 1.14 (s, 2H, H_{20}), 0.95 (s, 2H, H_{18}), 0.62 (s, 9H, H_{21}), 0.23 (s, 9H, H_{19}). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6, 293 K): δ 158.5 (C_{13}), 158.0 (C_5), 148.0 (C_1), 137.1 (C_3), 132.0 (C_{11}), 128.1 (C_9), 126.6 (C_{10}), 125.7 (C_{12}), 123.4 (C_8), 121.5 (C_2), 120.6 (C_4), 63.0 (C_7), 58.4 (C_6), 54.4 (C_{18}), 53.7 (C_{20}), 20.5 (C_{15}), 16.8 (C_{14}), 3.7 (C_{21}), 3.1 (C_{19}). IR (Nujol mull): ν (cm^{-1}) 1604 (m), 1320 (w), 1161 (m), 1059 (w), 1013 (w), 859 (m), 823 (s), 751(m), 677 (w), 640(w), 624 (w), 588 (m), 552 (m), 520 (m). MS-EI (*m/z*): 625 (15%) $[M - CH_3]^+$. Anal. Found (Calcd for $C_{32}H_{48}N_2O_2Si_2Zr$): C 58.95 (60.04), H 7.73 (7.56), N 4.23 (4.38). The low %C found for this compound and its homologue **8b** may be due to incomplete combustion and carbide formation.

$Zr(CH_2SiMe_3)_2(O_2NN'^{tBu})$ (8b). Method A. 8b was formed by a procedure analogous with that for $Zr(CH_2SiMe_3)_2(O_2NN'^{Me})$, with $H_2O_2NN'^{tBu}$ (0.375 g, 0.69 mmol) and $Zr(CH_2SiMe_3)_4$ (0.305 g, 0.69 mmol) in benzene (20 mL). After evaporation of the volatiles, the crude product was washed with 30 mL of dry pentane to give a white powder. Yield: 0.40 g (71%).

Method B (NMR tube scale). **8b** was formed by a procedure analogous with that for $Zr(CH_2SiMe_3)_2(O_2NN'^{Me})$, with $LiCH_2SiMe_3$ (4.2 mg, 44 μmol) in C_6D_6 (1 mL) and $ZrCl_2(O_2NN'^{tBu})$ (15.1 mg, 21.4 μmol).

^1H NMR (300.18 MHz, C_6D_6, 293 K): δ 8.26 (d, $^3J_{H1-H2}$ = 5.4 Hz, 1H, H_1), 7.36 (d, $^4J_{H11-H9}$ = 2.4 Hz, 2H, H_{11}), 6.94 (d, $^4J_{H9-H11}$ = 2.4 Hz, 2H, H_9), 6.29 (ddd, $^3J_{H3-H4}$ = 7.8 Hz, $^3J_{H3-H2}$ = 7.6 Hz, $^4J_{H3-H1}$ = 1.7 Hz, 1H, H_3), 6.03 (dd, $^3J_{H2-H1}$ = 5.4 Hz, $^3J_{H2-H3}$ = 7.6 Hz, 1H, H_2), 5.54 (d, $^3J_{H4-H3}$ = 7.8 Hz, 1H, H_4), 4.51 (d, $^2J_{H7-H7'}$ = 12.8 Hz, 2H, $H_{7or7'}$), 3.01 (s, 2H, H_6), 2.87 (d, $^2J_{H7-H7'}$ = 12.8 Hz, 2H, $H_{7or7'}$), 1.59 (s, 18H, H_{15}), 1.31 (s, 18H, H_{17}), 1.14 (s, 2H, H_{20}), 0.95 (s, 2H, H_{18}), 0.62 (s, 9H, H_{21}), 0.23 (s, 9H, H_{19}). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6, 293 K): δ 159.0 (C_{13}), 158.8 (C_5), 149.5 (C_1), 140.2 (C_{10}), 137.2 (C_3), 136.6 (C_{12}), 125.1 (C_9), 124.8 (C_8), 124.5 (C_{11}), 121.5 (C_2), 120.4 (C_4), 63.3 (C_7), 61.7 (C_{18}), 57.7 (C_6), 52.2 (C_{20}), 35.4 (C_{14}), 34.3 (C_{16}), 32.0 (C_{17}), 30.4 (C_{15}), 3.6 (C_{21}), 3.3 (C_{19}). IR (Nujol mull): ν (cm^{-1}) 1605 (m), 1413 (w), 1242 (m), 1201 (w), 1169 (w), 1131 (w), 1059 (w), 974 (w), 916 (m), 898 (m), 846 (m), 762 (w), 750 (w), 676 (w), 629 (w), 549 (m). MS-EI (*m/z*): 794 (35%) $[MH - CH_3]^+$. Anal. Found (Calcd for $C_{44}H_{72}N_2O_2Si_2Zr$): C 64.63 (65.37), H 9.15 (8.98), N 3.32 (3.47).

$Zr(CH_2CMe_3)_2(O_2NN'^{Me})$ (9a). A solution of $H_2O_2NN'^{Me}$ (0.15 g, 0.40 mmol) in benzene (15 mL) was added dropwise to $Zr(CH_2CCMe_3)_4$ (0.15 g, 0.40 mmol) in benzene (15 mL) with cooling using an ice/water bath. The mixture was allowed to warm to room temperature and stirred for a further 2 h. The volatiles were then removed under reduced pressure. The crude product was extracted into pentane (20 mL). The resulting solution was filtered, concentrated to 10 mL, and cooled to −30 °C to yield a white powder after drying. Yield: 0.10 g (40%).

^1H NMR (499.99 MHz, C_6D_6, 293 K): δ 8.54 (d, $^3J_{H1-H2}$ = 5.3 Hz, 1H, H_1), 6.70 (d, $^4J_{H11-H9}$ = 1.5 Hz, 2H, H_{11}), 6.51 (d, $^4J_{H9-H11}$ = 1.5 Hz, 2H, H_9), 6.35 (ddd, $^3J_{H3-H4}$ = $^3J_{H3-H2}$ = 7.6 Hz, $^4J_{H3-H1}$ = 1.8 Hz, 1H, H_3), 6.12 (dd, $^3J_{H2-H1}$ = 5.3 Hz, $^3J_{H2-H3}$ = 7.6 Hz, 1H, H_2), 5.60 (d, $^3J_{H4-H3}$ = 7.6 Hz, 1H, H_4), 4.38 (d, $^2J_{H7-H7'}$ = 12.9 Hz, 2H, $H_{7or7'}$), 3.04 (s, 2H, H_6), 2.72 (d, $^2J_{H7-H7'}$ = 12.9 Hz, 2H, $H_{7or7'}$), 2.34 (s, 6H, H_{14}), 2.17 (s, 6H, H_{15}), 1.92 (s, 2H, H_{21}), 1.67 (s, 9H, H_{23}), 1.45 (s, 11H, H_{18} and H_{20}). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6, 293 K): δ 158.7 (C_{13}), 158.4 (C_5), 148.6 (C_1), 137.1 (C_3), 132.1 (C_{11}), 128.5 (C_9), 126.6 (C_{10}), 125.9 (C_{12}), 123.8 (C_8), 121.5 (C_2), 120.8 (C_4), 85.6 (C_{21}), 84.5 (C_{18}), 63.4 (C_7), 58.9 (C_6), 35.6 (C_{23}), 35.4 (C_{20}), 35.1 (C_{22}), 35.0 (C_{19}), 20.6 (C_{15}), 17.2 (C_{14}). IR (Nujol mull): ν (cm^{-1}) 1604 (m), 1570 (w), 1354 (w), 1322 (w), 1230 (w), 1218 (w), 1054 (w), 1012 (w), 960(m), 902 (w), 856 (m), 824 (s), 756 (m), 728 (m), 640 (w), 624 (w), 588 (m), 552 (m), 518 (w). Anal. Found (Calcd for $C_{34}H_{48}N_2O_2Zr{\cdot}(C_5H_{12})_{0.60}$): C 68.53 (68.24), H 7.18 (7.54), N 4.49 (4.30).

$Zr(CH_2CMe_3)_2(O_2NN'^{tBu})$ (9b). 9b was formed by a procedure analogous with that for $Zr(CH_2CMe_3)_2(O_2NN'^{Me})$, with $H_2O_2NN'^{tBu}$ (0.214 g, 0.392 mmol) and $Zr(CH_2CMe_3)_4$ (0.15 g, 0.393 mmol) in benzene (30 mL). After evaporation of the volatiles, the crude product was washed with 30 mL of dry pentane to give a white powder. Yield: 0.15 g (49%).

^1H NMR (499.99 MHz, C_6D_6, 293 K): δ 8.44 (d, $^3J_{H1-H2}$ = 4.5 Hz, 1H, H_1), 7.38 (d, $^4J_{H11-H9}$ = 2.5 Hz, 2H, H_{11}), 6.94 (d, $^4J_{H9-H11}$ = 2.5 Hz, 2H, H_9), 6.31 (ddd, $^3J_{H3-H4}$ = 7.7 Hz, $^3J_{H3-H2}$ = 7.4 Hz, $^4J_{H3-H1}$ = 1.7 Hz, 1H, H_3), 6.11 (dd, $^3J_{H2-H1}$ = 4.5 Hz, $^3J_{H2-H3}$ = 7.4 Hz, 1H, H_2), 5.57 (d, $^3J_{H4-H3}$ = 7.7 Hz, 1H, H_4), 4.61 (d, $^2J_{H7-H7'}$ = 12.8 Hz, 2H, $H_{7or7'}$), 3.05 (s, 2H, H_6), 2.83 (d, $^2J_{H7-H7'}$ = 12.8 Hz, 2H, $H_{7or7'}$), 1.81 (s, 2H, H_{21}), 1.72 (s, 9H, H_{23}), 1.70 (s, 2H, H_{18}), 1.65 (s, 18H, H_{15}), 1.39 (s, 9H, H_{20}), 1.37 (s, 18H, H_{17}). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6, 293 K): δ 159.0 (C_{13}), 158.8 (C_5), 149.3 (C_1), 140.0 (C_{10}), 137.1 (C_3), 136.7 (C_{12}), 125.3 (C_9), 125.1 (C_8), 124.4 (C_{11}), 121.5 (C_2), 120.5 (C_4), 96.0 (C_{18}), 83.1 (C_{21}), 63.9 (C_7), 57.9 (C_6), 36.4, 36.1, 35.7, 35.4 (C_{14}), 35.2, 34.3 (C_{16}), 32.0 (C_{17}), 30.5 (C_{15}). IR (Nujol mull): ν (cm^{-1}) 1604 (m), 1568 (w), 1414 (w), 1364 (w), 1290 (w), 1238 (m), 1202 (m), 1168 (w), 1130 (w), 1058 (w), 1010 (w), 932 (w), 912 (w), 878 (m), 854 (m), 772 (w), 760 (s), 750 (m), 676 (w), 644 (w), 628 (w), 600 (w), 564 (s), 546 (m). Anal. Found (Calcd for $C_{46}H_{72}N_2O_2Zr$): C, 71.21 (71.17), H 10.95 (9.35), N 3.33 (3.61).

$Zr(CH_2C_6H_5)_2(O_2NN'^{Me})$ (10a). Method A. A solution of $H_2O_2NN'^{Me}$ (0.195 g, 0.52 mmol) in benzene (15 mL) was added dropwise to $Zr(CH_2C_6H_5)_4$ (0.247 g, 0.54 mmol) in benzene (15 mL) with cooling using an ice/water bath. The mixture was allowed to warm to room temperature and stirred for a further 2 h with exclusion of light. The volatiles were then removed under reduced pressure. The crude product was extracted into ether (20 mL). The resulting solution was filtered and cooled to −30 °C to yield yellow plates after drying. Yield: 0.15 g (45%). Crystals suitable for X-ray diffraction study were grown from a saturated ether solution at −30 °C.

Method B (NMR tube scale). At room temperature, $C_6H_5CH_2MgCl$ 1.25 M in ether (46 μL, 57 mmol) was added via microsyringe to a suspension of $ZrCl_2(O_2NN'^{Me})$ (15.3 mg, 28.5 μmol) in C_6D_6 (1 mL). The latter progressively dissolved, and a slightly cloudy solution was obtained after 10 min. After filtration, the ^1H NMR spectrum indicated the formation of pure **10a**.

^1H NMR (499.99 MHz, C_6D_6, 293 K): δ 8.17 (d, $^3J_{H1-H2}$ = 5.6 Hz, 1H, H_1), 7.65 (d, $^3J_{H25-H26}$ = 7.6 Hz, 2H, H_{25}), 7.34 (dd, $^3J_{H26-H25}$ = $^3J_{H26-H27}$ = 7.6 Hz, 2H, H_{26}), 7.05 (m, 3H, H_{20} and H_{27}), 6.96 (dd, $^3J_{H21-H22}$ = 8.8 Hz, $^3J_{H21-H20}$ = 7.6 Hz, 2H, H_{21}), 6.71 (t, $^3J_{H22-H21}$ = 8.8 Hz, 1H, H_{22}), 6.69 (d, $^4J_{H11-H9}$ = 1.7

Hz, 2H, H$_{11}$), 6.40 (d, $^4J_{H9-H11} = 1.7$ Hz, 2H, H$_9$), 6.32 (ddd, $^3J_{H3-H4} = 7.6$ Hz, $^3J_{H3-H2} = 7.8$ Hz, $^4J_{H3-H1} = 1.7$ Hz, 1H, H$_3$), 6.06 (dd, $^3J_{H2-H1} = 5.6$ Hz, $^3J_{H2-H3} = 7.8$ Hz, 1H, H$_2$), 5.57 (d, $^3J_{H4-H3} = 7.6$ Hz, 1H, H$_4$), 3.71 (d, $^2J_{H7-H7'} = 13.2$ Hz, 2H, H$_{7or7'}$), 3.02 (s, 2H, H$_{23}$), 2.89 (s, 2H, H$_6$), 2.53 (d, $^2J_{H7-H7'} = 13.2$ Hz, 2H, H$_{7or7'}$), 2.49 (s, 2H, H$_{18}$), 2.27 (s, 6H, H$_{14}$), 2.11 (s, 6H, H$_{15}$). ^{13}C{^{1}H} NMR (125.74 MHz, C$_6$D$_6$, 293 K): δ 158.3 (C$_{13}$), 158.2 (C$_5$), 149.3 (C$_{19}$), 148.2 (C$_1$), 146.4 (C$_{24}$), 137.2 (C$_3$), 131.8 (C$_{11}$), 129.3 (C$_{26}$), 128.8 (C$_{25}$), 128.5 (C$_{21}$), 128.1 (C$_9$), 127.8 (C$_{20}$), 127.0 (C$_{10}$), 125.5 (C$_{12}$), 123.7 (C$_8$), 122.6 (C$_{27}$), 121.9 (C$_2$), 120.8 (C$_4$), 120.6 (C$_{22}$), 65.6 (C$_{18}$), 65.3 (C$_{23}$), 63.1 (C$_7$), 59.7 (C$_6$), 20.6 (C$_{15}$), 16.6 (C$_{14}$). IR (Nujol mull): ν (cm^{-1}) 1604 (m), 1592 (s), 1568 (w), 1250 (m), 1208 (m), 1176 (w), 1122 (vw), 1088 (w), 1058 (w), 1014 (w), 1004 (w), 958 (s), 854 (s), 820 (s), 794 (m), 761 (m), 746 (s), 703 (m), 696 (s), 640 (w), 622 (vw), 590 (m), 556 (m), 542 (m), 516 (m). MS-EI (*m*/*z*): 555 (20%) [M − C$_7$H$_7$]$^+$, 464 (5%) [M − 2C$_7$H$_7$]$^+$. Anal. Found (Calcd for C$_{38}$H$_{40}$N$_2$O$_2$Zr): C, 69.91 (70.44), H 6.19 (6.22), N 4.31 (4.32).

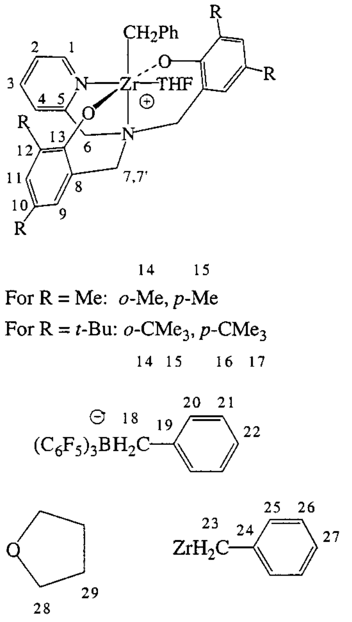
Zr(CH$_2$C$_6$H$_5$)$_2$(O$_2$NN′^{tBu}) (10b). Method A. 10b was formed by a procedure analogous with that for Zr(CH$_2$C$_6$H$_5$)$_2$(O$_2$NN′^{Me}), with H$_2$O$_2$NN′^{tBu} (0.3 g, 0.55 mmol) and Zr(CH$_2$C$_6$H$_5$)$_4$ (0.25 g, 0.545 mmol) in benzene (30 mL). After evaporation of the volatiles, the crude product was extracted into ether (80 mL). The resulting solution was filtered, concentrated to 60 mL, and cooled to −30 °C to yield a yellow crystalline powder. Yield: 0.24 g (54%).

Method B (NMR tube scale). **10b** was formed by a procedure analogous with that for Zr(CH$_2$C$_6$H$_5$)$_2$(O$_2$NN′^{Me}), with C$_6$H$_5$CH$_2$MgCl (34 mL, 42.5 μmol) and ZrCl$_2$(O$_2$NN′^{tBu}) (15.3 mg, 28.5 μmol) in C$_6$D$_6$ (1 mL). The complete conversion of the starting materials into **10b** took 3 h.

^{1}H NMR (499.99 MHz, C$_6$D$_6$, 293 K): δ 8.18 (d, $^3J_{H1-H2} = 4.7$ Hz, 1H, H$_1$), 7.83 (d, $^3J_{H25-H26} = 7.6$ Hz, 2H, H$_{25}$), 7.40 (dd, $^3J_{H26-H25} = 7.6$ Hz, $^3J_{H26-H27} = 7.4$ Hz, 2H, H$_{26}$), 7.35 (d, $^4J_{H11-H9} = 2.4$ Hz, 2H, H$_{11}$), 7.08 (t, $^3J_{H26-H27} = 7.4$ Hz, 1H, H$_{27}$), 7.04 (d, $^3J_{H20-H21} = 7.6$ Hz, 2H, H$_{20}$), 6.89 (dd, $^3J_{H21-H22} = 7.4$ Hz, $^3J_{H21-H20} = 7.6$ Hz, 2H, H$_{21}$), 6.80 (d, $^4J_{H9-H11} = 2.4$ Hz, 2H, H$_9$), 6.65 (t, $^3J_{H22-H21} = 7.4$ Hz, 1H, H$_{22}$), 6.32 (ddd, $^3J_{H3-H4} = 8.0$ Hz, $^3J_{H3-H2} = 7.4$ Hz, $^4J_{H3-H1} = 1.7$ Hz, 1H, H$_3$), 6.08 (dd, $^3J_{H2-H1} = 4.7$ Hz, $^3J_{H2-H3} = 7.4$ Hz, 1H, H$_2$), 5.57 (d, $^3J_{H4-H3} = 8.0$ Hz, 1H, H$_4$), 3.75 (d, $^2J_{H7-H7'} = 13.2$ Hz, 2H, H$_{7or7'}$), 3.21 (s, 2H, H$_{23}$), 2.88 (s, 2H, H$_6$), 2.59 (d, $^2J_{H7-H7'} = 13.2$ Hz, 2H, H$_{7or7'}$), 2.56 (s, 2H, H$_{18}$), 1.67 (s, 18H, H$_{15}$), 1.28 (s, 18H, H$_{17}$). ^{13}C{^{1}H} NMR (125.74 MHz, C$_6$D$_6$, 293 K): δ 158.7 (C$_{13}$), 158.6 (C$_5$), 149.9 (C$_{19}$), 149.3 (C$_1$), 146.4 (C$_{24}$), 140.6 (C$_{10}$), 137.3 (C$_3$), 136.3 (C$_{12}$), 129.4 (C$_{26}$), 128.6 (C$_{25}$), 128.4 (C$_{21}$), 127.5 (C$_{20}$), 124.9 (C$_9$), 124.85 (C$_8$), 124.2 (C$_{11}$), 122.9 (C$_{27}$), 121.7 (C$_2$), 120.9 (C$_4$), 120.4 (C$_{22}$), 67.6 (C$_{23}$), 67.0 (C$_{18}$), 63.7 (C$_7$), 58.8 (C$_6$), 35.4 (C$_{14}$), 34.2 (C$_{16}$), 31.9 (C$_{17}$), 30.3 (C$_{15}$). IR (Nujol mull): ν (cm^{-1}) 1603 (w), 1593 (s), 1568 (w), 1416 (w), 1241 (m), 1213 (m), 1171 (m), 1132 (w), 1059 (vw), 1000 (m), 977 (s), 916 (m), 882 (m), 855 (w), 843 (s), 763 (w), 746 (vw), 697 (vs), 644 (w), 630 (w), 597 (vw), 572 (m), 547 (m), 518 (vw), 502 (vw). MS-EI (*m*/*z*): 723 (100%) [M − C$_7$H$_7$]$^+$, 631 (15%) [M − 2C$_7$H$_7$]$^+$. Anal. Found (Calcd for C$_{50}$H$_{64}$N$_2$O$_2$Zr): C, 73.39 (73.57), H 7.88 (7.90), N 3.40 (3.43).

{[Zr(CH$_2$Ph)(THF)(O$_2$NN′^{Me})][PhCH$_2$B(C$_6$F$_5$)$_3$]} (11a). Method A. A solution of B(C$_6$F$_5$)$_3$ (0.036 g, 0.071 mmol) in CH$_2$Cl$_2$ (2 mL) was added at room temperature to Zr(CH$_2$Ph)$_2$-(O$_2$NN′^{Me}) (0.046 g, 0.071 mmol) in CH$_2$Cl$_2$ (4 mL) in the presence of THF (6 μL, 0.073 mmol). After 90 min at room temperature, the solvent was removed under reduced pressure to yield a white-yellow powder. Yield: 0.08 g (95%).

Method B (NMR tube scale). At room temperature, a solution of B(C$_6$F$_5$)$_3$ (0.0078 g, 0.015 mmol) in CD$_2$Cl$_2$ (0.5 mL) was added to Zr(CH$_2$Ph)$_2$(O$_2$NN′^{Me}) (0.01 g, 0.015 mmol) in CD$_2$Cl$_2$ (0.5 mL) in the presence of THF (1.3 μL, 0.016 mmol). The compound **11a** was formed quantitatively.



^{1}H NMR (499.99 MHz, CD$_2$Cl$_2$, 293 K): δ 8.61 (d, $^3J_{H1-H2} = 5.6$ Hz, 1H, H$_1$), 7.62−7.55 (m, 5H, H$_3$, H$_{25}$, and H$_{26}$), 7.33 (t, $^3J_{H26-H27} = 7.2$ Hz, 1H, H$_{27}$), 7.15 (dd, $^3J_{H2-H1} = 5.6$ Hz, $^3J_{H2-H3} = 7.4$ Hz, 1H, H$_2$), 6.88 (apparent triplet, $^3J_{H21-H22} = {}^3J_{H21-H20} = 7.4$ Hz, 2H, H$_{21}$), 6.83 (s, 2H, H$_{11}$), 6.82 (1H, H$_4$), 6.79 (t, $^3J_{H22-H21} = 7.4$ Hz, 1H, H$_{22}$), 6.76 (s, 2H, H$_9$), 6.74 (d, $^3J_{H20-H21} = 7.4$ Hz, 2H, H$_{20}$), 3.98 (vbr s, 4H, H$_{28}$), 3.96 (d, $^2J_{H7-H7'} = 13.7$ Hz, 2H, H$_{7or7'}$), 3.83 (s, 2H, H$_6$), 3.51 (d, $^2J_{H7-H7'} = 13.7$ Hz, 2H, H$_{7or7'}$), 3.27 (s, 2H, H$_{23}$), 2.79 (br s, 2H, H$_{18}$), 2.15 (s, 12H, H$_{14}$ and H$_{15}$), 1.95 (vbr s, 4H, H$_{29}$). ^{13}C{^{1}H} NMR (125.74 MHz, CD$_2$Cl$_2$, 293 K): δ 159.7 (C$_5$), 156.2 (C$_{13}$), 150.1 (C$_1$), 148.9 (C$_{19}$), 148.4 ($^1J_{13C-19F} = 226$ Hz, o-C$_6$F$_5$), 140.8 (C$_3$), 138.1 ($^1J_{13C-19F} = 245$ Hz, p-C$_6$F$_5$), 136.7 ($^1J_{13C-19F} = 235$ Hz, m-C$_6$F$_5$), 136.5 (C$_{24}$), 133.2 (C$_{25}$), 132.6 (C$_{11}$), 131.8 (C$_{26}$), 130.6 (C$_{10}$ or C$_{12}$), 129.0 (C$_{20}$), 128.1 (C$_{27}$), 127.1 (C$_9$ and C$_{21}$), 125.3 (C$_{10}$ or C$_{12}$), 123.9 (C$_2$), 122.7 (C$_8$), 122.3 (C$_4$ and C$_{22}$), 75.7 (br, C$_{28}$), 70.0 (C$_{23}$), 63.9 (C$_7$), 59.7 (C$_6$), 32.1 (C$_{18}$), 25.9 (C$_{29}$), 20.4 (C$_{15}$), 16.3 (C$_{14}$). ^{19}F NMR (300 MHz, CD$_2$Cl$_2$, 293 K): δ −131.17 (d, $^3J_{oF-mF} = 21.2$ Hz, 6F, o−F), −164.32 (t, $^3J_{pF-mF} = 20.4$ Hz, 3F, p-F), −167.15 (m, 6F, m-F). Anal. Found (Calcd for C$_{60}$H$_{48}$-BF$_{15}$N$_2$O$_3$Zr·0.2CH$_2$Cl$_2$): C, 57.49 (57.90), H 3.71 (3.90), N 2.18 (2.24).

{[Zr(CH$_2$Ph)(THF)(O$_2$NN′^{tBu})][PhCH$_2$B(C$_6$F$_5$)$_3$]} (11b). Method A. 11b was formed by a procedure analogous with that for {[Zr(CH$_2$Ph)(O$_2$NN′^{Me})][PhCH$_2$B(C$_6$F$_5$)$_3$]}, with Zr(CH$_2$-Ph)$_2$(O$_2$NN′^{tBu}) (0.07 g, 0.086 mmol), B(C$_6$F$_5$)$_3$ (0.044 g, 0.086 mmol), and THF (7 μL, 0.086 mmol) in CD$_2$Cl$_2$ (6 mL). Yield = 0.10 g (85%).

Method B (NMR tube scale). At room temperature, a solution of B(C$_6$F$_5$)$_3$ (0.0063 g, 0.012 mmol) in CD$_2$Cl$_2$ (0.5 mL) was added to Zr(CH$_2$Ph)$_2$(O$_2$NN′^{tBu}) (0.01 g, 0.012 mmol) in CD$_2$Cl$_2$ (0.5 mL) in the presence of THF (1.0 μL, 0.012 mmol). The product **11b** formed quantitatively.

^{1}H NMR (499.99 MHz, CD$_2$Cl$_2$, 293 K): δ 8.51 (d, $^3J_{H1-H2} = 5.2$ Hz, 1H, H$_1$), 7.76 (d, $^3J_{H25-H26} = 7.2$ Hz, 2H, H$_{25}$), 7.59 (dd, $^3J_{H26-H25} = 7.2$ Hz, $^3J_{H26-H27} = 7.5$ Hz, 2H, H$_{26}$), 7.56 (ddd, $^3J_{H3-H4} = {}^3J_{H3-H2} = 7.7$ Hz, $^4J_{H3-H1} = 1.5$ Hz, 1H, H$_3$), 7.32 (t, $^3J_{H26-H27} = 7.5$ Hz, 1H, H$_{27}$), 7.24 (d, $^4J_{H11-H9} = 2.5$ Hz, 2H, H$_{11}$), 7.16 (dd, $^3J_{H2-H1} = 5.2$ Hz, $^3J_{H2-H3} = 7.7$ Hz, 1H, H$_2$), 7.06 (d, $^4J_{H9-H11} = 2.5$ Hz, 2H, H$_9$), 6.87 (dd, $^3J_{H21-H22} = 7.8$ Hz, $^3J_{H21-H20} = 6.9$ Hz, 2H, H$_{21}$), 6.78 (d, $^3J_{H4-H3} = 7.7$ Hz, 1H, H$_4$), 6.775 (t, $^3J_{H22-H21} = 7.8$ Hz, 1H, H$_{22}$), 6.75 (d, $^3J_{H20-H21} = 6.9$ Hz, 2H, H$_{20}$), 3.97 (d, $^2J_{H7-H7'} = 13.5$ Hz, 2H, H$_{7or7'}$), 3.91 (s, 2H, H$_6$), 3.80 (vbr s, 4H, H$_{28}$), 3.61 (d, $^2J_{H7-H7'} = 13.5$ Hz, 2H, H$_{7or7'}$), 3.29 (s, 2H, H$_{23}$), 2.81 (br s, 2H, H$_{18}$), 1.87 (vbr s, 4H, H$_{29}$), 1.44 (s, 18H, H$_{15}$), 1.23 (s, 18H, H$_{17}$). ^{13}C{^{1}H} NMR (125.74 MHz, CD$_2$Cl$_2$, 293 K): δ 159.6 (C$_5$), 156.3 (C$_{13}$), 150.6 (C$_1$), 148.6 (C$_{19}$), 148.4 ($^1J_{13C-19F} = 226$ Hz, o-C$_6$F$_5$), 143.8 (C$_{10}$), 140.6 (C$_3$), 138.1 ($^1J_{13C-19F} = 245$ Hz, p-C$_6$F$_5$), 136.7 ($^1J_{13C-19F} = 235$ Hz, m-C$_6$F$_5$), 136.5 (C$_{24}$), 135.9 (C$_{12}$), 132.3 (C$_{25}$), 131.2

Table 1. X-ray Data Collection and Processing Parameters for $ZrCl_2(O_2NN'^{Me})$ (3a), $ZrCl_2(O_2NN'^{t}Bu)\cdot 0.35C_6H_{14}$ (3b·0.35C$_6$H$_{14}$), $Zr(O_2NN'^{Me})_2\cdot 2C_6H_6$ (4a·2C$_6$H$_6$), $Zr(NMe_2)_2(O_2NN'^{t}Bu)$ (5b), $ZrMe_2(O_2NN'^{Me})$ (6a), $ZrMe_2(O_2NN'^{t}Bu)$ (6b), and $Zr(CH_2Ph)_2(O_2NN'^{Me})$ (10a)

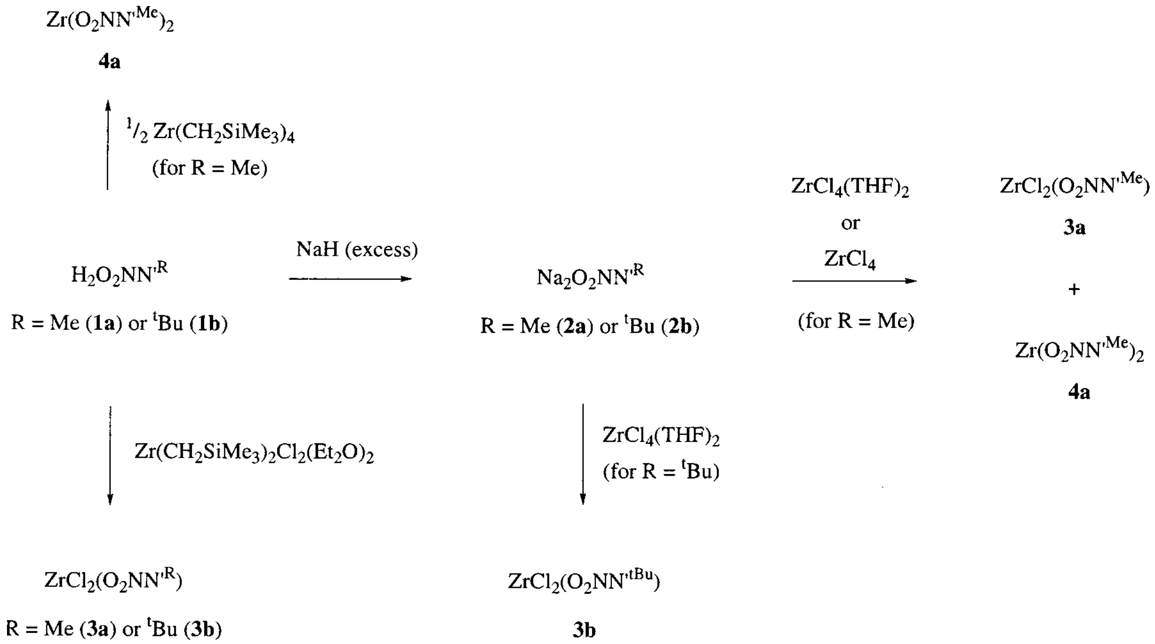
	3a	**3b**·0.35C$_6$H$_{14}$	**4a**·2C$_6$H$_6$
molecular formula	$C_{24}H_{26}Cl_2N_2O_2Zr$	$C_{36}H_{50}Cl_2N_2O_2Zr\cdot 0.35\ C_6H_{14}$	$C_{48}H_{52}N_4O_4Zr\cdot 2\ C_6H_6$
fw	536.61	735.10	996.41
cryst syst	triclinic	monoclinic	tetragonal
space group	$P\bar{1}$	$C2/c$	$P4_2/n$
Z	2	8	8
a/Å	8.7656(3)	36.3440(5)	24.919(1)
b/Å	12.3126(4)	13.7738(2)	24.919(1)
c/Å	15.8989(6)	18.1546(3)	18.1356(8)
α/deg	71.051(2)	90	90
β/deg	76.120(2)	117.4049(7)	90
γ/deg	79.316(2)	90	90
volume/Å^3	1564.7(1)	8068.2(2)	11261.6(8)
density(calcd)/mg m^{-3}	1.14	1.21	1.18
temperature/K	293	150	150
μ (Mo Kα, λ = 0.71073 Å)/mm^{-1}	0.54	0.44	0.24
no. of reflns collected	10 196	17 293	20 380
no. of ind reflns	7061	9210	12 440
obsd reflns [$I > 3\sigma(I)$]	4167	6783	5028
no. of params refined	281	401	623
final R indices[a] [$I>3\sigma(I)$]	$R_1 = 0.0539$ $R_w = 0.0579$	$R_1 = 0.0426$ $R_w = 0.0490$	$R_1 = 0.0802$ $R_w = 0.0771$
largest residual peaks/e Å^{-3}	0.95 and −0.62	0.92 and −0.80	0.95 and −0.71

	5b	**6a**	**6b**
molecular formula	$C_{40}H_{62}NO_2Zr$	$C_{26}H_{32}N_2O_2Zr$	$C_{38}H_{56}N_2O_2Zr$
fw	722.18	495.77	664.10
cryst syst	triclinic	tetragonal	monoclinic
space group	$P\bar{1}$	$P42_1c$	$C2/c$
Z	2	8	8
a/Å	10.1513(1)	18.8350(7)	31.5313(4)
b/Å	10.2107(1)	18.8350(7)	14.2743(2)
c/Å	19.7534(3)	13.8284(3)	16.9292(2)
α/deg	104.8043(5)	90	90
β/deg	97.6019(5)	90	108.1635(6)
γ/deg	95.2271(7)	90	90
volume/Å^3	1945.37(4)	4905.7(3)	7239.9(2)
density(calcd)/Mg m^{-3}	1.23	1.34	1.22
temperature/K	150	150	150
μ (Mo Kα, λ = 0.71073 Å)/mm^{-1}	0.32	0.47	0.34
no. of reflns collected	16 332	10 209	15 932
no. of ind reflns	8867	9992	8195
no. of obsd reflns [$I > 3\sigma(I)$]	7362	6016	5502
no. of params refined	425	281	388
final R indices[a] [$I>3\sigma(I)$]	$R_1 = 0.0329$ $R_w = 0.0382$	$R_1 = 0.0415$ $R_w = 0.0457$	$R_1 = 0.0352$ $R_w = 0.0390$
largest residual peaks/e Å^{-3}	0.72 and −0.79	0.69 and −0.57	0.66 and −0.63

	10a
molecular formula	$C_{38}H_{40}N_2O_2Zr$
fw	647.97
cryst syst	monoclinic
space group	$P2_1/n$
Z	4
a/Å	11.1165(2)
b/Å	21.9660(5)
c/Å	13.7130(2)
α/deg	90
β/deg	103.512(1)
γ/deg	90
volume/Å^3	3255.8(1)
density(calcd)/Mg m^{-3}	1.32
temperature/K	150
μ (Mo Kα, λ = 0.71073 Å)/mm^{-1}	0.37
no. of reflns collected	12 142
no. of ind reflns	7436
no. of obsd reflns [$I > 3\sigma(I)$]	4957
no. of params refined	415
final R indices[a] [$I > 3\sigma(I)$]	$R_1 = 0.0348$ $R_w = 0.0374$
largest residual peaks/e Å^{-3}	0.43 and −0.47

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum(w|F_o|^2\}^{1/2}$.

Scheme 1. Synthesis of Sodium Salts of the Diamine−Bis(phenolate) Ligands, and Zirconium Mono(diamine−bis(phenolate)) Dichloride and Bis(diamine−bis(phenolate)) Complexes



(C_{26}), 128.7 (C_{20}), 127.6 (C_{27}), 126.7 (C_{21}), 125.7 (C_9), 125.3 (C_{11}), 123.6 (C_2), 123.4 (C_8), 122.3 and 122.0 (C_4 and C_{22}), 76.2 (C_{28}), 71.6 (C_{23}), 64.5 (C_7), 58.7 (C_6), 35.3 (C_{14}), 34.6 (C_{16}), 31.9 (C_{18}), 31.6 (C_{17}), 30.1 (C_{15}), 26.0 (C_{29}). ^{19}F NMR (300 MHz, CD_2Cl_2, 293 K): δ −131.18 (d, $^3J_{oF-mF}$ = 21.2 Hz, 6F, o-F), −164.44 (t, $^3J_{pF-mF}$ = 20.4 Hz, 3F, p-F), −167.20 (m, 6F, m-F). IR (Nujol mull): ν (cm^{-1}) 1639 (m), 1610 (w), 1600 (vw), 1510 (s), 1305 (w), 1240 (w), 1204 (w), 1168 (m), 1128 (w), 1079 (s), 1026 (w), 973 (m), 838 (m), 808 (m), 754 (m), 724 (m), 701 (m), 679 (w), 650 (w), 633 (vw), 597 (w), 569 (m), 552 (m). Anal. Found (Calcd for $C_{72}H_{72}BF_{15}N_2O_3Zr{\cdot}0.15CH_2Cl_2$): C, 61.02 (61.32), H 5.41 (5.15), N 1.85 (1.98).

Crystal Structure Determinations for $ZrCl_2(O_2NN'^{Me})$ (3a), $ZrCl_2(O_2NN'^{tBu}){\cdot}0.35C_6H_{14}$ (3b·0.35C_6H_{14}), $Zr(O_2NN'^{Me})_2{\cdot}2C_6H_6$ (4a·2C_6H_6), $Zr(NMe_2)_2(O_2NN'^{tBu})$ (5b), $ZrMe_2(O_2NN'^{Me})$ (6a), $ZrMe_2(O_2NN'^{tBu})$ (6b), and $Zr(CH_2Ph)_2(O_2NN'^{Me})$ (10a). 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 Kappa CCD diffractometer equipped with an Oxford Cryosystems low-temperature device.[36] 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.[37] Corrections for Lorentz−polarization effects and absorption were performed, and the structures were solved by direct methods using SIR92.[38] Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Hydrogen atoms were either placed geometrically and refined in a riding model or (for **10a**) located from Fourier maps and refined as indicated below. Extinction corrections were applied as required,[39] and examination of the refined Flack parameter[40] for **4a** and **6a** confirmed the correct polarity.

For **3b**·0.35C_6H_{14} residual electron density was modeled as a 70% chemical occupancy hexane molecule of crystallization (lying across a crystallographic 2-fold rotation axis). The disordered atoms were refined isotropically. For **4a**·2C_6H_6 the benzene molecules of crystallization were refined anisotropically subject to similarity restraints on the C−C distances and general vibrational restraints. For **10b** all H atoms were located from Fourier diffrence syntheses. The H atoms of the benzylic CH_2 groups were positionally and isotropically refined. All others were refined in a riding model with equivalent isotropic displacement parameters for chemically related groups of H atoms. There are no unusual features concerning the benzylic CH_2 group H atoms.

Crystallographic calculations were performed using SIR92[38] and CRYSTALS.[41] A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for **3a**, **3b**, **4a**, **5b**, **6a**, **6b**, and **10a** has been deposited at the Cambridge Crystallographic Data Center. See Notice to Authors, Issue No. 1.

Results and Discussion

Ligand Precursors and their Disodium Salts. An independent synthesis of the *tert*-butyl-substituted ligand precursor $H_2O_2NN'^{tBu}$ (**1b**, Chart 1) has been described very recently.[28] In our hands the multigram scale syntheses of $H_2O_2NN'^R$ [R = Me (**1a**) or ^tBu (**1b**)] were readily achieved by a Mannich condensation between paraformaldehyde, $(2\text{-}C_5H_4N)CH_2NH_2$, and the appropriate 2,4-disubstituted phenol HO-2,4-$C_6H_2R_2$ (R = Me or ^tBu) in a 1:1:2 molar ratio in ethanol in a sealed ampule at 110 °C for 3 days. Typical yields of 50−55% are readily achieved in this way, affording **1a** and **1b** as white microcrystalline solids. If the reaction is carried out under open reflux conditions (water-cooled condenser), then incomplete conversions of $(2\text{-}C_5H_4N)CH_2NH_2$ and 2,4-disubstituted phenol are observed, consistent with the partial loss of paraformaldehyde from the reaction mixture.

The protio-ligands $H_2O_2NN'^R$ were smoothly converted to their disodium derivatives $Na_2O_2NN'^R$ [R = Me (**2a**) or ^tBu (**2b**)] by reaction with an excess of sodium hydride in THF (Scheme 1). Filtering and evaporation

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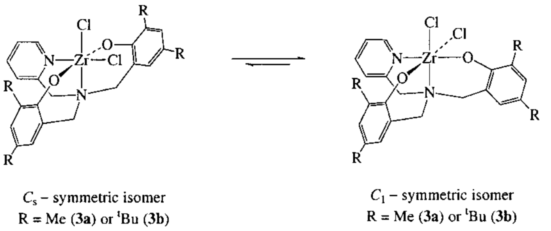
of the solvents yielded **2a** or **2b** as mildly air-sensitive white solids soluble and stable in aromatic and nonhalogenated donor solvents. Despite prolonged drying at 90 °C under vacuum, the dimethyl derivative **2a** contained small, nonstoichiometric quantities of THF (determined by ^{1}H NMR integration). Both compounds are formulated for convenience as $Na_2O_2NN'^R$, but since we were unable to obtain diffraction-quality crystals, we cannot comment on their actual nuclearity. NMR studies have proved inconclusive in these regards. Both the protio (**1a**, **1b**) and disodium (**2a**, **2b**) derivatives are useful precursors to new zirconium complexes.

Zirconium Dichloride Complexes of Diamine−Bis(phenolate) Ligands. The reactions between $H_2O_2NN'^R$ (**1a**, **1b**) or $Na_2O_2NN'^R$ (**2a**, **2b**) and a number of zirconium precursor complexes are summarized in Scheme 1. The course and outcome of the reaction chemistry is dependent on the identity of the phenoxide ring substituents, presumably because of the different steric factors involved.

Protonolysis reactions of either **1a** or **1b** with $Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2$ [31] in benzene lead to elimination of $SiMe_4$ and formation of the dichloride complexes $ZrCl_2(O_2NN'^R)$ (R = Me (**3a**) or ^{t}Bu (**3b**)) in 69 and 63% isolated yield, respectively. Both of these compounds have been crystallographically characterized, and the structures are discussed below. Reaction of the disodium salts $Na_2O_2NN'^R$ (**2a**, **2b**) with $ZrCl_4$ or $ZrCl_4(THF)_2$ with the aim of forming **3a** and **3b** was successful only for the *tert*-butyl-substituted system **3b**, this being obtained in 50% yield. For the methyl-substituted ligand these reactions gave mixtures of $ZrCl_2(O_2NN'^{Me})$ (**3a**) and the eight coordinate bis(diamine−bis(phenolate)) complex $Zr(O_2NN'^{Me})_2$ (**4a**). The latter has been isolated in 42% yield by treating $ZrCl_4(THF)_2$ with 2 equiv of $Na_2O_2NN'^{Me}$. Compound **4a** can also be obtained in a similar yield by an $SiMe_4$ elimination reaction between $Zr(CH_2SiMe_3)_4$ and 2 equiv of $H_2O_2NN'^{Me}$. All attempts to make the *tert*-butyl-substituted analogue of **4a** were unsuccessful, reflecting the greater steric demands of the $O_2NN'^{tBu}$ ligand. Compound **4a** has been structurally characterized, and the solid-state structure is discussed below.

At room temperature the ^{1}H and ^{13}C NMR spectra of $ZrCl_2(O_2NN'^R)$ (R = Me (**3a**) or ^{t}Bu (**3b**)) in CD_2Cl_2 are broad and relatively uninformative. However, cooling to −60 °C leads to a considerable sharpening of the resonances. These NMR spectra are consistent with the presence of two isomers, one having C_1 symmetry and the other having C_s symmetry. For the two compounds **3a** and **3b** these are present in the ratios ca. 95:5 and 65:35, respectively, by ^{1}H NMR integration. The relative amounts of each isomer do not depend on the actual method of preparation; nor do they change with temperature, suggesting that there is a negligible entropic contribution to the Gibbs free energies involved. The two isomers are illustrated in eq 1, which also shows the proposed dynamic equilibrium between them. That the two isomers are in dynamic exhange is apparent from the variable-temperature NMR spectra. For example, at low temperature the ^{1}H NMR spectra show two pyridyl group *ortho* (to N) H atom resonances for **3a** and **3b**; on warming, these coalesce to a weighted average chemical shift.



(1)

The ^{1}H NMR spectra of **3a** and **3b** readily distinguish between the C_1 and C_s symmetry isomers. For example, the former has two chemically distinct phenoxide ring environments (one *trans* to chloride, the other *trans* to the pyridyl group), whereas in the latter isomer the mutually *trans* phenoxide groups give rise to a single set of resonances. It is not surprising that the *tert*-butyl-substituted complex **3b** has proportionally less of the C_1 symmetry isomer since this places the phenoxide ligands mutually *cis* to each other, an arrangement that should become less favorable as the steric bulk of the phenoxide ring substituents is increased. The nature of the fluxional processes responsible for the broad NMR spectra of **3a** and **3b** at room temperature is as yet unknown. Addition of either 1 or 10 equiv of $^nBu_4Cl$ (a chloride ion source) does not influence the spectral line widths or equilibrium position between C_1 and C_s symmetry isomers, militating against a mechanism involving dissociation of chloride ions. However, it is in principle possible that pyridyl group dissociation can occur on the NMR time scale and that this would give a five-coordinate intermediate through which one phenoxide and the pyridyl donor could exchange positions (i.e., to be *cis* or *trans* to the other phenoxide group).

To probe further the mechanism of interconversion between the C_1 and C_s symmetry isomers of **3b**, we carried out a variable-temperature, ^{1}H NMR line shape analysis in dichloromethane-d_2 solution, using all four pairs of exchanging resonances of the two different pyridyl groups. Selected examples of the observed and simulated[42] spectra in this region are illustrated in Figure 1. Analysis of a set of 10 first-order rate constants (between −30 and 20 °C) for **3b** using standard (Eyring plot) procedures[43] afforded the following activation parameters: $\Delta H^\ddagger = 35.9(8)$ kJ mol^{-1}; $\Delta S^\ddagger = -102(5)$ J mol^{-1} K^{-1}; $\Delta G^\ddagger_{(298K)} = 66(2)$ kJ mol^{-1}. The somewhat negative entropy of activation disfavors a dissociatively activated mechanism (e.g., by chloride or pyridyl donor loss), as does the relatively modest enthalpy of activation.[44] Rather, the activation parameters are more in favor of a nondissociative rearrangement (for example, via a trigonal prismatic transition state or intermediate[45]), possibly with a somewhat ordered transition state (although the effects of differing extents of solvation cannot be disregarded). Furthermore, we found that the NMR line widths are independent of sample concentration in the concentration range 0.014 to 0.045 mmol of **3b**, consistent with an intramolecular exchange mechanism.

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(43) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1992.

(44) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*; VCH: Weinheim, 1991.

(45) Muetterties, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5097.

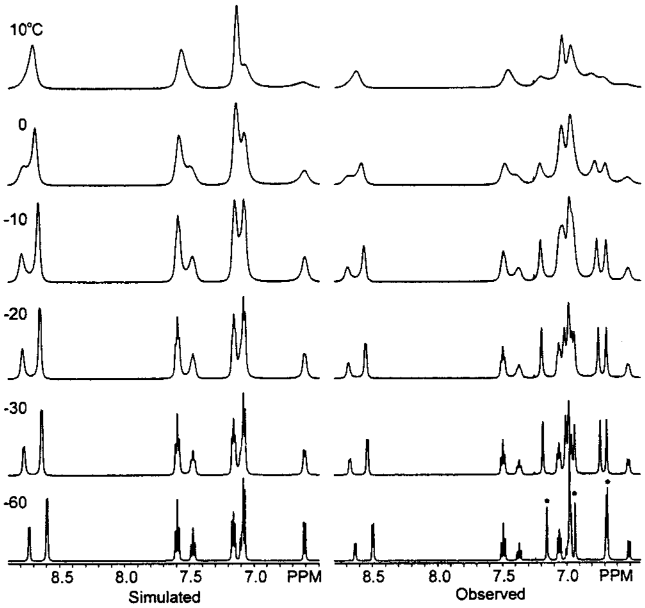

Figure 1. Selected simulated (left) and observed variable-temperature ^{1}H NMR spectra of the aromatic region of $ZrCl_2(O_2NN'^{Me})$ (**3a**) in dichloromethane-d_2. The observed resonances (marked with a "*") for the $C_6H_2Bu^t_2$ ring protons were not included in the simulation and are therefore "missing" from the simulated spectra.

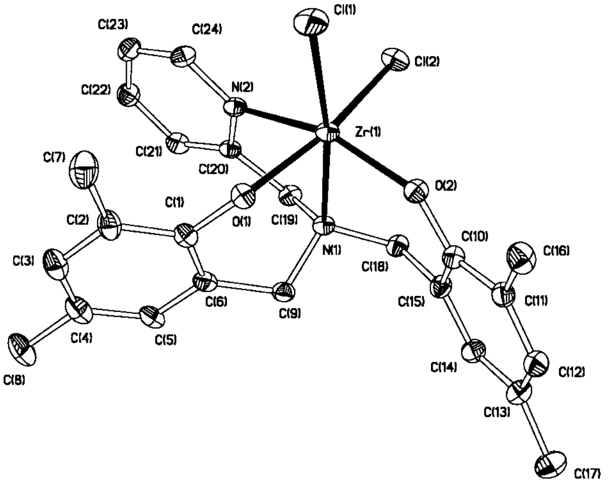

Figure 2. Displacement ellipsoid plot (15% probablility) of $ZrCl_2(O_2NN'^{Me})$ (**3a**) with hydrogen atoms omitted.

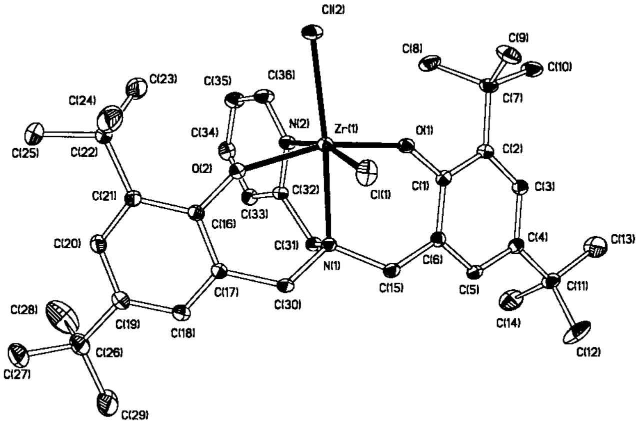

Figure 3. Displacement ellipsoid plot (25% probablility) of $ZrCl_2(O_2NN'^{tBu})$ (**3b**) with hydrogen atoms and hexane molecule of crystallization omitted.

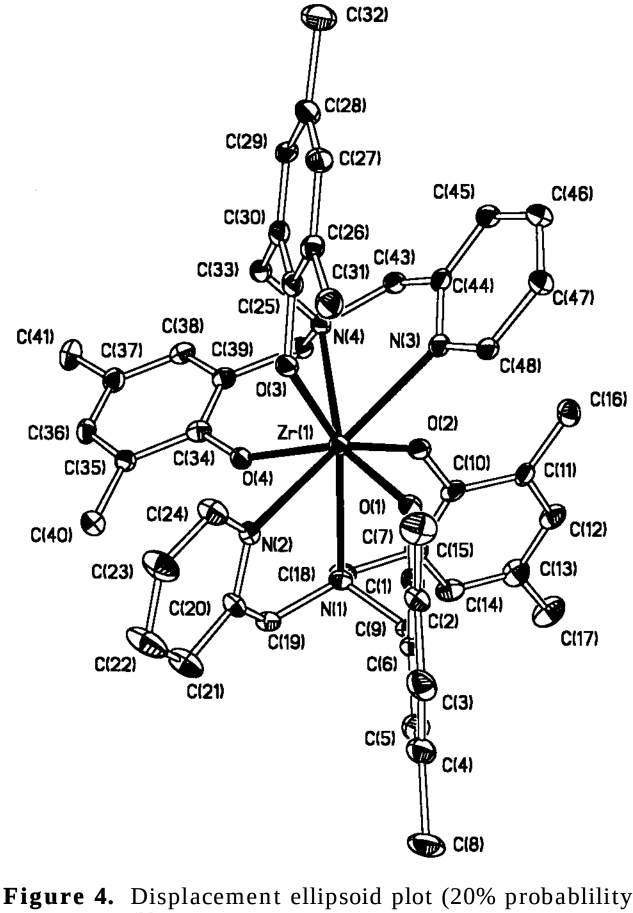

Figure 4. Displacement ellipsoid plot (20% probablility) of $Zr(O_2NN'^{Me})_2$ (**4a**) with hydrogen atoms and benzene molecules of crystallization omitted.

The NMR spectra of the homoleptic complex $Zr(O_2NN'^{Me})_2$ (**4a**) are sharp at room temperature and feature one set of $O_2NN'^{Me}$ ligand resonances with the two phenoxide groups in chemically inequivalent environments. This suggests that these phenoxide groups adopt a mutually *cis* disposition (as in the C_1 symmetric isomers of **3a** and **3b**) and that the two $O_2NN'^{Me}$ ligands are related by a molecular symmetry element (or undergo rapid exchange on the NMR time scale). Cooling a ^{1}H NMR sample of **4a** to −60 °C resulted in no significant change to the spectrum. In all of the complexes **3a**, **3b** (both isomers), and **4a** the ^{1}H chemical shifts of the *ortho* hydrogen of the pyridyl moiety are consistent with coordination of this group to the metal center in solution. This was also confirmed by the two-dimensional NOESY (nuclear Overhauser effect correlation spectroscopy) spectra of **3a** and **4a**, which revealed NOE interactions between these pyridyl *ortho* hydrogens and the *ortho* methyl hydrogens of a phenoxide group (most probably those attached to C(15) or C(31) in Figure 4).

The solid-state structures of $ZrCl_2(O_2NN'^{Me})$ (**3a** as the C_1 symmetric isomer), $ZrCl_2(O_2NN'^{tBu})$ (**3b** as the C_s symmetric isomer) and $Zr(O_2NN'^{Me})_2$ (**4a**) have all been determined and are shown in Figures 2−4. Selected bond lengths and angles are listed in Tables 2−4. Crystals of **3b** and **4a** contain hexane or benzene molecules of crystallization, but there are no unusual contacts between these and the metal complexes.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $ZrCl_2(O_2NN'^{Me})$ (3a)

Distances			
Zr(1)−Cl(1)	2.422(1)	Zr(1)−O(2)	1.935(3)
Zr(1)−Cl(2)	2.483(1)	Zr(1)−N(1)	2.409(3)
Zr(1)−O(1)	1.983(3)	Zr(1)−N(2)	2.332(3)
Angles			
Cl(1)−Zr(1)−Cl(2)	94.37(4)	O(1)−Zr(1)−N(1)	80.80(11)
Cl(1)−Zr(1)−O(1)	94.83(8)	O(2)−Zr(1)−N(1)	80.69(11)
Cl(2)−Zr(1)−O(1)	159.41(8)	Cl(1)−Zr(1)−N(2)	100.08(8)
Cl(1)−Zr(1)−O(2)	107.40(8)	Cl(2)−Zr(1)−N(2)	80.45(8)
Cl(2)−Zr(1)−O(2)	95.09(9)	O(1)−Zr(1)−N(2)	79.84(11)
O(1)−Zr(1)−O(2)	99.65(12)	O(2)−Zr(1)−N(2)	152.44(11)
Cl(1)−Zr(1)−N(1)	171.44(9)	N(1)−Zr(1)−N(2)	72.0(1)
Cl(2)−Zr(1)−N(1)	87.54(8)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $ZrCl_2(O_2NN'^tBu)$ (3b)

Distances			
Zr(1)−Cl(1)	2.4205(6)	Zr(1)−O(2)	1.997(2)
Zr(1)−Cl(2)	2.4309(6)	Zr(1)−N(1)	2.397(2)
Zr(1)−O(1)	1.966(2)	Zr(1)−N(2)	2.377(2)
Angles			
Cl(1)−Zr(1)−Cl(2)	102.06(3)	N(1)−Zr(1)−O(1)	78.63(6)
Cl(1)−Zr(1)−N(1)	95.33(5)	N(2)−Zr(1)−O(1)	86.69(7)
Cl(2)−Zr(1)−N(1)	162.57(5)	Cl(1)−Zr(1)−O(2)	94.81(5)
Cl(1)−Zr(1)−N(2)	167.26(5)	Cl(2)−Zr(1)−O(2)	98.88(5)
Cl(2)−Zr(1)−N(2)	90.41(5)	N(1)−Zr(1)−O(2)	80.65(6)
N(1)−Zr(1)−N(2)	72.28(7)	N(2)−Zr(1)−O(2)	80.50(7)
Cl(1)−Zr(1)−O(1)	93.89(5)	O(1)−Zr(1)−O(2)	158.16(7)
Cl(2)−Zr(1)−O(1)	98.83(5)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Zr(O_2NN'^{Me})_2$ (4a)

Distances			
Zr(1)−O(1)	2.074(6)	Zr(1)−N(1)	2.524(7)
Zr(1)−O(2)	2.054(5)	Zr(1)−N(2)	2.462(7)
Zr(1)−O(3)	2.101(5)	Zr(1)−N(3)	2.451(7)
Zr(1)−O(4)	2.058(6)	Zr(1)−N(4)	2.547(7)
Angles			
O(1)−Zr(1)−O(2)	94.5(2)	O(1)−Zr(1)−N(3)	77.8(2)
O(1)−Zr(1)−O(3)	95.6(2)	O(2)−Zr(1)−N(3)	73.5(2)
O(2)−Zr(1)−O(3)	141.6(2)	O(3)−Zr(1)−N(3)	72.6(2)
O(1)−Zr(1)−O(4)	140.8(2)	O(4)−Zr(1)−N(3)	141.2(2)
O(2)−Zr(1)−O(4)	101.1(2)	N(1)−Zr(1)−N(3)	135.8(2)
O(3)−Zr(1)−O(4)	94.0(2)	O(1)−Zr(1)−N(4)	146.5(2)
O(1)−Zr(1)−N(1)	77.5(2)	O(2)−Zr(1)−N(4)	74.4(2)
O(2)−Zr(1)−N(1)	72.7(2)	O(3)−Zr(1)−N(4)	76.8(2)
O(3)−Zr(1)−N(1)	145.7(2)	O(4)−Zr(1)−N(4)	72.7(2)
O(4)−Zr(1)−N(1)	73.4(2)	N(1)−Zr(1)−N(4)	126.2(2)
O(1)−Zr(1)−N(2)	72.9(2)	N(2)−Zr(1)−N(3)	134.9(2)
O(2)−Zr(1)−N(2)	141.3(2)	N(2)−Zr(1)−N(4)	134.3(2)
O(3)−Zr(1)−N(2)	77.0(2)	N(3)−Zr(1)−N(4)	68.8(2)
O(4)−Zr(1)−N(2)	72.5(2)	N(1)−Zr(1)−N(2)	68.9(2)

The structures found for $ZrCl_2(O_2NN'^{Me})$ (**3a**) and $ZrCl_2(O_2NN'^{tBu})$ (**3b**) in the solid state are fully consistent with the solution NMR data for the C_1 symmetric isomer of **3a** and C_s symmetric isomer of **3b**. By inference, the assignment of the remaining peaks in the NMR spectra of **3a** and **3b** to the other isomer (i.e., C_s symmetric or C_1 symmetric, respectively) is therefore supported in each case. The zirconium centers in **3a** and **3b** are approximately octahedral and show that the pyridyl moiety is tightly bound in each case. The two chloride ligands and nitrogen donors in each compound adopt mutually *cis* dispositions. But whereas the phenoxide ligands are also mutually *cis* in the C_1 symmetric isomer of **3a**, they are mutually *trans* in the C_s symmetric **3b**. This has some significant effects on the zirconium−donor atom bond lengths due the different *trans* influences of the various donors. For example, the Zr(1)−Cl(2) (chloride *trans* to phenoxide) distance of 2.483(1) Å in **3a** is significantly longer that the other Zr−Cl distance in **3a** [2.422(1) Å, *trans* to the amine donor N(1)] and the two Zr−Cl distances of 2.4205(6) and 2.4309(6) Å in **3b** (both Zr−Cl bonds being *trans* to neutral N-donor atoms). Similarly the Zr(1)−O(2) (*trans* to neutral pyridyl) distance of 1.935(3) Å in **3a** is significantly shorter than the three other Zr−O distances in **3a** and **3b** (range 1.966(2)−1.997(2) Å) for phenoxide groups *trans* to anionic donors.

The solid-state structure of $Zr(O_2NN'^{Me})_2$ (**4a**) is consistent with the solution NMR data discussed above and features two tetradentate $O_2NN'^{Me}$ ligands, each with mutually *cis* phenoxide donors. In the solid state **4a** possesses approximate C_2 symmetry; Figure 4 shows a view of **4a** approximately along the molecular 2-fold axis that relates the two $O_2NN'^{Me}$ ligands. The geometry at zirconium is best described as a square anti-prism, with atoms O(1), N(2), O(3), and N(3) forming one of the (approximately) square faces and atoms O(2), N(1), O(4), and N(4) forming the other. The Zr−O and Zr−N_{amine} and Zr−$N_{pyridyl}$ distances in **4a** are all significantly longer than the corresponding distances in six-coordinate **3a** and **3b**. This reflects the increased coordination number and steric crowding in **4a**. For all three compounds **3a**, **3b**, and **4a** the intramolecular distances and angles are within previously reported ranges.[46]

The tendency of the zirconium dichloride complexes of $O_2NN'^R$ (i.e., **3a**, **3b**, and **4a**) to exist as isomeric mixtures and also to form the bis($O_2NN'^{Me}$) derivative **4a** is reminiscent of previously reported group 4 complexes of chelating (bi- or tetradentate) O,N-donor ligands[11−21] and appears to be an intrinsic feature of these systems.

Zirconium Bis(dimethylamide) and Organometallic Complexes with Diamine−Bis(phenolate) Ligands. Scheme 2 summarizes other new zirconium complexes prepared in this work. Two synthetic strategies have been evaluated. These are (i) protonolysis reactions of $H_2O_2NN'^R$ (**1a**, **1b**) with ZrR'_4 (R′ = NMe_2, CH_2SiMe_3, CH_2CMe_3, or CH_2Ph), and (ii) chloride substitution reactions of $ZrCl_2(_2O_2NN'^R)$ (**3a**, **3b**) with organolithium or Grignard reagents.

Reaction of $Zr(NMe_2)_4$ with $H_2O_2NN'^{Me}$ (**1a**) in cold benzene gave elimination of $HNMe_2$ (observed by ^1H NMR), but no well-defined zirconium complex could be isolated. The problem appears to be one of thermal stablilty since ^1H NMR analysis of crude mixtures immediately after reaction showed resonances attributable to the desired product $Zr(NMe_2)_2(_2O_2NN'^{Me})$. However, on further handling at room temperature and/or attempted purification, the spectra became increasingly ill-defined. In contrast, reaction of $Zr(NMe_2)_4$ with the more sterically encumbered $H_2O_2NN'^{tBu}$ (**1b**) in benzene gave $Zr(NMe_2)_2(O_2NN'^{tBu})$ (**5b**) as a white crystalline material in 80% yield. Diffraction-quality crystals were obtained by slow evaporation of a benzene solution. The molecular structure is shown in Figure 5, and selected bond lengths and angles are listed in Table 5.

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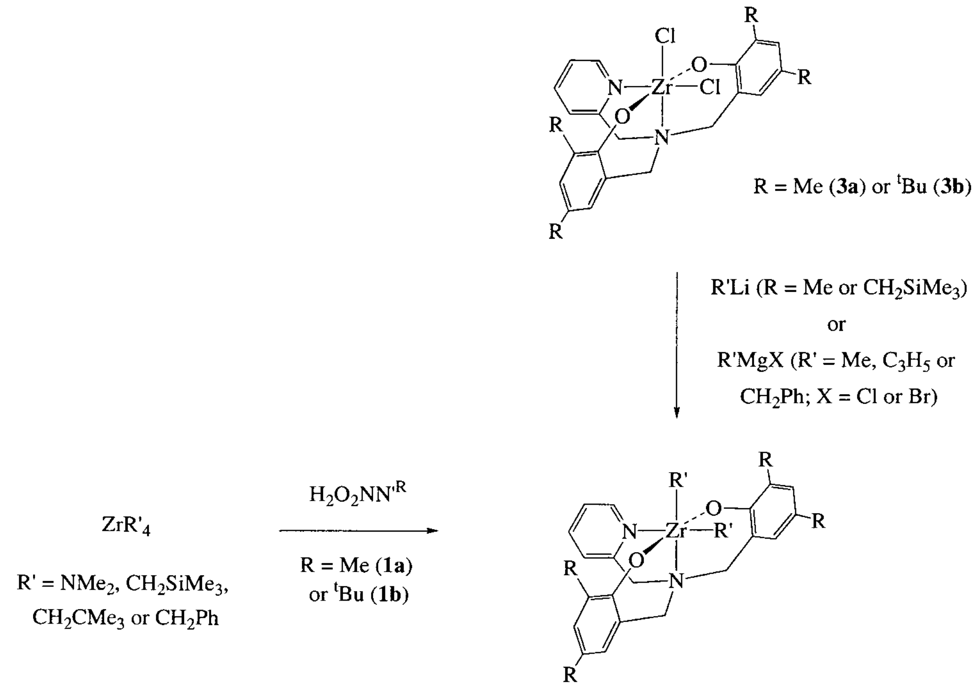
(46) Fletcher, D. A.; McMeeking, R. F.; Parkin, D. The United Kingdom Chemical Database Service. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746. Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 1&31.

Scheme 2. Synthesis of Bis(dimethylamide) and Organometallic Zirconium Complexes of Diamine–Bis(phenolate) Ligands



R' = NMe_2, R = ${}^tBu$ (**5b**); R' =Me, R = Me (**6a**) or ${}^tBu$ (**6b**);
R' = η^3-C_3H_5, R = ${}^tBu$ (**7b**); R' = CH_2SiMe_3, R = Me (**8a**) or ${}^tBu$ (**8b**);
R' = CH_2CMe_3, R = Me (**9a**) or ${}^tBu$ (**9b**); R' = CH_2Ph, R = Me (**10a**) or ${}^tBu$ (**10b**)

Molecules of **5b** contain approximately octahedral zirconium centers with mutually *cis* NMe_2 ligands and *trans* phenoxide groups. The N_{amine} and $N_{pyridyl}$ donors are therefore also mutually *cis*, and the compound possess approximate C_s symmetry in the solid state. A comparison of the Zr–O and Zr–$N_{amine/pyridyl}$ distances in **5b** with those of $ZrCl_2(O_2NN'^{tBu})$ (**3b**, Table 3) shows that those for **5b** are all significantly longer. This is consistent with the superior σ- and π-donor ability of NMe_2 in comparison with Cl as a ligand to transition metal centers. The Zr–N_{amide} distances are within previously reported ranges for six-coordinate zirconium.

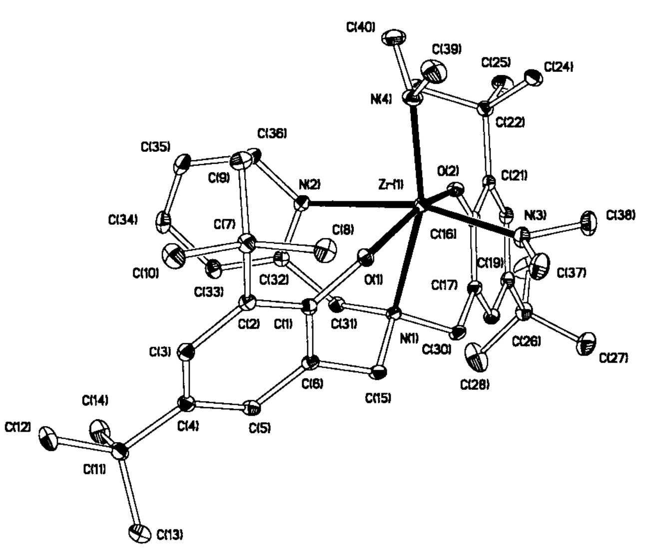


Figure 5. Displacement ellipsoid plot (20% probablility) of $Zr(NMe_2)_2(O_2NN'^{tBu})$ (**5b**) with hydrogen atoms omitted.

The sum of the angles subtended at the NMe_2 nitrogens [359.3(4)° for N(3) and 359.7(5)° for N(4)] show that they are sp^2 hybridized and potentially capable of π-donating to the d^0 metal center. The carbon atoms of the NMe_2 ligand bound *trans* to the pyridyl group are effectively coplanar with the "equatorial" (as drawn) {O(1), O(2), N(2), N(3)} plane. To maximize π-donation from the *other* NMe_2 ligand (i.e., to avoid competition with the NMe_2 *trans* to pyridyl for metal "t_{2g}" π-acceptor orbitals), it would be expected that its methyl groups would lie in the {N(1), N(2), N(3), N(4)} plane. This would give an orthogonal (nonmutually competing) arrangement of the NMe_2 nitrogen lone pair $2p_\pi$ orbitals. In **5b**, however, the methyl carbons of the axial NMe_2 effectively bisect the N(2)–Zr(1)–O(2) and O(1)–Zr(1)–N(3) angles so that some competition between the two NMe_2 nitrogen lone pairs presumably arises. The orientation of the

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $Zr(NMe_2)_2(O_2NN'{}^tBu)$ (5b)

Distances			
Zr(1)–O(1)	2.0380(11)	Zr(1)–N(2)	2.4597(14)
Zr(1)–O(2)	2.0245(11)	Zr(1)–N(3)	2.0706(14)
Zr(1)–N(1)	2.4670(13)	Zr(1)–N(4)	2.0832(14)
Angles			
O(1)–Zr(1)–O(2)	156.70(5)	O(2)–Zr(1)–N(4)	99.70(5)
O(1)–Zr(1)–N(1)	81.14(4)	N(1)–Zr(1)–N(4)	159.69(6)
O(2)–Zr(1)–N(1)	76.06(4)	N(2)–Zr(1)–N(4)	91.20(5)
O(1)–Zr(1)–N(2)	79.51(4)	N(3)–Zr(1)–N(4)	103.23(6)
O(2)–Zr(1)–N(2)	87.82(5)	Zr(1)–N(3)–C(37)	126.65(12)
N(1)–Zr(1)–N(2)	68.95(4)	Zr(1)–N(3)–C(38)	122.50(12)
O(1)–Zr(1)–N(3)	90.89(5)	C(37)–N(3)–C(38)	110.1(2)
O(2)–Zr(1)–N(3)	96.53(5)	Zr(1)–N(4)–C(39)	120.86(14)
N(1)–Zr(1)–N(3)	97.01(5)	Zr(1)–N(4)–C(40)	128.09(13)
N(2)–Zr(1)–N(3)	163.93(5)	C(39)–N(4)–C(40)	110.8(2)
O(1)–Zr(1)–N(4)	100.03(5)		

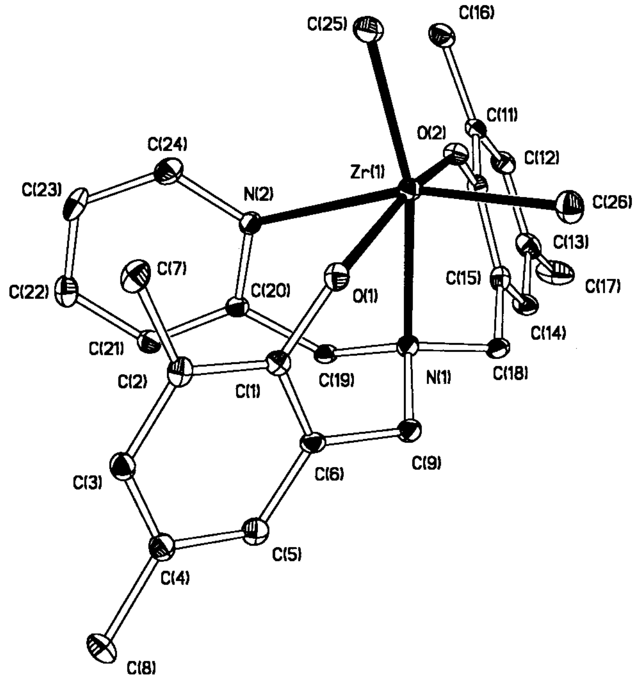


Figure 6. Displacement ellipsoid plot (20% probablility) of $ZrMe_2(O_2NN'^{Me})$ (**6a**) with hydrogen atoms omitted.

methyl groups of the axial NMe_2 ligand therefore attempts to balance between optimizing electronic and steric factors (putting the non-H atoms of the axial NMe_2 ligand in the {N(1), N(2), N(3), N(4)} plane would apparently place one of the methyl groups prohibitively close to the pyridyl group *ortho* hydrogen atoms).

The solution NMR spectra of **5b** are consistent with the C_s symmetric structure found in the solid state. There is no evidence for another isomer, unlike the dichloride analogue $ZrCl_2(O_2NN'^{tBu})$ (**3b**). The resonances in both the ^1H and ^{13}C spectra of **5b** are very sharp, unlike those of **3b**. There are two NMe_2 group environments (giving rise to two singlets for the two distinct NMe_2 ligands). The ^1H NMR subspectrum for $O_2NN'^{tBu}$ shows two equivalent 2-O-3,5-$C_6H_2{}^tBu_2$ moieties; the CH_2 protons adjacent to the pyridyl group appear as a singlet, whereas the other CH_2 group protons give rise to a pair of mutually coupled doublets.

Attempts to convert the bis(dimethylamide) compound **5b** to the corresponding dichloride **3b** by reaction with Me_3SiCl or HCl (1 M solution in diethyl ether) gave only unidentified mixtures. Attempts to prepare a dimethyl zirconium complex $ZrMe_2(O_2NN'^{tBu})$ by reaction of **5b** with $AlMe_3$ or $AlMe_3$·py in benzene were also unsuccessful. However, the target dimethyl complexes $ZrMe_2(O_2NN'^{R})$ [R = Me (**6a**) or ^{t}Bu (**6b**)] could be fairly easily obtained from the corresponding dichlorides $ZrCl_2(O_2NN'^{R})$ (**3a**, **3b**) via transmetalation reactions with methyllithium or methyl Grignard reagents (Scheme 2). Isolated yields are typically in the range 30−55%, and the white crystalline products so prepared are mildly air- and moisture-sensitive. Diffraction-quality crystals of both **6a** and **6b** were obtained, and the molecular structures are shown in Figures 6 and 7; selected bond lengths and angles are presented in Tables 6 and 7.

Both complexes **6a** and **6b** possess six-coordinate metal centers in an approximately octahedral geometry analogous to that described for **3b** and **5b** above. The phenoxide groups lie mutually *trans* to each other, and the molecules possess approximate C_s symmetry. The Zr−N and Zr−O distances are comparable to those of **5b** but longer than in **3b**, reflecting the better donor nature of methyl groups in comparison with Cl and NMe_2. The ^1H and ^{13}C NMR spectra are consistent with the solid-state structures and resemble those of $Zr(NMe_2)_2(O_2NN'^{tBu})$. The two methyl groups in **6a** and **6b** are in chemically different environments and give rise to two distinct singlets in the range 1.2−0.8 ppm. NOESY spectroscopy was used to assign the two different methyl group resonances, the most shielded methyl groups lying *trans* to the pyridyl moiety.

Reaction of $ZrCl_2(O_2NN'^{Me})$ (**3a**) with allylmagnesium chloride gave intractable mixtures. However, the cor-

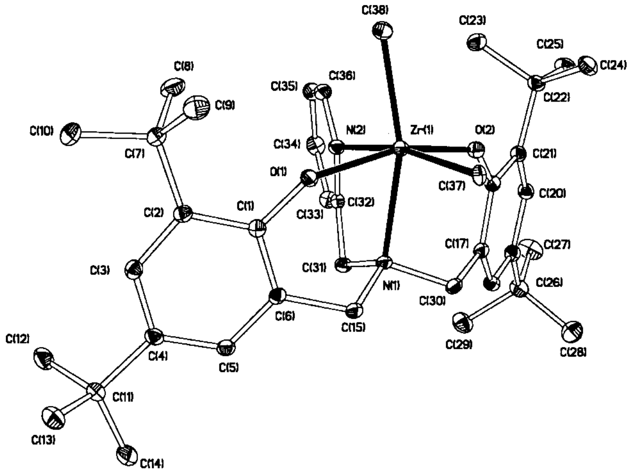


Figure 7. Displacement ellipsoid plot (25% probablility) of $ZrMe_2(O_2NN'^{tBu})$ (**6b**) with hydrogen atoms omitted.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $ZrMe_2(O_2NN'^{Me})$ (6a)

	Distances		
Zr(1)−C(25)	2.241(4)	Zr(1)−O(2)	1.988(3)
Zr(1)−C(26)	2.278(4)	Zr(1)−N(1)	2.504(3)
Zr(1)−O(1)	2.003(3)	Zr(1)−N(2)	2.452(3)
	Angles		
N(1)−Zr(1)−N(2)	68.2(1)	O(1)−Zr(1)−C(25)	103.05(14)
N(1)−Zr(1)−O(1)	80.7(1)	O(2)−Zr(1)−C(25)	95.15(14)
N(2)−Zr(1)−O(1)	76.0(1)	N(1)−Zr(1)−C(26)	96.81(13)
N(1)−Zr(1)−O(2)	77.2(1)	N(2)−Zr(1)−C(26)	163.18(14)
N(2)−Zr(1)−O(2)	88.0(1)	O(1)−Zr(1)−C(26)	94.52(13)
O(1)−Zr(1)−O(2)	156.4(1)	O(2)−Zr(1)−C(26)	96.34(13)
N(1)−Zr(1)−C(25)	160.6(2)	C(25)−Zr(1)−C(26)	101.8(2)
N(2)−Zr(1)−C(25)	93.95(14)		

Table 7. Selected Bond Lengths (Å) and Angles (deg) for $ZrMe_2(O_2NN'^tBu)$ (6b)

	Distances		
Zr(1)−C(37)	2.343(2)	Zr(1)−O(2)	2.009(2)
Zr(1)−C(38)	2.267(2)	Zr(1)−N(1)	2.446(2)
Zr(1)−O(1)	2.002(2)	Zr(1)−N(2)	2.497(2)
	Angles		
O(1)−Zr(1)−O(2)	158.85(7)	N(1)−Zr(1)−C(37)	99.63(7)
O(1)−Zr(1)−N(1)	78.95(6)	N(2)−Zr(1)−C(37)	166.95(7)
O(2)−Zr(1)−N(1)	80.65(7)	O(1)−Zr(1)−C(38)	96.98(8)
O(1)−Zr(1)−N(2)	87.90(6)	O(2)−Zr(1)−C(38)	99.14(8)
O(2)−Zr(1)−N(2)	79.45(7)	N(1)−Zr(1)−C(38)	154.99(8)
N(1)−Zr(1)−N(2)	68.51(6)	N(2)−Zr(1)−C(38)	86.78(8)
O(1)−Zr(1)−C(37)	95.28(7)	C(37)−Zr(1)−C(38)	105.32(9)
O(2)−Zr(1)−C(37)	93.57(7)		

responding reaction of $ZrCl_2(O_2NN'^{tBu})$ (**3b**) gave moderate yields of a bis(allyl)zirconium derivative formulated as $Zr(\eta^3\text{-}C_3H_5)_2(O_2NN'^{tBu})$ (**7b**). This compound is highly fluxional and also fairly unstable in solution. The latter feature meant that pure samples for elemental analysis could not be obtained, and so **7b** was characterized by only ^1H and ^{13}C NMR, and also IR, spectroscopy. The NMR spectra of **7b** show resonances typical of a C_s symmetric compound as illustrated. There are two different allyl environments in the NMR spectrum. At room temperature, one allyl ligand gives rise to an apparent quintet (integrating as 1 H) at 6.25 ppm and a time-averaged doublet (4 H) at 3.71; the other also gives an apparent quintet (1 H, at 7.09 ppm) which is associated with a broad signal (4 H) at ca. 3.83 ppm. On warming the sample to ca. 60 °C, this latter resonance sharpens and becomes a doublet; significant sample decomposition also sets in rapidly at this temperature. On cooling to −60 °C, this signal broadens into the baseline (as does the doublet for the other allyl ligand), but no new signals appear before the solvent (toluene-d_8) freezing point is reached. The appearance of each allyl ligand's resonances as an apparent quintet and a doublet is typical of fluxional systems undergoing rapid η^3- ↔ η^1- ↔ η^3-bound allyl group interconversions.[47] The apparent quintet corresponds to the "central" methine hydrogen; the NMR time scale-averaged doublets arise from the four "terminal" methylene hydrogens. We cannot tell if the allyl ligands in **7b** are η^3- or η^1-coordinated in the ground state. The solid-state IR spectra are uninformative in this regard because the absorptions for the $O_2NN'^{tBu}$ ligand itself mask the relevant region for allyl ligand absorptions. On balance we favor the formulation of **7b** as $Zr(\eta^3\text{-}C_3H_5)_2(O_2NN'^{tBu})$ with two η^3-bound allyl groups. Structurally characterized zirconium complexes possessing one,[48] two,[49] or three[50] η^3-allyl ligands have been reported previously.

Both of the protio ligand $H_2O_2NN'^R$ (**1a**, **1b**) undergo smooth protonolysis reactions with the tetra-alkyl or -benzyl zirconium compounds ZrR'_4 (R = CH_2SiMe_3,[32] CH_2CMe_3,[33] or CH_2Ph[34,35]). As shown in Scheme 2 these reactions form $ZrR'_2(O_2NN'^R)$ [R' = CH_2SiMe_3 (**8a**, **8b**), CH_2CMe_3 (**9a**, **9b**), or CH_2Ph (**10a**, **10b**); R = Me (suffix **a**) or ^{t}Bu (suffix **b**)], which are obtained in reasonable to good isolated yields as white or pale yellow microcrystalline solids. NMR tube scale reactions showed that **8a**, **8b**, **10a**, and **10b** are also formed quantitatively by the reaction of the dichloride complexes $ZrCl_2(O_2NN'^R)$ (**3a**, **3b**) with $LiCH_2SiMe_3$ or $PhCH_2MgCl$ in C_6D_6. While this work was in progress, the synthesis and X-ray structure of compound **10b** was reported by Kol, Goldschmidt, and co-workers, but no other chemistry of the $O_2NN'^R$ ligands was described.[22]

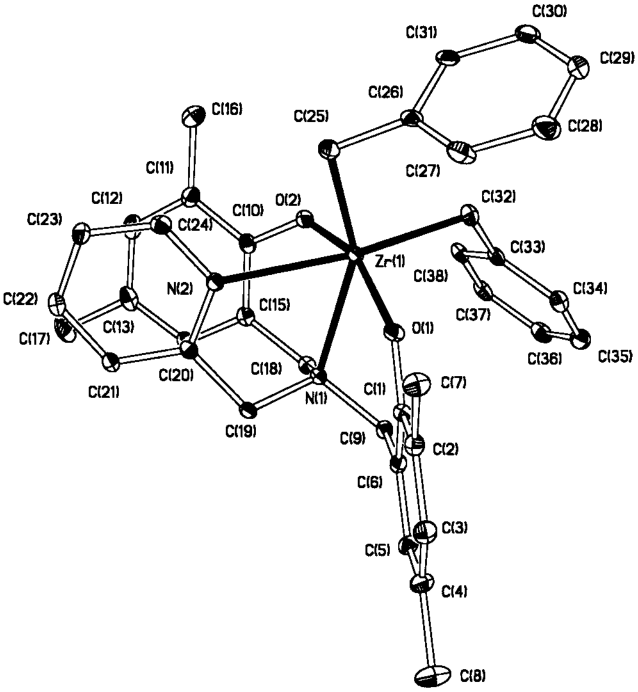


Figure 8. Displacement ellipsoid plot (20% probablility) of $Zr(CH_2Ph)_2(O_2NN'^{Me})$ (**10a**) with hydrogen atoms omitted.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for $Zr(CH_2Ph)_2(O_2NN'^{Me})$ (10a)

Distances			
Zr(1)−C(25)	2.300(3)	Zr(1)−O(1)	1.990(2)
Zr(1)−C(32)	2.312(3)	Zr(1)−O(2)	2.022(2)
Zr(1)···C(26)	3.006(2)	Zr(1)−N(1)	2.447(2)
Zr(1)···C(33)	3.288(2)	Zr(1)−N(2)	2.476(2)
Angles			
O(1)−Zr(1)−O(2)	157.25(7)	N(2)−Zr(1)−C(25)	81.15(8)
O(1)−Zr(1)−N(1)	76.86(7)	O(1)−Zr(1)−C(32)	100.17(9)
O(2)−Zr(1)−N(1)	80.42(7)	O(2)−Zr(1)−C(32)	88.51(9)
O(1)−Zr(1)−N(2)	93.54(7)	N(1)−Zr(1)−C(32)	110.06(8)
O(2)−Zr(1)−N(2)	77.33(7)	N(2)−Zr(1)−C(32)	165.77(9)
N(1)−Zr(1)−N(2)	69.27(6)	C(25)−Zr(1)−C(32)	100.9(1)
O(1)−Zr(1)−C(25)	96.63(9)	Zr(1)−C(25)−C(26)	103.2(2)
O(2)−Zr(1)−C(25)	102.37(9)	Zr(1)−C(32)−C(33)	118.9(2)
N(1)−Zr(1)−C(25)	149.04(8)		

For the purposes of comparison with **10b**, we determined the X-ray crystal structure of the less sterically crowded analogue $Zr(CH_2Ph)_2(O_2NN'^{Me})$ (**10a**). The molecular structure is shown in Figure 8, and selected bond distances and angles are given in Table 8. Molecules of **10a** possess approximately octahedrally coordinated metal centers and C_s symmetry. The bond distances and angles associated with the $Zr(O_2NN'^{Me})$ moiety are comparable with those described above for other systems containing the $Zr(O_2NN'^R)$ fragment. All of the distances and angles for **10a** are comparable to those reported previously for **10b**. In **10a** the phenyl *ipso* carbon C(26) of the "axial" benzyl group is loosely associated [Zr(1)···C(26) = 3.006(2) Å] with the metal center. The corresponding $Zr-CH_2-Ph$ angle for this ligand is 103.2(2)°, which is significantly more acute than for the "equatorial" benzyl ligand [Zr(1)−C(32)−C(33) = 118.9(2)°, Zr(1)···C(33) = 3.288(2) Å]. In **10b** the axial benzyl ligand also features a $Zr\cdots C_{ipso}$ interaction, although in this complex the extent of interaction is apparently greater [$Zr-CH_2-Ph$ = 92.2(3)°; $Zr\cdots C_{ipso}$ = 2.771(5) Å]. The origin of the loose $Zr\cdots C_{ipso}$ interactions in **10a** and **10b** is likely to be electronic in nature since the Zr centers in these compounds otherwise possess only 12 valence electron counts (discounting any likely $O_{2p(\pi)} \rightarrow Zr_{4d(\pi)}$ π-interactions). It is not clear why

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the Zr···C$_{ipso}$ interaction in **10b** is stronger than in the less sterically crowded homologue **10a**, but the influences of intermolecular packing effects may be important in these systems.

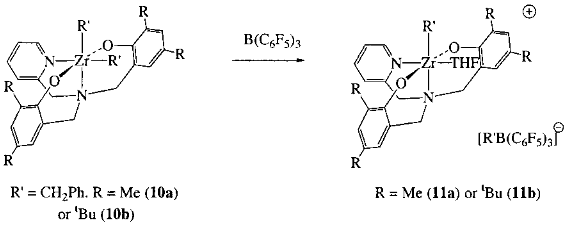
The ^{1}H and ^{13}C NMR spectra of all the compounds ZrR′$_2$(O$_2$NN′^{R}) (**8a**−**10b**) are fully consistent with the C_s-symmetrical structures depicted in Scheme 2 and the structures found in the solid state for **10a** and **10b**. As for the dimethyl compounds ZrMe$_2$(O$_2$NN′^{R}) (**6a**, **6b**) the two alkyl groups in **8a**−**10b** are in chemically inequivalent sites and give rise to two different sets of resonances in the NMR spectra. One-dimensional NOE experiments were used to assign unambiguously the two alkyl groups (in each compound an NOE interaction is observed between the pyridyl group *ortho* hydrogen and the CH$_2$ group of the *cis*-alkyl substituent). By analogy with the dimethyl complexes **6a** and **6b**, the CH$_2$ protons of the alkyl groups *trans* to pyridyl in **8a**−**10b** are in all cases the more shielded.

In addition, the ^{13}C data for the CH$_2$Ph groups of **10a** and **10b** appear to reflect the slight η^2-coordination (i.e., through Zr−CH$_2$ and Zr···C$_{ipso}$ interactions) of the *cis* (with respect to pyridyl) benzyl groups. The C$_{ispo}$ resonances for the weakly η^2-bound *cis* benzyl groups appear at 146.4 ppm in both **10a** and **10b**, whereas those for the *trans* benzyls appear at 149.3 and 149.9 ppm, respectively. We note that there is a much smaller difference between the *cis* and *trans* CH$_2$ group carbons (*cis* to pyridyl: 65.3 and 67.6; *trans* to pyridyl: 65.6 and 67.0, for **10a** and **10b** respectively); furthermore, while the differences between *cis* and *trans* benzyl C$_{ipso}$ chemical shifts are ca. 3−3.5 ppm, the differences between other pairs of ring carbon shifts (namely *ortho*, *meta*, and *para*) are in the range 0.1−2.0 ppm.

Screening of the new dichloride (**3a**, **3b**) or dibenzyl (**10a**, **10b**) or dimethyl (**6b**) complexes for ethylene polymerization (toluene solvent with 5−7 atm pressure C$_2$H$_4$) in the presence of methylaluminoxane (for **3a**, **3b** and **10b**; Zr:Al ratio ca. 1:1500) or B(C$_6$F$_5$)$_3$ (for **6b** and **10a**, **10b**; Zr:B ratio ca. 1:1) were effectively unsuccessful, and only trace amounts of polymer were obtained.

We note that Kol and Goldschmidt[22] have reported the successful polymerization of 1-hexene with **10b**. We attribute the difference between our results (negative, i.e., attempted ethylene polymerization in toluene) and theirs to the fact that these authors carried out their polymerizations in *neat* 1-hexene (for **10b**: activity 5700 g poly(1-hexene) mmol^{-1} h^{-1} with $M_w/M_n = 4.5$); on dilution of the 1-hexene monomer to 30% 1-hexene/70% heptane the activity dropped by an order of magnitude to 650 g mmol^{-1} h^{-1}. There is a larger dilution effect in our case using 5−7 bar C$_2$H$_4$ (headspace pressure), and so despite the fact that α-olefins intrinsically give lower polymerization rates, the dilution effects in our screening experiments possibly outweigh the expected higher activity of ethylene over 1-hexene.

Attempts to generate stable cationic organozirconium complexes with B(C$_6$F$_5$)$_3$ on an NMR tube scale from the dimethyl or dibenzyl species ZrR′$_2$(O$_2$NN′^{R}) (**6a**, **6b** or **10a**, **10b**) gave only ill-defined mixtures. However, reaction of Zr(CH$_2$Ph)$_2$(O$_2$NN′^{R}) (**10a**, **10b**) with B(C$_6$F$_5$)$_3$ in the presence of THF (eq 2) gave the fully characterized cationic complexes [Zr(CH$_2$Ph)(THF)(O$_2$NN′^{R})]$^+$ as the [PhCH$_2$B(C$_6$F$_5$)$_3$]$^-$ salts (**11a**, **11b**). In contrast, the reaction of the dimethyl compounds **6a**, **6b** with B(C$_6$F$_5$)$_3$ in the presence of THF gave only ill-defined mixtures.



(2)

^{1}H NMR NOE analyses of **11a**, **11b** established that the benzyl groups in both cations are positioned *cis* to the pyridyl donor group. The ^{1}H and ^{19}F NMR spectra of the previously reported[51] anion [PhCH$_2$B(C$_6$F$_5$)$_3$] in **11a**, **11b** suggest that there is no significant interaction between it and the cation.[52] The ^{13}C NMR data for the zirconium-bound benzyl groups in **11a**, **11b** suggest an interaction between the *ipso* carbons and the cationic zirconium centers, with the *ispo* carbon resonances appearing ca. 10 ppm *upfield* of the analogous positions in the dibenzyls **10a**, **10b** (the other resonances for the CH$_2$Ph groups of **11a**, **11b** appear *downfield* of them). Indeed, on the basis of the X-ray structures of the neutral dibenzyl complexes **10a**, **10b** it would appear likely that such interactions would exist also in the [Zr(CH$_2$Ph)(THF)(O$_2$NN′^{R})]$^+$ cations of **11a**, **11b**. Since it is only the *cis*-positioned benzyl groups in both **10a**, **10b** that exhibit a Zr···C$_{ipso}$ interaction, we believe (i) that this helps to account for the observation that the remaining benzyl group preferentially occupies the *cis* coordination site (although other factors such as the greater *trans* labilizing effect of the pyridyl N-donor may also contribute) and (ii) that the intramolecular stabilization through an *ipso* carbon interaction may explain why stable cationic complexes can be prepared from the dibenzyl complexes **10a**, **10b** but not from the dimethyl homologues **6a**, **6b**.

Conclusions

The readily available H$_2$O$_2$NN′^{R} (**1a**, **1b**) and Na$_2$O$_2$NN′^{R} (**2a**, **2b**) provide useful entry points to new organometallic and coordination complexes of zirconium. A series of six- or eight-coordinate derivatives have been prepared and crystallographically characterized. Attempts to generate catalytically active systems for the polymerization of ethylene were unsuccessful, although THF-stabilized benzyl cations have been identified. We are continuing to explore the early transition metal chemistry of the O$_2$NN′^{R} ligand systems, and this work 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 **3a**, **3b**, **4a**, **5b**, **6a**, **6b**, and **10a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010982W

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