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 diaminebis(phenolate) ligands $O_2NN'^{Me}$ and $O_2NN'^{tBu}$ are reported $[H_2O_2NN'^{R} = (2-C_5H_4N)CH_2N (CH_2-2-HO-3,5-C_6H_2R_2)_2$, 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 H2O2NN'R with Zr(CH2SiMe3)2Cl2(Et2O)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 Na₂O₂NN'^{tBu} and ZrCl₄(THF)₂, but reaction of Na₂O₂NN'^{Me} with either $ZrCl_4$ in benzene or $ZrCl_4(THF)_2$ in THF gives mixtures of **3a** and the eightcoordinate bis(diamine-bis(phenolate)) complex Zr(O₂NN'^{Me})₂ (4a). The latter can also be prepared from 2 equiv of H₂O₂NN'^{Me} and Zr(CH₂SiMe₃)₄. Treatment of Zr(NMe₂)₄ with H₂O₂-NN'tBu leads to the bis(dimethylamide) derivative Zr(NMe₂)₂(O₂NN'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' = CH₂SiMe₃ (8a, 8b), CH₂- CMe_3 (9a, 9b), or CH_2Ph (10a, 10b); R = Me (suffix a) or 'Bu (suffix b)]. The dichloride complexes ZrCl₂(O₂NN'^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 $ZrR'_{2}(O_{2}NN'^{R})$ [R' = Me (6a, 6b), η^{3} -C₃H₅ (7b), CH₂SiMe₃ (8a, 8b), CH₂Ph (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 chemistry¹ 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 particular²⁻⁹ 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

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M = Sc, Y, Ti, Zr, Hf, Nb, Ta; neutral or cationic; A, B = single- or multipy-bonded ligand; $R = Me \text{ or } {}^{t}Bu$



II $M = Ti, Zr; X = Cl, NMe_2 \text{ or } CH_2SiMe_3$

 $R = Me: H_2O_2NN^{Me} (1a)$ $\mathbf{R} = {}^{\mathrm{t}}\mathbf{B}\mathbf{u}: \ \mathbf{H}_2\mathbf{O}_2\mathbf{N}\mathbf{N}^{\mathrm{t}\mathbf{B}\mathbf{u}} \ (\mathbf{1b})$



M = Y, n = 2, $R = \mu_2$ -Cl, L = py

In our group we have been developing new diaminebis(amide) ligands of the type (2-C₅H₄N)CH₂N(CH₂CH₂- $NSiMe_2R)_2$ (abbreviated as N_2NN' , 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 $M(A)(B)(N_2NN')$ and $M(A)(N_2NN')$ (I, Chart 1). We have developed in parallel studies the diamine-bis-(alkoxide) ligand (2-C₅H₄N)CH₂N(CH₂CMe₂O)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 $O_2NN'^{Me}$ and $O_2NN'^{tBu}$ [H₂O₂NN'^R = (2-C₅H₄N)CH₂N- $(CH_2-2-HO-3,5-C_6H_2R_2)_2$, where R = Me (1a) or ^tBu (1b);²⁸ see Chart 1]. The more sterically demanding ligand O2NN'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 airand/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 (C₆D₆) or calcium hydride (CD₂Cl₂ and C₅D₅N), 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.

¹H and ¹³C{¹H} NMR spectra were recorded on Varian Venus 300 or Varian Unity Plus 500 spectrometers. ¹H and ¹³C assignments were confirmed when necessary with the use of one-dimensional NOE experiments and of two-dimensional ¹H-¹H COSY, ¹H-¹H NOESY, ¹³C-¹H HSQC, and HMBC NMR experiments. All spectra were referenced internally to residual protio-solvent (1H) or solvent (13C) resonances and are reported relative to trimethylsilane ($\delta = 0$ 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 H₂O₂NN'tBu (1b),²⁸ ZrCl₄(THF)₂,³⁰ Zr(CH₂SiMe₃)₂Cl₂(Et₂O)₂,³¹ Zr(CH₂-SiMe₃)₄,³² Zr(CH₂CMe₃)₄,³³ and Zr(CH₂Ph)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.



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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%).

¹H NMR (300.18 MHz, CDCl₃, 293 K): δ 10.42 (s, 2H, OH), 8.69 (d, ³*J*_{H1-H2} = 5.8 Hz, 1H, H₁), 7.68 (ddd, ³*J*_{H3-H4} = 8.2 Hz, ³*J*_{H3-H2} = 7.0 Hz, ⁴*J*_{H3-H1} = 1.8 Hz, 1H, H₃), 6.26 (dd, ³*J*_{H2-H1} = 5.8 Hz, ³*J*_{H2-H3} = 7.0 Hz, 1H, H₂), 7.10 (d, ³*J*_{H4-H3} = 8.2 Hz, 1H, H₄), 6.90 (d, ⁴*J*_{H11-H9} = 1.2 Hz, 2H, H₁₁), 6.74 (d, ⁴*J*_{H9-H11} = 1.2 Hz, 2H, H₉), 3.82 (s, 2H, H₆), 3.74 (s, 4H, H₇), 2.28 (s, 3H, H₁₄), 2.21 (s, 3H, H₁₅). ¹³C{¹H} NMR (75.48 MHz, CDCl₃, 293 K): δ 156.1 (C₅), 153.1 (C₁₃), 148.2 (C₁), 137.4 (C₃), 131.1 (C₁₁), 128.4 (C₉), 127.4 (C₁₂), 125.4 (C₁₀), 123.6 (C₄), 122.4 (C₂), 120.7 (C₈), 56.4 (C₇), 55.4 (C₆), 20.3 (C₁₅), 16.2 (C₁₄). MS-EI (*m*/*z*): 377 (50%) [MH]⁺, 243 (70%) [MH - CH₂(C₆H₂-(CH₃)₂O]⁺. Anal. Found (Calcd for C₂₄H₂₈N₂O₂): 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 (Na₂O₂NN'^{Me}, 2a). A solution of H₂O₂-NN'^{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 ¹H NMR spectrum.

¹H NMR (300.18 MHz, C₅D₅N, 293 K): δ 8.16 (d, ³J_{H1-H2} = 4.7 Hz, 1H, H₁), 7.42 (dd, ${}^{3}J_{H3-H4} = 8.2$ Hz, ${}^{3}J_{H3-H2} = 7.6$ Hz, 1H, H₃), 7.10 (d, ${}^{3}J_{H4-H3} = 8.2$ Hz, 1H, H₄), 7.08 (br s, 2H, H₁₁), 6.87 (br s, 2H, H₉), 6.74 (dd, ${}^{3}J_{H2-H3} = 7.6$ Hz, ${}^{3}J_{H2-H1} = 4.7$ Hz, 1H, H₂), 3.82 (vbr s, 4H, H_{6 or 7,7'}), 2.90 (vbr s, 2H, H₇ or 7'), 2.38 (s, 3H, H₁₄), 2.34 (s, 3H, H₁₅). ¹³C{¹H} NMR (75.43 MHz, C₅D₅N, 293 K): δ 166.9 (C₁₃), 161.0 (C₅), 150.5 (C₁), 137.7 (C₃), 133.0 (C₉), 132.3 (C₁₁), 126.1 (C₁₂), 125.3 (C₄), 122.5 (C₂), 119.4 (C10), 62.5 (C6), 61.2 (vbr,C7), 20.1 (C15), 19.8 (C14) (C8 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 C24H26N2O2Na2 (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 (Na₂O₂NN'^{tBu}, 2b). 2b was produced by a procedure analogous with that for Na₂O₂NN'^{Me}, with H₂O₂-NN'^{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%).

¹H NMR (300.18 MHz, C_5D_5N , 293 K): δ 7.61 (d, ${}^3J_{H1-H2} =$ 4.5 Hz, 1H, H₁), 7.37 (ddd, ${}^3J_{H3-H4} =$ 7.7 Hz, ${}^3J_{H3-H2} =$ 7.4 Hz, ${}^4J_{H3-H1} =$ 1.9 Hz, 1H, H₃), 7.32 (d, ${}^4J_{H11-H9} =$ 2.7 Hz, 2H, H₁₁), 7.19 (d, ${}^3J_{H4-H3} =$ 7.7 Hz, 1H, H₄), 6.98 (d, ${}^4J_{H9-H11} =$ 2.7 Hz, 2H, H₉), 6.63 (dd, ${}^3J_{H2-H1} =$ 4.5 Hz, ${}^3J_{H2-H3} =$ 7.4 Hz, 1H, H₂), 4.71 (br s, 2H, H₇₀₇₇), 4.14 (s, 2H, H₆), 3.39 (br s, 2H, H₇₀₇₇), 1.63 (s, 18H, H₁₅), 1.33 (s, 18H, H₁₇). ¹³C{¹H} NMR (75.43 MHz, C₅D₅N, 293 K): δ 168.9 (C₁₃), 162.2 (C₅), 149.1 (C₁), 137.0 (C₃), 136.7 (C₁₂), 126.95 and 126.9 (C₈ and C₉), 123.5 (C₄), 123.0 (C₁₁), 121.6 (C₂), 66.1 (C₇₀₇₇), 62.8 (C₆), 36.1 (C₁₄), 34.3 (C₁₆), 32.9 (C₁₇), 30.7 (C₁₅). 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 $C_{36}H_{50}N_2O_2Na_2)\colon$ 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(O₂NN'^{Me})₂ (4a). Method A. A suspension of ZrCl₄ (0.13 g, 0.56 mmol) and Na₂O₂NN'^{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.

¹H NMR (499.99 MHz, CD₂Cl₂, 293 K): δ 9.75 (d, ³J_{H1-H2} = 5.7 Hz, 1H, H₁), 7.43 (ddd, ${}^{3}J_{H3-H4} = 7.8$ Hz, ${}^{3}J_{H3-H2} = 7.5$ Hz, ${}^{4}J_{\text{H3}-\text{H1}} = 1.7$ Hz, 1H, H₃), 7.02 (dd, ${}^{3}J_{\text{H2}-\text{H1}} = 5.7$ Hz, ${}^{3}J_{\text{H2}-\text{H3}}$ = 7.5 Hz, 1H, H₂), 6.81 (d, ${}^{3}J_{H4-H3}$ = 7.8 Hz, 1H, H₄), 6.72 (d, ${}^{4}J_{H11'-H9'} = 2.2$ Hz, 1H, H_{11'}), 6.64 (d, ${}^{4}J_{H9'-H11'} = 2.2$ Hz, 1H, H₉), 6.51 (d, ${}^{4}J_{H9-H11} = 2.2$ Hz, 1H, H₉), 6.36 (d, ${}^{4}J_{H11-H9} = 2.2$ Hz, 1H, H₁₁), 4.84 (d, ${}^{2}J_{H6-H6'} = 15.0$ Hz, 1H, H_{60r6'}), 4.75 (d, ${}^{2}J_{\text{H7"-H7"'}} = 12.8$ Hz, 1H, H_{7"or7"'}), 3.91 (d, ${}^{2}J_{\text{H7-H7'}} = 12.2$ Hz, 1H, H_{7or7'}), 3.61 (d, ${}^{2}J_{H6-H6'}$ = 15.0 Hz, 1H, H_{6or6'}), 3.10 (d, ${}^{2}J_{\text{H7"-H7"}} = 12.8$ Hz, 1H, H_{7"or7"}), 2.57 (d, ${}^{2}J_{\text{H7-H7'}} = 12.2$ Hz, 1H, H_{70r7}), 2.15 (s, 3H, H₁₄), 2.12 (s, 3H, H₁₅), 2.03 (s, 3H, H₁₅), 1.42 (s, 3H, H₁₄). ¹³C{¹H} NMR (125.74 MHz, CD₂Cl₂, 293 K): δ 160.8 (C_{13'}), 158.2 (C₁₃), 157.2 (C₅), 148.4 (C₁), 137.1 (C₃), 131.4 (C_{11'}), 131.1 (C₁₁), 127.9 (C₉), 127,8 (C₉), 125.1 (C_{12'}), 125.0 (C10'), 124.9 (C8), 124.8 and 124.75 (C10 and C12), 124.2 (C8'), 121.8 (C₂), 120.8 (C₄), 65.9 (C₆), 64.1 (C_{7"}), 60.3 (C₇), 20.5 (C_{15"}), 20.3 (C₁₅), 18.4 (C₁₄), 16.6 (C₁₄). 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 C48H52N4O4Zr (C6H6)0.25): C 69.06 (69.15), H 6.35 (6.27), N 6.37 (6.51).

ZrCl₂(O₂NN^{'Me}) (3a). A solution of $H_2O_2NN'^{Me}$ (1.17 g, 3.1 mmol) in benzene (25 mL) was added dropwise to $ZrCl_2(CH_2-SiMe_3)_2 \cdot (Et_2O)_2$ (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 = t-Bu: o-CMe₃, p-CMe₃

¹H NMR (499.99 MHz, CD₂Cl₂, 213 K): C₁ symmetry isomer: δ 8.76 (d, ${}^{3}J_{\text{H1}-\text{H2}} = 5.2$ Hz, 1H, H₁), 7.63 (ddd, ${}^{3}J_{\text{H3}-\text{H4}} = {}^{3}J_{\text{H3}-\text{H2}}$ = 7.8 Hz, ${}^{4}J_{H3-H1}$ = 1.7 Hz, 1H, H₃), 7.21 (dd, ${}^{3}J_{H2-H1}$ = 5.2 Hz, ${}^{3}J_{H2-H3} = 7.8$ Hz, 1H, H₂), 7.00 (d, ${}^{3}J_{H4-H3} = 7.8$ 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, H₁₁), 4.97 (d, ${}^{2}J_{H7''-H7''} = 13.4$ Hz, 1H, H_{7''or7'''}), 4.62 (d, ${}^{2}J_{\text{H6-H6'}} = 15.4 \text{ Hz}, 1\text{H}, \text{H}_{60r6'}$, 3.82 (d, ${}^{2}J_{\text{H6-H6'}} = 15.4 \text{ Hz}, 1\text{H},$ H_{60r6'}), 3.82 (d, ${}^{2}J_{H7-H7'} = 12.9$ Hz, 1H, H_{70r7'}), 3.55 (d, ${}^{2}J_{H7''-H7'''}$ = 13.4 Hz, 1H, $H_{7or7'}$), 2.97 (d, ${}^{2}J_{H7-H7'}$ = 12.9 Hz, 1H, $H_{7or7'}$), 2.24 (s, 3H, H₁₄), 2.23 (s, 3H, H₁₅), 2.00 (s, 3H, H₁₅), 1.84 (s, 3H, H₁₄). C_s symmetry isomer: δ 8.82 (d, ${}^{3}J_{\text{H1-H2}} = 5.8$ Hz, 1H, H₁), 7.48 (ddd, ${}^{3}J_{H3-H4} = 8.3$ Hz, ${}^{3}J_{H3-H2} = 7.4$ Hz, ${}^{4}J_{H3-H1} =$ 1.7 Hz, 1H, H₃), 7.11 (dd, ${}^{3}J_{H2-H1} = 5.8$ Hz, ${}^{3}J_{H2-H3} = 7.4$ Hz, 1H, H₂), 6.82 (s, 2H, H₁₁), 6.75 (s, 2H, H₉), 6.57 (d, ${}^{3}J_{H4-H3} =$ 8.3 Hz, 1H, H₄), 4.74 (d, ${}^{2}J_{H7-H7'} = 13.4$ Hz, 2H, H_{7or7'}), 3.78 (s, 2H, H₆), 3.53 (d, ${}^{2}J_{H7-H7'}$ = 13.4 Hz, 2H, H_{7or7'}), 2.15 (s, 6H, H₁₄), 1.96 (s, 6H, H₁₅). $^{13}C{^{1}H}$ NMR (125.74 MHz, CD₂Cl₂, 233 K): C_1 symmetry isomer: δ 156.0 (C_{13}), 155.6 (C_5), 153.9 (C13), 146.0 (C1), 140.0 (C3), 131.6 (C11), 131.4 (C11), 129.9 (C10), 128.6 (C10), 127.8 (C9), 127.1 (C9), 125.4 (C12), 124.4 (C12), 123.3 (C2), 123.0 (C8), 122.7 (C8), 122.2 (C4), 64.1 (C6), 63.4 (C7"), 60.0 (C7), 20.4 (C15'), 20.1 (C15), 15.9(C14'), 15.3 (C14). 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%) $[M - CH_2(C_6H_2(CH_3)_2O)]^+$. Anal. Found (Calcd for C₂₄H₂₆Cl₂N₂O₂Zr): C 53.43 (53.72), H 4.99 (4.88), N 4.97 (5.22).

ZrCl₂(O₂NN'^{tBu}) (3b). Method A. 3b was formed by a procedure analogous with that for $ZrCl_2(O_2NN'^{Me})$, with H_2O_2 -NN'^{tBu} (1.65 g, 3.03 mmol) and $ZrCl_2(CH_2SiMe_3)_2(Et_2O)_2$ (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 $Na_2O_2NN'^{tBu}$ (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 CH₂Cl₂ (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 ¹³C spectrum.

 $^1\mathrm{H}$ NMR (499.99 MHz, CD2Cl2, 213 K): δ 8.73 (C_{s} d, $^3J_{\mathrm{H1-H2}}$ = 5.2 Hz, 1H, H₁), 8.59 (C_1 , d, ${}^{3}J_{H1-H2}$ = 5.4 Hz, 1H, H₁), 7.60 $(C_1, \text{ ddd}, {}^{3}J_{\text{H3}-\text{H4}} = 7.9 \text{ Hz}, {}^{3}J_{\text{H3}-\text{H2}} = 7.6 \text{ Hz}, {}^{4}J_{\text{H3}-\text{H1}} = 1.5 \text{ Hz},$ 1H, H₃), 7.47 (C_s , ddd, ${}^{3}J_{H3-H4} = 8.0$ Hz, ${}^{3}J_{H3-H2} = 7.4$ Hz, ${}^{4}J_{\text{H3}-\text{H1}} = 1.7 \text{ Hz}, 1\text{H}, \text{H}_{3}$), 7.26 (*C*₁, d, 1\text{H}), 7.16 (*C*₁, dd, ${}^{3}J_{\text{H2}-\text{H1}}$ = 5.5 Hz, ${}^{3}J_{\text{H2}-\text{H3}}$ = 7.6 Hz, 1H, H₂), 7.09 (*C*_s, dd, ${}^{3}J_{\text{H2}-\text{H1}}$ = 5.6 Hz, ${}^{3}J_{\text{H2-H3}} = 7.4$ Hz, 1H, H₂), 7.08–7.05 (m, 3H), 7.03 (d, 1H), 6.78 (m, 2H), 6.61 (C_s , d, ${}^{3}J_{H4-H3} = 8.0$ Hz, 1H, H₄), 5.02 (C_1 , d, ${}^{2}J_{H7''-H7'''} = 13.5$ Hz, 1H, $H_{7''or7''}$), 4.76 (*C_s*, d, ${}^{2}J_{H7-H7'} = 14.0$ Hz, 2H, H_{70r7}), 4.73 (C_1 , d, ${}^2J_{H6-H6'} = 15.5$ Hz, 1H, H_{60r6}), 3.94 $(C_1, d, {}^2J_{H6-H6'} = 15.5 Hz, 1H, H_{60r6'}), 3.93 (C_s, s, 4H, H_6), 3.74$ $(C_1, d, {}^2J_{H7-H7'} = 13.1 \text{ Hz}, 1H, H_{70r7'}), 3.60 (C_s, d, {}^2J_{H7-H7'} =$ 14.0 Hz, 2H, $H_{7or7'}$), 3.57 (C_1 , d, ${}^2J_{H7''-H7'''}$ = 13.5 Hz, 1H, $H_{7or7'}$), 3.00 (C_1 , d, ${}^2J_{\text{H7-H7'}} = 13.1$ Hz, 1H, $H_{7\text{or}7'}$), 1.41 (s, 9H), 1.20 (s, 18H), 1.18 (s, 9H), 1.16 (s, 9H), 1.02 (s, 9H). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.48 MHz, CD₂Cl₂, 223 K): δ 157.5, 156.7, 156.1, 155.0, 150.7 (C_s, C₁), 147.3 (C₁, C₁), 143.1, 142.3, 141.7, 140.4 (C_s and C₁, 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 (Cs, C4), 64.8 (C1, C6), 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 $C_{36}H_{50}Cl_2N_2O_2Zr):\ C\ 61.12$ (61.34), H 7.12 (7.15), N 3.80 (3.97).

 $Zr(NMe_2)_2(O_2NN'^{tBu})$ (5b). A solution of $H_2O_2NN'^{tBu}$ (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.

¹H NMR (300.18 MHz, C₆D₆, 293 K): δ 8.29 (d, ³J_{H1-H2} = 5.3 Hz, 1H, H₁), 7.33 (d, ${}^{4}J_{H11-H9} = 3$ Hz, 2H, H₁₁), 6.91 (d, ${}^{4}J_{\text{H9-H11}} = 3$ Hz, 2H, H₉), 6.41 (ddd, ${}^{3}J_{\text{H3-H4}} = 7.6$ Hz, ${}^{3}J_{\text{H3-H2}}$ = 7.6 Hz, ${}^{4}J_{H3-H1}$ = 1.8 Hz, 1H, H₃), 6.17 (dd, ${}^{3}J_{H2-H1}$ = 5.3 Hz, ${}^{3}J_{H2-H3} = 7.6$ Hz, 1H, H₂), 5.68 (d, ${}^{3}J_{H4-H3} = 7.6$ Hz, 1H, H₄), 4.44 (d, ${}^{2}J_{H7-H7'}$ = 12.3 Hz, 2H, H_{70r7'}), 3.63 (s, 6H, H_{190r18}), 3.34 (s, 6H, H₁₈₀₁₉), 3.16 (s, 2H, H₆), 2.90 (d, ${}^{2}J_{H7-H7'} = 12.3$ Hz, 2H, H_{70r7'}), 1.60 (s, 18H, H₁₅), 1.37 (s, 18H, H₁₇). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 293 K): δ 159.2 (C₁₃), 158.4 (C₅), 149.7 (C1), 138.9 (C10), 137.2 (C3), 136.6 (C12), 125.1 (C9), 124.7 (C8), 123.8 (C₁₁), 121.5 (C₂), 120.9 (C₄), 64.1 (C₇), 57.5 (C₆), 45.9 (C₁₈₀₇₁₉), 44.7 (C₁₉₀₇₁₈), 35.3 (C₁₄), 34.2 (C₁₆), 32.1 (C₁₇), 30.1 (C₁₅). 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 C₄₀H₆₂N₄O₂Zr): 66.53; H, 8.65; N, 7.76. Found: C 66.18 (66.53), H 8.74 (8.65), N 7.37 (7.76).

ZrMe₂(O₂NN^{'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 ZrCl₂(O₂NN^{'Me}) (0.30 g, 0.56 mmol) in benzene (25 mL) with cooling using an ice/water bath. The mixture was



14 15 For R = Me: *o*-Me, *p*-Me For R = *t*-Bu: *o*-CMe₃, *p*-CMe₃ 14 15 16 17

18 19
For
$$X = NMe_2$$
: $NMe_{2(trans)}$ $NMe_{2(cis)}$

18 19 For X = Me: $Me_{(trans)}$, $Me_{(cis)}$

For $X = CH(CH_2)_2$: $CH(CH_2)_{2(trans)}$ $CH(CH_2)_{2(cis)}$

18

$$18 \quad 19 \qquad 20 \quad 21$$

For X = CH₂SiMe₃: CH₂SiMe_{3(tenne)} CH₂SiMe_{3(cic)}

 $18 \quad 19 \quad 21 \qquad 22 \quad 23 \quad 24$ For X = CH₂CMe₃: CH₂CMe_{3(trans)} CH₂CMe_{3(cis)}

For X = CH₂Ph: trans to pyridyl H_2C cis to pyridyl H_2C 23 242727

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 $\text{ZrCl}_2(\text{O}_2\text{NN}^{\text{Me}})$ (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%).

¹H NMR (499.99 MHz, C₆D₆, 293 K): δ 8.18 (d, ³*J*_{H1-H2} = 5.4 Hz, 1H, H₁), 6.71 (s, 2H, H₁₁), 6.50 (s, 2H, H₉), 6.30 (ddd, ³*J*_{H3-H4} = 7.8 Hz, ³*J*_{H3-H2} = 7.6 Hz, ⁴*J*_{H3-H1} = 0.9 Hz, 1H, H₃), 6.01 (dd, ³*J*_{H2-H1} = 5.4 Hz, ³*J*_{H2-H3} = 7.6 Hz, 1H, H₂), 5.54 (d, ³*J*_{H4-H3} = 7.8 Hz, 1H, H₄), 4.11 (d, ²*J*_{H7-H7'} = 12.9 Hz, 2H, H_{70r7'}), 2.97 (s, 2H, H₆), 2.66 (d, ²*J*_{H7-H7'} = 12.9 Hz, 2H, H_{70r7'}), 2.97 (s, 2H, H₆), 2.66 (d, ²*J*_{H7-H7'} = 12.9 Hz, 2H, H_{70r7'}), 2.26 (s, 6H, H₁₄), 2.15 (s, 6H, H₁₅), 1.11 (s, 3H, H₁₉), 0.85 (s, 3H, H₁₈). ¹³C{¹H} NMR (125.74 MHz, C₆D₆, 293 K): δ 158.7 (C₁₃), 158.3 (C₅), 148.1 (C₁), 137.2 (C₃), 132.0 (C₁₁), 128.2 (C₉), 126.5 (C₁₀), 125.8 (C₁₂), 123.6 (C₈), 121.8 (C₂), 120.4 (C₄), 62.7 (C₇), 58.2 (C₆), 38.6 (C₁₉), 38.2 (C₁₈), 20.6 (C₁₅), 16.1 (C₁₄). 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.)

ZrMe₂(O₂NN'^{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%).

¹H NMR (499.99 MHz, C₆D₆, 293 K): δ 8.19 (d, ³J_{H1-H2} = 5.6 Hz, 1H, H₁), 7.36 (d, ${}^{4}J_{H11-H9} = 2.6$ Hz, 2H, H₁₁), 6.86 (d, ${}^{4}J_{\text{H9-H11}} = 2.6 \text{ Hz}, 2\text{H}, \text{H}_{9}$, 6.32 (ddd, ${}^{3}J_{\text{H3-H4}} = 8.0 \text{ Hz}, {}^{3}J_{\text{H3-H2}}$ = 7.6 Hz, ${}^{4}J_{H3-H1}$ = 1.7 Hz, 1H, H₃), 6.05 (dd, ${}^{3}J_{H2-H1}$ = 5.6 Hz, ${}^{3}J_{H2-H3} = 7.6$ Hz, 1H, H₂), 5.56 (d, ${}^{3}J_{H4-H3} = 8.0$ Hz, 1H, H₄), 4.07 (d, ${}^{2}J_{\text{H7-H7'}} = 12.9$ Hz, 2H, H_{7or7'}), 2.97 (s, 2H, H₆), 2.65 (d, ${}^{2}J_{\text{H7-H7'}} = 12.9$ Hz, 2H, H_{70r7'}), 1.62 (s, 18H, H₁₅), 1.34 (s, 18H, H₁₇), 1.16 (s, 3H, H₁₉), 0.88 (s, 3H, H₁₈). ${}^{13}C{}^{1}H$ NMR (75.48 MHz, C₆D₆, 293 K): δ 159.2 (C₁₃), 158.7 (C₅), 149.4 (C₁), 140.1 (C10), 137.2 (C3), 136.5 (C12), 125.0 (C9), 124.7 (C8), 124.3 (C₁₁), 121.6 (C₂), 120.4 (C₄), 63.3 (C₇), 57.7 (C₆), 41.1 (C₁₉), 37.6 (C18), 35.4 (C14), 34.3 (C16), 32.0 (C17), 30.1 (C15). IR (Nujol mull): v (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(η³-**C**₃**H**₅)₂(**O**₂**NN**^{'tBu}) (7b). A 1.73 M solution of C₃H₅-MgCl in THF (0.5 mL, 0.42 mmol) was added dropwise to a suspension of ZrCl₂(O₂NN^{'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.

¹H NMR (499.99 MHz, C₆D₆, 293 K): δ 8.90 (d, ³J_{H1-H2} = 5.6 Hz, 1H, H₁), 7.23 (d, ${}^{4}J_{H11-H9} = 2.4$ Hz, 2H, H₁₁), 7.09 (apparent quintet, apparent ${}^{3}J_{H20-H21} = 11$ Hz, 1H, H₂₀), 6.79 $(d, {}^{4}J_{H9-H11} = 2.4 \text{ Hz}, 2H, H_{9}), 6.43 (ddd, {}^{3}J_{H3-H4} = 7.8 \text{ Hz},$ ${}^{3}J_{\text{H3}-\text{H2}} = 7.6$ Hz, ${}^{4}J_{\text{H3}-\text{H1}} = 1.7$ Hz, 1H, H₃), 6.25 (apparent quintet, apparent ${}^{3}J_{\text{H18}-\text{H19}} = 12.4$ Hz, 1H, H₁₈), 6.21 (dd, ${}^{3}J_{H2-H1} = 5.6 \text{ Hz}, {}^{3}J_{H2-H3} = 7.6 \text{ Hz}, 1H, H_2), 5.79 \text{ (d, } {}^{3}J_{H4-H3} = 7.8 \text{ Hz}, 1H, H_4), 4.51 \text{ (d, } {}^{2}J_{H7-H7'} = 13.2 \text{ Hz}, 2H, H_{70r7'}), 3.83$ (br s, 4H, H₂₁), 3.71 (d, ${}^{2}J_{H19-H18} = 13.2$ Hz, 4H, H₁₉), 3.17 (s, 2H, H₆), 2.76 (d, ${}^{2}J_{\text{H7-H7'}} = 13.2$ Hz, 2H, H_{70r7'}), 1.35 (s, 18H, H₁₅), 1.31 (s, 18H, H₁₇). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 293 K): δ 158.5 (C₅), 158.3 (C₁₃), 150.3 (C₁), 145.8 (C₂₀), 141.2 (C₁₈), 140.0 (C10), 137.2 (C3), 136.3 (C12), 125.1 (C9), 124.6 (C8), 123.8 (C11), 122.0 (C2), 121.2 (C4), 81.3 (C19), 79.2 (vb, C21), 66.2 (C7), 60.9 (C₆), 35.1 (C₁₄), 34.2 (C₁₆), 32.0 (C₁₇), 30.2 (C₁₅). 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(CH₂SiMe₃)₂(O₂NN'^{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(CH₂SiMe₃)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 LiCH₂SiMe₃ (5.3 mg, 55.6 μ mol) in C₆D₆ (1 mL) was added to ZrCl₂(O₂NN^{/Me}) (14.9 mg, 27.8 μ mol). 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, C₆D₆, 293 K): δ 8.30 (d, ³J_{H1-H2} = 5.5 Hz, 1H, H₁), 6.71 (d, ${}^{4}J_{H11-H9} = 1.5$ Hz, 2H, H₁₁), 6.50 (d, ${}^{4}J_{H9-H11} = 1.5$ Hz, 2H, H₉), 6.34 (ddd, ${}^{3}J_{H3-H4} = 8.0$ Hz, ${}^{3}J_{H3-H2}$ = 7.5 Hz, ${}^{4}J_{H3-H1}$ = 1.8 Hz, 1H, H₃), 6.10 (dd, ${}^{3}J_{H2-H1}$ = 5.5 Hz, ${}^{3}J_{H2-H3} = 7.5$ Hz, 1H, H₂), 5.57 (d, ${}^{3}J_{H4-H3} = 8.0$ Hz, 1H, H₄), 4.21 (d, ${}^{2}J_{H7-H7'} = 13.2$ Hz, 2H, H_{7or7'}), 3.00 (s, 2H, H₆), 2.73 (d, ${}^{2}J_{H7-H7'}$ = 13.2 Hz, 2H, H_{7or7'}), 2.33 (s, 6H, H₁₄), 2.17 (s, 6H, H_{15}), 1.14 (s, 2H, H_{20}), 0.95 (s, 2H, H_{18}), 0.62 (s, 9H, H₂₁), 0.23 (s, 9H, H₁₉). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 293 K): δ 158.5 (C₁₃), 158.0 (C₅), 148.0 (C₁), 137.1 (C₃), 132.0 (C₁₁), 128.1 (C₉), 126.6 (C₁₀), 125.7 (C₁₂), 123.4 (C₈), 121.5 (C₂), 120.6 (C₄), 63.0 (C₇), 58.4 (C₆), 54.4 (C₁₈), 53.7 (C₂₀), 20.5 (C₁₅), 16.8 (C₁₄), 3.7 (C₂₁), 3.1 (C₁₉). 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 - CH₃]⁺. Anal. Found (Calcd for C32H48N2O2Si2Zr): 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(CH₂SiMe₃)₂(O₂NN'^{tBu}) (8b). Method A. 8b was formed by a procedure analogous with that for Zr(CH₂SiMe₃)₂(O₂-NN'^{Me}), with H₂O₂NN'^{tBu} (0.375 g, 0.69 mmol) and Zr(CH₂-SiMe₃)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 LiCH₂-SiMe₃ (4.2 mg, 44 μ mol) in C₆D₆ (1 mL) and ZrCl₂(O₂NN'^{tBu}) (15.1 mg, 21.4 μ mol).

¹H NMR (300.18 MHz, C₆D₆, 293 K): δ 8.26 (d, ³J_{H1-H2} = 5.4 Hz, 1H, H₁), 7.36 (d, ${}^{4}J_{H11-H9} = 2.4$ Hz, 2H, H₁₁), 6.94 (d, ${}^{4}J_{H9-H11} = 2.4$ Hz, 2H, H₉), 6.29 (ddd, ${}^{3}J_{H3-H4} = 7.8$ Hz, ${}^{3}J_{H3-H2}$ = 7.6 Hz, ${}^{4}J_{H3-H1}$ = 1.7 Hz, 1H, H₃), 6.03 (dd, ${}^{3}J_{H2-H1}$ = 5.4 Hz, ${}^{3}J_{H2-H3} = 7.6$ Hz, 1H, H₂), 5.54 (d, ${}^{3}J_{H4-H3} = 7.8$ Hz, 1H, H₄), 4.51 (d, ${}^{2}J_{H7-H7'} = 12.8$ Hz, 2H, H_{70r7'}), 3.01 (s, 2H, H₆), 2.87 (d, ${}^{2}J_{\text{H7-H7'}} = 12.8$ Hz, 2H, H_{7or7'}), 1.59 (s, 18H, H₁₅), 1.31 (s, 18H, H_{17}), 1.14 (s, 2H, H_{20}), 0.95 (s, 2H, H_{18}), 0.62 (s, 9H, H₂₁), 0.23 (s, 9H, H₁₉). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 293 K): δ 159.0 (C₁₃), 158.8 (C₅), 149.5 (C₁), 140.2 (C₁₀), 137.2 (C₃), 136.6 (C12), 125.1 (C9), 124.8 (C8), 124.5 (C11), 121.5 (C2), 120.4 (C₄), 63.3 (C₇), 61.7 (C₁₈), 57.7 (C₆), 52.2 (C₂₀), 35.4 (C₁₄), 34.3 (C₁₆), 32.0 (C₁₇), 30.4 (C₁₅), 3.6 (C₂₁), 3.3 (C₁₉). 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 -CH₃]⁺. Anal. Found (Calcd for C44H72N2O2Si2Zr): C 64.63 (65.37), H 9.15 (8.98), N 3.32 (3.47).

Zr(CH₂CMe₃)₂(O₂NN'^{Me}) (9a). A solution of $H_2O_2NN'^{Me}$ (0.15 g, 0.40 mmol) in benzene (15 mL) was added dropwise to Zr(CH₂CCMe₃)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, C₆D₆, 293 K): δ 8.54 (d, ³J_{H1-H2} = 5.3 Hz, 1H, H₁), 6.70 (d, ${}^{4}J_{H11-H9} = 1.5$ Hz, 2H, H₁₁), 6.51 (d, ${}^{4}J_{\text{H9-H11}} = 1.5$ Hz, 2H, H₉), 6.35 (ddd, ${}^{3}J_{\text{H3-H4}} = {}^{3}J_{\text{H3-H2}} = 7.6$ Hz, ${}^{4}J_{H3-H1} = 1.8$ Hz, 1H, H₃), 6.12 (dd, ${}^{3}J_{H2-H1} = 5.3$ Hz, ${}^{3}J_{\text{H2}-\text{H3}} = 7.6$ Hz, 1H, H₂), 5.60 (d, ${}^{3}J_{\text{H4}-\text{H3}} = 7.6$ Hz, 1H, H₄), 4.38 (d, ${}^{2}J_{\text{H7}-\text{H7}'}$ = 12.9 Hz, 2H, H_{70r7}), 3.04 (s, 2H, H₆), 2.72 (d, ${}^{2}J_{H7-H7'} = 12.9$ Hz, 2H, H_{70r7}), 2.34 (s, 6H, H₁₄), 2.17 (s, 6H, H₁₅), 1.92 (s, 2H, H₂₁), 1.67 (s, 9H, H₂₃), 1.45 (s, 11H, H₁₈ and H₂₀). ${}^{13}C{}^{1}H$ NMR (75.48 MHz, C₆D₆, 293 K): δ 158.7 (C13), 158.4 (C5), 148.6 (C1), 137.1 (C3), 132.1 (C11), 128.5 (C9), 126.6 (C10), 125.9 (C12), 123.8 (C8), 121.5 (C2), 120.8 (C4), 85.6 (C21), 84.5 (C18), 63.4 (C7), 58.9 (C6), 35.6 (C23), 35.4 (C20), 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(CH₂CMe₃)₂(O₂NN'^{tBu}) (9b). 9b was formed by a procedure analogous with that for Zr(CH₂CMe₃)₂(O₂NN'^{Me}), with H₂O₂NN'^{tBu} (0.214 g, 0.392 mmol) and Zr(CH₂CMe₃)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, C₆D₆, 293 K): δ 8.44 (d, ³J_{H1-H2} = 4.5 Hz, 1H, H₁), 7.38 (d, ${}^{4}J_{H11-H9} = 2.5$ Hz, 2H, H₁₁), 6.94 (d, ${}^{4}J_{H9-H11} = 2.5$ Hz, 2H, H₉), 6.31 (ddd, ${}^{3}J_{H3-H4} = 7.7$ Hz, ${}^{3}J_{H3-H2}$ = 7.4 Hz, ${}^{4}J_{H3-H1}$ = 1.7 Hz, 1H, H₃), 6.11 (dd, ${}^{3}J_{H2-H1}$ = 4.5 Hz, ${}^{3}J_{H2-H3} = 7.4$ Hz, 1H, H₂), 5.57 (d, ${}^{3}J_{H4-H3} = 7.7$ Hz, 1H, H₄), 4.61 (d, ${}^{2}J_{H7-H7'} = 12.8$ Hz, 2H, H_{7or7'}), 3.05 (s, 2H, H₆), 2.83 (d, ${}^{2}J_{H7-H7'} = 12.8$ Hz, 2H, H_{70r7'}), 1.81 (s, 2H, H₂₁), 1.72 (s, 9H, H₂₃), 1.70 (s, 2H, H₁₈), 1.65 (s, 18H, H₁₅), 1.39 (s, 9H, H₂₀), 1.37 (s, 18H, H₁₇). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 293 K): δ 159.0 (C₁₃), 158.8 (C₅), 149.3 (C₁), 140.0 (C₁₀), 137.1 (C₃), 136.7 (C12), 125.3 (C9), 125.1 (C8), 124.4 (C11), 121.5 (C2), 120.5 (C₄), 96.0 (C₁₈), 83.1 (C₂₁), 63.9 (C₇), 57.9 (C₆), 36.4, 36.1, 35.7, 35.4 (C14), 35.2, 34.3 (C16), 32.0 (C17), 30.5 (C15). 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 C46H72N2O2Zr): C, 71.21 (71.17), H 10.95 (9.35), N 3.33 (3.61).

Zr(CH₂C₆H₅)₂(O₂NN^{'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(CH₂C₆H₅)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_5 -CH₂MgCl 1.25 M in ether (46 μ L, 57 mmol) was added via microsyringe to a suspension of ZrCl₂(O₂NN^{Me}) (15.3 mg, 28.5 μ mol) 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, C₆D₆, 293 K): δ 8.17 (d, ³J_{H1-H2} = 5.6 Hz, 1H, H₁), 7.65 (d, ³J_{H25-H26} = 7.6 Hz, 2H, H₂₅), 7.34 (dd, ³J_{H26-H25} = ³J_{H26-H27} = 7.6 Hz, 2H, H₂₆), 7.05 (m, 3H, H₂₀ and H₂₇), 6.96 (dd, ³J_{H21-H22} = 8.8 Hz, ³J_{H21-H20} = 7.6 Hz, 2H, H₂₁), 6.71 (t, ³J_{H22-H21} = 8.8 Hz, 1H, H₂₂), 6.69 (d, ⁴J_{H11-H9} = 1.7

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Hz, 2H, H₁₁), 6.40 (d, ${}^{4}J_{H9-H11} = 1.7$ Hz, 2H, H₉), 6.32 (ddd, ${}^{3}J_{\text{H3}-\text{H4}} = 7.6 \text{ Hz}, \, {}^{3}J_{\text{H3}-\text{H2}} = 7.8 \text{ Hz}, \, {}^{4}J_{\text{H3}-\text{H1}} = 1.7 \text{ Hz}, \, 1\text{H}, \, \text{H}_{3}),$ 6.06 (dd, ${}^{3}J_{\text{H2}-\text{H1}} = 5.6$ Hz, ${}^{3}J_{\text{H2}-\text{H3}} = 7.8$ Hz, 1H, H₂), 5.57 (d, ${}^{3}J_{\text{H4-H3}} = 7.6$ Hz, 1H, H₄), 3.71 (d, ${}^{2}J_{\text{H7-H7}'} = 13.2$ Hz, 2H, $H_{70r7'}$), 3.02 (s, 2H, H_{23}), 2.89 (s, 2H, H_6), 2.53 (d, ${}^2J_{H7-H7'}$ = 13.2 Hz, 2H, H_{70r7}), 2.49 (s, 2H, H₁₈), 2.27 (s, 6H, H₁₄), 2.11 (s, 6H, H₁₅). ¹³C{¹H} NMR (125.74 MHz, C₆D₆, 293 K): δ 158.3 (C13), 158.2 (C5), 149.3 (C19), 148.2 (C1), 146.4 (C24), 137.2 (C3), 131.8 (C11), 129.3 (C26), 128.8 (C25), 128.5 (C21), 128.1 (C9), 127.8 (C20), 127.0 (C10), 125.5 (C12), 123.7 (C8), 122.6 (C27), 121.9 (C2), 120.8 (C₄), 120.6 (C₂₂), 65.6 (C₁₈), 65.3 (C₂₃), 63.1 (C₇), 59.7 (C₆), 20.6 (C₁₅), 16.6 (C₁₄). 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 -C₇H₇]⁺, 464 (5%) [M - 2C₇H₇]⁺. Anal. Found (Calcd for C38H40N2O2Zr): C, 69.91 (70.44), H 6.19 (6.22), N 4.31 (4.32).

Zr(CH₂C₆H₅)₂(O₂NN'^(Bu)) (10b). Method A. 10b was formed by a procedure analogous with that for Zr(CH₂C₆H₅)₂(O₂NN'^{Me}), with H₂O₂NN'^(Bu) (0.3 g, 0.55 mmol) and Zr(CH₂C₆H₅)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 $Zr(CH_2C_6H_5)_2(O_2NN'^{Me})$, with $C_6H_5CH_2MgCl$ (34 mL, 42.5 μ mol) and $ZrCl_2(O_2NN'^{tBu})$ (15.3 mg, 28.5 μ mol) in C_6D_6 (1 mL). The complete conversion of the starting materials into **10b** took 3 h.

¹H NMR (499.99 MHz, C₆D₆, 293 K): δ 8.18 (d, ³J_{H1-H2} = 4.7 Hz, 1H, H₁), 7.83 (d, ${}^{3}J_{H25-H26} = 7.6$ Hz, 2H, H₂₅), 7.40 (dd, ${}^{3}J_{\text{H26-H25}} = 7.6$ Hz, ${}^{3}J_{\text{H26-H27}} = 7.4$ Hz, 2H, H₂₆), 7.35 (d, ${}^{4}J_{\text{H11-H9}}$ = 2.4 Hz, 2H, H₁₁), 7.08 (t, ${}^{3}J_{H26-H27}$ = 7.4 Hz, 1H, H₂₇), 7.04 (d, ${}^{3}J_{H20-H21} = 7.6$ Hz, 2H, H₂₀), 6.89 (dd, ${}^{3}J_{H21-H22} = 7.4$ Hz, ${}^{3}J_{\text{H21-H20}} = 7.6$ Hz, 2H, H₂₁), 6.80 (d, ${}^{4}J_{\text{H9-H11}} = 2.4$ Hz, 2H, H₉), 6.65 (t, ${}^{3}J_{H22-H21} = 7.4$ Hz, 1H, H₂₂), 6.32 (ddd, ${}^{3}J_{H3-H4} =$ 8.0 Hz, ${}^{3}J_{H3-H2} = 7.4$ Hz, ${}^{4}J_{H3-H1} = 1.7$ Hz, 1H, H₃), 6.08 (dd, ${}^{3}J_{\text{H2}-\text{H1}} = 4.7$ Hz, ${}^{3}J_{\text{H2}-\text{H3}} = 7.4$ Hz, 1H, H₂), 5.57 (d, ${}^{3}J_{\text{H4}-\text{H3}} =$ 8.0 Hz, 1H, H₄), 3.75 (d, ${}^{2}J_{H7-H7'} = 13.2$ Hz, 2H, H_{7or7'}), 3.21 (s, 2H, H₂₃), 2.88 (s, 2H, H₆), 2.59 (d, ${}^{2}J_{H7-H7'} = 13.2$ Hz, 2H, H_{7or7'}), 2.56 (s, 2H, H_{18}), 1.67 (s, 18H, H_{15}), 1.28 (s, 18H, H_{17}). $^{13}\mathrm{C}\text{--}$ {¹H} NMR (125.74 MHz, C₆D₆, 293 K): δ 158.7 (C₁₃), 158.6 (C₅), 149.9 (C19), 149.3 (C1), 146.4 (C24), 140.6 (C10), 137.3 (C3), 136.3 (C₁₂), 129.4 (C₂₆), 128.6 (C₂₅), 128.4 (C₂₁), 127.5 (C₂₀), 124.9 (C₉), 124.85 (C₈), 124.2 (C₁₁), 122.9 (C₂₇), 121.7 (C₂), 120.9 (C₄), 120.4 (C22), 67.6 (C23), 67.0 (C18), 63.7 (C7), 58.8 (C6), 35.4 (C14), 34.2 (C₁₆), 31.9 (C₁₇), 30.3 (C₁₅). 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%) $[M - C_7H_7]^+$, 631 (15%) $[M - 2C_7H_7]^+$. Anal. Found (Calcd for C₅₀H₆₄N₂O₂Zr): C, 73.39 (73.57), H 7.88 (7.90), N 3.40 (3.43).

{[**Zr**(**CH**₂**Ph**)(**THF**)(**O**₂**NN**^{*M*}**e**)][**PhCH**₂**B**(**C**₆**F**₅)₃]} (11a). **Method A.** A solution of B(C₆F₅)₃ (0.036 g, 0.071 mmol) in CH₂Cl₂ (2 mL) was added at room temperature to Zr(CH₂Ph)₂-(O₂NN^{*M*}**e**) (0.046 g, 0.071 mmol) in CH₂Cl₂ (4 mL) in the presence of THF (6 μ L, 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 $B(C_6F_5)_3$ (0.0078 g, 0.015 mmol) in CD_2Cl_2 (0.5 mL) was added to $Zr(CH_2Ph)_2(O_2NN'^{Me})$ (0.01 g, 0.015 mmol) in CD_2Cl_2 (0.5 mL) in the presence of THF (1.3 μ L, 0.016 mmol). The compound **11a** was formed quantitatively.

¹H NMR (499.99 MHz, CD₂Cl₂, 293 K): δ 8.61 (d, ³*J*_{H1-H2} = 5.6 Hz, 1H, H₁), 7.62–7.55 (m, 5H, H₃, H₂₅, and H₂₆), 7.33 (t, ³*J*_{H26-H27} = 7.2 Hz, 1H, H₂₇), 7.15 (dd, ³*J*_{H2-H1} = 5.6 Hz, ³*J*_{H2-H3}



= 7.4 Hz, 1H, H₂), 6.88 (apparent triplet, ${}^{3}J_{H21-H22} = {}^{3}J_{H21-H20}$ = 7.4 Hz, 2H, H₂₁), 6.83 (s, 2H, H₁₁), 6.82 (1H, H₄), 6.79 (t, ${}^{3}J_{\text{H22-H21}} = 7.4$ Hz, 1H, H₂₂), 6.76 (s, 2H, H₉), 6.74 (d, ${}^{3}J_{\text{H20-H21}}$ = 7.4 Hz, 2H, H₂₀), 3.98 (vbr s, 4H, H₂₈), 3.96 (d, ${}^{2}J_{H7-H7'}$ = 13.7 Hz, 2H, H_{70r7}), 3.83 (s, 2H, H₆), 3.51 (d, ${}^{2}J_{H7-H7} = 13.7$ Hz, 2H, H70r7'), 3.27 (s, 2H, H23), 2.79 (br s, 2H, H18), 2.15 (s, 12H, H₁₄ and H₁₅), 1.95 (vbr s, 4H, H₂₉). ¹³C{¹H} NMR (125.74 MHz, CD₂Cl₂, 293 K): δ 159.7 (C₅), 156.2 (C₁₃), 150.1 (C₁), 148.9 (C₁₉), 148.4 (${}^{1}J_{13C-19F} = 226$ Hz, o-C₆F₅), 140.8 (C₃), 138.1 $({}^{1}J_{13C-19F} = 245 \text{ Hz}, \text{ p-C}_{6}\text{F}_{5}), 136.7 ({}^{1}J_{13C-19F} = 235 \text{ Hz}, \text{ m-C}_{6}\text{F}_{5}),$ 136.5 (C24), 133.2 (C25), 132.6 (C11), 131.8 (C26), 130.6 (C10 or C₁₂), 129.0 (C₂₀), 128.1 (C₂₇), 127.1 (C₉ and C₂₁), 125.3 (C₁₀ or C12), 123.9 (C2), 122.7 (C8), 122.3 (C4 and C22), 75.7 (br, C28), 70.0 (C₂₃), 63.9 (C₇), 59.7 (C₆), 32.1 (C₁₈), 25.9 (C₂₉), 20.4 (C₁₅), 16.3 (C14). $^{19}\mathrm{F}$ NMR (300 MHz, CD2Cl2, 293 K): δ –131.17 (d, $^{3}J_{\rm oF-mF}$ = 21.2 Hz, 6F, o–F), –164.32 (t, $^{3}J_{\rm pF-mF}$ = 20.4 Hz, 3F, p-F), –167.15 (m, 6F, m-F). Anal. Found (Calcd for C_{60}H_{48}-BF15N2O3Zr·0.2CH2Cl2): C, 57.49 (57.90), H 3.71 (3.90), N 2.18 (2.24).

{**[Zr(CH₂Ph)(THF)(O₂NN'^{tBu})]**[**PhCH₂B(C₆F₅)₃]**} (11b). **Method A. 11b** was formed by a procedure analogous with that for {[Zr(CH₂Ph)(O₂NN'^{Me})]]PhCH₂B(C₆F₅)₃]}, with Zr(CH₂-Ph)₂(O₂NN'^{tBu}) (0.07 g, 0.086 mmol), B(C₆F₅)₃ (0.044 g, 0.086 mmol), and THF (7 μ L, 0.086 mmol) in CD₂Cl₂ (6 mL). Yield = 0.10 g (85%).

Method B (NMR tube scale). At room temperature, a solution of $B(C_6F_5)_3$ (0.0063 g, 0.012 mmol) in CD_2Cl_2 (0.5 mL) was added to $Zr(CH_2Ph)_2(O_2NN'^{tBu})$ (0.01 g, 0.012 mmol) in CD_2Cl_2 (0.5 mL) in the presence of THF (1.0 μ L, 0.012 mmol). The product **11b** formed quantitatively.

¹H NMR (499.99 MHz, CD₂Cl₂, 293 K): δ 8.51 (d, ³J_{H1-H2} = 5.2 Hz, 1H, H₁), 7.76 (d, ${}^{3}J_{H25-H26} = 7.2$ Hz, 2H, H₂₅), 7.59 (dd, ${}^{3}J_{\rm H26-H25}$ = 7.2 Hz, ${}^{3}J_{\rm H26-H27}$ = 7.5 Hz, 2H, H₂₆), 7.56 (ddd, ${}^{3}J_{\text{H3}-\text{H4}} = {}^{3}J_{\text{H3}-\text{H2}} = 7.7 \text{ Hz}, \, {}^{4}J_{\text{H3}-\text{H1}} = 1.5 \text{ Hz}, \, 1\text{H}, \, \text{H}_{3}$), 7.32 (t, ${}^{3}J_{\text{H26-H27}} = 7.5$ Hz, 1H, H₂₇), 7.24 (d, ${}^{4}J_{\text{H11-H9}} = 2.5$ Hz, 2H, H₁₁), 7.16 (dd, ${}^{3}J_{H2-H1} = 5.2$ Hz, ${}^{3}J_{H2-H3} = 7.7$ Hz, 1H, H₂), 7.06 (d, ${}^{4}J_{H9-H11} = 2.5$ Hz, 2H, H₉), 6.87 (dd, ${}^{3}J_{H21-H22} = 7.8$ Hz, ${}^{3}J_{H21-H20} = 6.9$ Hz, 2H, H₂₁), 6.78 (d, ${}^{3}J_{H4-H3} = 7.7$ Hz, 1H, H₄), 6.775 (t, ${}^{3}J_{H22-H21} = 7.8$ Hz, 1H, H₂₂), 6.75 (d, ${}^{3}J_{H20-H21}$ = 6.9 Hz, 2H, H₂₀), 3.97 (d, ${}^{2}J_{H7-H7'}$ = 13.5 Hz, 2H, H_{7or7'}), 3.91 (s, 2H, H₆), 3.80 (vbr s, 4H, H₂₈), 3.61 (d, ${}^{2}J_{H7-H7'} = 13.5$ Hz, 2H, H70r7'), 3.29 (s, 2H, H23), 2.81 (br s, 2H, H18), 1.87 (vbr s, 4H, H₂₉), 1.44 (s, 18H, H₁₅), 1.23 (s, 18H, H₁₇). ¹³C{¹H} NMR (125.74 MHz, CD₂Cl₂, 293 K): δ 159.6 (C₅), 156.3 (C₁₃), 150.6 (C₁), 148.6 (C₁₉), 148.4 (${}^{1}J_{13C-19F} = 226$ Hz, o-C₆F₅), 143.8 (C₁₀), 140.6 (C₃), 138.1 (${}^{1}J_{13C-19F} = 245$ Hz, p-C₆F₅), 136.7 (${}^{1}J_{13C-19F}$ = 235 Hz, m-C₆F₅), 136.5 (C₂₄), 135.9 (C₁₂), 132.3 (C₂₅), 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 $\cdot 0.35C_6H_{14}$), $Zr(O_2NN'^{Me})_2 \cdot 2C_6H_6$ (4a $\cdot 2C_6H_6$), $Zr(NMe_2)_2(O_2NN'^{t}Bu)$ (5b), $ZrMe_2(O_2NN'^{Me})$ (6a), $ZrMe_2(O_2NN'^{t}Bu)$ (6b), and $Zr(CH_2Ph)_2(O_2NN'^{Me})$ (10a)

) (\mathbf{u}), $\mathbf{Linic}_{\mathcal{L}}(\mathbf{o}_{\mathcal{L}})$ $\mathbf{b}\mathbf{u}$)) (104)
	3a	$3b \cdot 0.35C_6H_{14}$	4a •2C ₆ H ₆
molecular formula	C24H26Cl2N2O2Zr	C36H50Cl2N2O2Zr.0.35 C6H14	C48H52N4O4Zr·2 C6H6
fw	536.61	735.10	996.41
cryst syst	triclinic	monoclinic	tetragonal
space group	$P\overline{1}$	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 K α , $\lambda = 0.71073$ 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 \hat{R} indices ^a $[I > 3\sigma(I)]$	$R_1 = 0.0539$	$R_1 = 0.0426$	$R_1 = 0.0802$
	$R_{\rm w} = 0.0579$	$R_{\rm w} = 0.0490$	$R_{\rm w} = 0.0771$
largest residual peaks/e Å ⁻³	0.95 and -0.62	0.92 and -0.80	0.95 and -0.71
с .			
	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	tr <u>i</u> clinic	tetragonal	monoclinic
space group	<i>P</i> 1	$P42_{1}c$	C2/c
Z_{\sim}	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 K $lpha$, 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 $[I > 3\sigma(I)]$	$R_1 = 0.0329$	$R_1 = 0.0415$	$R_1 = 0.0352$
-	$R_{ m w}=0.0382$	$R_{ m w} = 0.0457$	$R_{ m w}=0.0390$
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 Ka, $\lambda = 0.71073$ 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 \hat{R} indices ^a $[I > 3\sigma(I)]$	$R_1 = 0.0348$
	$R_{\rm w} = 0.0374$
largest residual peaks/e Å ⁻³	0.43 and -0.47

^a $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|; R_w = \{ \sum w(|F_0| - |F_c|)^2 / \sum (w|F_0|^2)^{1/2}.$

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

 $Zr(O_2NN'^{Me})_2$ 4a ¹/₂ Zr(CH₂SiMe₃)₄ (for R = Me)ZrCl₄(THF)₂ $ZrCl_2(O_2NN'^{Me})$ or 3a NaH (excess) ZrCl₄ H₂O₂NN'^R Na₂O₂NN'^R (for R = Me) $R = Me (1a) \text{ or }^{t}Bu (1b)$ $\mathbf{R} = \mathbf{Me} (\mathbf{2a}) \text{ or }^{\mathsf{t}} \mathbf{Bu} (\mathbf{2b})$ $Zr(O_2NN'^{Me})_2$ 4a ZrCl₄(THF)₂ $Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2$ (for $R = {}^{t}Bu$)

$ZrCl_2(O_2NN'^R)$

ZrCl₂(O₂NN'^{tBu}) 3b

$R = Me (3a) \text{ or }^{t}Bu (3b)$

(C26), 128.7 (C20), 127.6 (C27), 126.7 (C21), 125.7 (C9), 125.3 (C11), 123.6 (C₂), 123.4 (C₈), 122.3 and 122.0 (C₄ and C₂₂), 76.2 (C₂₈), 71.6 (C₂₃), 64.5 (C₇), 58.7 (C₆), 35.3 (C₁₄), 34.6 (C₁₆), 31.9 (C₁₈), 31.6 (C17), 30.1 (C15), 26.0 (C29). ¹⁹F NMR (300 MHz, CD2Cl2, 293 K): δ -131.18 (d, ${}^{3}J_{oF-mF}$ = 21.2 Hz, 6F, o-F), -164.44 (t, ${}^{3}J_{\rm pF-mF} = 20.4$ 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 C72H72BF15N2O3Zr·0.15CH2Cl2): C, 61.02 (61.32), H 5.41 (5.15), N 1.85 (1.98).

Crystal Structure Determinations for ZrCl₂(O₂NN^{/Me}) (3a), $ZrCl_2(O_2NN'^{tBu}) \cdot 0.35C_6H_{14}$ (3b $\cdot 0.35C_6H_{14}$), $Zr(O_2-$ NN'Me)2.2C6H6 (4a.2C6H6), Zr(NMe2)2(O2NN'tBu) (5b), ZrMe2-(O₂NN^{'Me}) (6a), ZrMe₂(O₂NN^{'tBu}) (6b), and Zr(CH₂Ph)₂-(O₂NN^{'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 Ka 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 parameter⁴⁰ for **4a** and **6a** confirmed the correct polarity.

For **3b**·0.35C₆H₁₄ 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.2C6H6 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 CH₂ 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 CH₂ group H atoms.

Crystallographic calculations were performed using SIR92³⁸ 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 H₂O₂NN'^{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-C₅H₄N)CH₂NH₂, and the appropriate 2,4-disubstituted phenol HO-2,4-C₆H₂R₂ (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-C₅H₄N)CH₂-NH₂ and 2,4-disubstituted phenol are observed, consistent with the partial loss of paraformaldehyde from the reaction mixture.

The protio-ligands H₂O₂NN'^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 ¹H NMR integration). Both compounds are formulated for convenience as Na₂O₂NN'^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 H₂O₂- NN'^{R} (1a, 1b) or $Na_{2}O_{2}NN'^{R}$ (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 $Zr(CH_2-$ SiMe₃)₂Cl₂(Et₂O)₂ ³¹ in benzene lead to elimination of SiMe₄ and formation of the dichloride complexes ZrCl₂(O₂- NN'^{R}) (R = Me (**3a**) or ^tBu (**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 ZrCl₂(O₂NN'^{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_2 -NN'Me. Compound 4a can also be obtained in a similar yield by an SiMe₄ elimination reaction between Zr(CH₂- $SiMe_3)_4$ 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 O₂-NN'tBu ligand. Compound 4a has been structurally characterized, and the solid-state structure is discussed below.

At room temperature the ¹H and ¹³C NMR spectra of $\operatorname{ZrCl}_2(O_2NN'^R)$ (R = Me (**3a**) or ^tBu (**3b**)) in CD₂Cl₂ 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 ¹H 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 ¹H 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.



The ¹H 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*-butylsubstituted 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 ⁿBu₄Cl (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, ¹H 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 simulated⁴² 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) procedures⁴³ afforded the following activation parameters: $\Delta H^{\ddagger} = 35.9(8) \text{ kJ mol}^{-1}; \Delta S^{\ddagger}$ $= -102(5) \text{ J mol}^{-1} \text{ K}^{-1}$; $\Delta G^{\ddagger}_{(298\text{K})} = 66(2) \text{ kJ mol}^{-1}$. 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 intermediate⁴⁵), 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.

⁽⁴²⁾ Budzelaar, P. H. M. gNMR for Windows v4.1; Cherwell Scientific Ltd.: Oxford, 1999.

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

⁽⁴⁴⁾ Wilkins, R. G. Kinetics and Mechanism of Reactions of Transi*tion Metal Complexes*; VCH: Weinheim, 1991. (45) Muetterties, E. L. J. Am. Chem. Soc. **1968**, *90*, 5097.



Figure 1. Selected simulated (left) and observed variabletemperature ¹H 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 $C_6H_2But_2$ ring protons were not included in the simulation and are therefore "missing" from the simulated spectra.



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

The NMR spectra of the homoleptic complex Zr(O₂- $NN^{\prime Me})_2$ (4a) are sharp at room temperature and feature one set of O₂NN'^{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 ¹H 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 ¹H 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 twodimensional NOESY (nuclear Overhauser effect correlation spectroscopy) spectra of 3a and 4a, which



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.

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 $\operatorname{ZrCl}_2(O_2 NN'^{Me})$ (**3a** as the C_1 symmetric isomer), $\operatorname{ZrCl}_2(O_2 NN'^{HBu})$ (**3b** as the C_s symmetric isomer) and $\operatorname{Zr}(O_2 NN'^{Me})_2$ (**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 ZrCl₂(O₂NN^{'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)		
	A	daa			
	Ang	gies			
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 ZrCl₂(O₂NN^{'t}Bu) (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)		
	Ang	les			
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)	
	An	øles		
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 C₁ 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 O₂NN^{'Me} ligands, each with mutually cis phenoxide donors. In the solid state **4a** possesses approximate C₂ symmetry; Figure 4 shows a view of 4a approximately along the molecular 2-fold axis that relates the two O₂NN'^{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 sixcoordinate 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 HNMe₂ (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(NMe₂)₄ with the more sterically encumbered H₂O₂NN'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.

⁽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.





$$\begin{split} R' &= NMe_2, R = {}^tBu \ (\textbf{5b}); R' = Me, R = Me \ (\textbf{6a}) \ or \ {}^tBu \ (\textbf{6b}); \\ R' &= \eta^3 - C_3H_5, R = {}^tBu \ (\textbf{7b}); R' = CH_2SiMe_3, R = Me \ (\textbf{8a}) \ or \ {}^tBu \ (\textbf{8b}); \\ R' &= CH_2CMe_3, R = Me \ (\textbf{9a}) \ or \ {}^tBu \ (\textbf{9b}); R' = CH_2Ph, R = Me \ (\textbf{10a}) \ or \ {}^tBu \ (\textbf{10b}) \end{split}$$

Molecules of **5b** contain approximately octahedral zirconium centers with mutually *cis* NMe₂ 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 ZrCl₂(O₂NN'^{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 NMe₂ 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 NMe₂ nitrogens [359.3(4)° for N(3) and 359.7(5)° for N(4)] show that they are sp² hybridized and potentially capable of π -donating to the d⁰ metal center. The carbon atoms of the NMe₂ ligand bound *trans* to the pyridyl group are effectively coplanar with the "equatorial" (as drawn) $\{O(1), O(2), O(2$ N(2), N(3)} plane. To maximize π -donation from the other NMe₂ ligand (i.e., to avoid competition with the NMe₂ 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 NMe₂ nitrogen lone pair $2p_{\pi}$ orbitals. In **5b**, however, the methyl carbons of the axial NMe₂ effectively bisect the N(2)-Zr(1)-O(2) and O(1)-Zr(1)-N(3) angles so that some competition between the two NMe₂ nitrogen lone pairs presumably arises. The orientation of the

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Zr(NMe₂)₂(O₂NN'^tBu) (5b)

Distances					
2.0380(11)	Zr(1)-N(2)	2.4597(14)			
2.0245(11)	Zr(1)-N(3)	2.0706(14)			
2.4670(13)	Zr(1)-N(4)	2.0832(14)			
Ar	ngles				
156.70(5)	O(2) - Zr(1) - N(4)	99.70(5)			
81.14(4)	N(1) - Zr(1) - N(4)	159.69(6)			
76.06(4)	N(2) - Zr(1) - N(4)	91.20(5)			
79.51(4)	N(3) - Zr(1) - N(4)	103.23(6)			
87.82(5)	Zr(1) - N(3) - C(37)	126.65(12)			
68.95(4)	Zr(1) - N(3) - C(38)	122.50(12)			
90.89(5)	C(37) - N(3) - C(38)	110.1(2)			
96.53(5)	Zr(1) - N(4) - C(39)	120.86(14)			
97.01(5)	Zr(1) - N(4) - C(40)	128.09(13)			
163.93(5)	C(39) - N(4) - C(40)	110.8(2)			
100.03(5)					
	$\begin{array}{r} \text{Dist}\\ 2.0380(11)\\ 2.0245(11)\\ 2.4670(13)\\ & \text{Ar}\\ 156.70(5)\\ 81.14(4)\\ 76.06(4)\\ 79.51(4)\\ 87.82(5)\\ 68.95(4)\\ 90.89(5)\\ 96.53(5)\\ 97.01(5)\\ 163.93(5)\\ 100.03(5)\\ \end{array}$	$\begin{array}{c c} \hline Distances \\ 2.0380(11) & Zr(1)-N(2) \\ 2.0245(11) & Zr(1)-N(3) \\ 2.4670(13) & Zr(1)-N(4) \\ \hline Angles \\ 156.70(5) & O(2)-Zr(1)-N(4) \\ 81.14(4) & N(1)-Zr(1)-N(4) \\ 76.06(4) & N(2)-Zr(1)-N(4) \\ 79.51(4) & N(3)-Zr(1)-N(4) \\ 87.82(5) & Zr(1)-N(3)-C(37) \\ 68.95(4) & Zr(1)-N(3)-C(38) \\ 90.89(5) & C(37)-N(3)-C(38) \\ 90.89(5) & C(37)-N(3)-C(38) \\ 96.53(5) & Zr(1)-N(4)-C(39) \\ 97.01(5) & Zr(1)-N(4)-C(40) \\ 163.93(5) & C(39)-N(4)-C(40) \\ 100.03(5) \\ \hline \end{array}$			



Figure 6. Displacement ellipsoid plot (20% probability) of ZrMe₂(O₂NN^{'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 $\text{ZrCl}_2(O_2\text{NN}'^{\text{tBu}})$ (**3b**). The resonances in both the ¹H and ¹³C spectra of **5b** are very sharp, unlike those of **3b**. There are two NMe₂ group environments (giving rise to two singlets for the two distinct NMe₂ ligands). The ¹H NMR subspectrum for $O_2\text{NN}'^{\text{tBu}}$ shows two equivalent 2-O-3,5-C₆H₂^tBu₂ moieties; the CH₂ protons adjacent to the pyridyl group appear as a singlet, whereas the other CH₂ 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 Me₃SiCl or HCl (1 M solution in diethyl ether) gave only unidentified mixtures. Attempts to prepare a dimethyl zirconium complex $ZrMe_2(\hat{O}_2NN'^{tBu})$ by reaction of **5b** with AlMe₃ or AlMe₃·py in benzene were also unsuccessful. However, the target dimethyl complexes $ZrMe_2(O_2NN'^R)$ [R = Me (**6a**) or ^tBu (**6b**)] could be fairly easily obtained from the corresponding dichlorides ZrCl₂(O₂NN'^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



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 ZrMe₂(O₂NN^{'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 ZrMe₂(O₂NN'^tBu) (6b)

	Dist	ances	
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)
	An	gles	
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)		

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 NMe₂. The ¹H and ¹³C NMR spectra are consistent with the solid-state structures and resemble those of Zr-(NMe₂)₂(O₂NN'^{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-

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responding reaction of ZrCl₂(O₂NN'tBu) (3b) gave moderate yields of a bis(allyl)zirconium derivative formulated as $Zr(\eta^3-C_3H_5)_2(O_2NN'^{tBu})$ (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 ¹³C 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 $\eta^{3} \leftrightarrow \eta^{1} \leftrightarrow \eta^{3}$ -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 O₂NN'tBu ligand itself mask the relevant region for allyl ligand absorptions. On balance we favor the formulation of **7b** as $Zr(\eta^3-C_3H_5)_2(O_2NN'^{tBu})$ with two η^3 -bound allyl groups. Structurally characterized zirconium complexes possessing one,48 two,49 or three⁵⁰ 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 = CH₂SiMe₃,³² CH₂CMe₃, ³³ or CH₂Ph^{34,35}). As shown in Scheme 2 these reactions form $ZrR'_2(O_2NN'^R)$ [R' = CH₂SiMe₃ (8a, 8b), CH_2CMe_3 (9a, 9b), or CH_2Ph (10a, 10b); R = Me (suffix **a**) or ^tBu (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 LiCH₂SiMe₃ or PhCH₂MgCl in C₆D₆. 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 O₂NN'^R ligands was described.²²

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



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	5 (Å)	and	Angles
(de	eg) for Zr(CH2Ph)2(O2NI	N'Me)	(10a	ı) Ŭ

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)	
	An	gles		
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)			

10a possess approximately octahedrally coordinated metal centers and C_s symmetry. The bond distances and angles associated with the Zr(O₂NN'Me) moiety are comparable with those described above for other systems containing the Zr(O₂NN'^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 $[Zr(1)\cdots C(26) = 3.006(2) \text{ Å}]$ with the metal center. The corresponding Zr-CH₂-Ph angle for this ligand is 103.2(2)°, which is significantly more acute than for the "equatorial" benzyl ligand [Zr(1)-C(32)- $C(33) = 118.9(2)^{\circ}, Zr(1)\cdots C(33) = 3.288(2) Å$]. In **10b** the axial benzyl ligand also features a Zr...Cipso interaction, although in this complex the extent of interaction is apparently greater [Zr-CH₂-Ph = 92.2(3)°; Zr···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 $O_{2p(\pi)} \rightarrow Zr_{4d(\pi)} \pi$ -interactions). It is not clear why

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the $Zr \cdots C_{ipso}$ 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 ¹H and ¹³C NMR spectra of all the compounds $ZrR'_2(O_2NN'^R)$ (**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 $ZrMe_2(O_2NN'^R)$ (**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 CH₂ group of the *cis*-alkyl substituent). By analogy with the dimethyl complexes **6a** and **6b**, the CH₂ protons of the alkyl groups *trans* to pyridyl in **8a**–**10b** are in all cases the more shielded.

In addition, the ¹³C data for the CH₂Ph groups of **10a** and **10b** appear to reflect the slight η^2 -coordination (i.e., through Zr–CH₂ 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* CH₂ 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_2H_4) in the presence of methylaluminoxane (for **3a**, **3b** and **10b**; Zr:Al ratio ca. 1:1500) or B(C_6F_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 Goldschmidt²² 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 C₂H₄ (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 $B(C_6F_5)_3$ on an NMR tube scale from the dimethyl or dibenzyl species $ZrR'_2(O_2NN'^R)$ (**6a**, **6b** or **10a**, **10b**) gave only ill-defined mixtures. However, reaction of $Zr(CH_2Ph)_2(O_2NN'^R)$ (**10a**, **10b**) with $B(C_6F_5)_3$ in the presence of THF (eq 2) gave the fully characterized cationic complexes $[Zr(CH_2Ph)(THF)(O_2NN'^R)]^+$ as the $[PhCH_2B(C_6F_5)_3]^-$ salts (**11a**, **11b**). In contrast, the

reaction of the dimethyl compounds **6a**, **6b** with $B(C_6F_5)_3$ in the presence of THF gave only ill-defined mixtures.



¹H NMR NOE analyses of **11a**, **11b** established that the benzyl groups in both cations are positioned *cis* to the pyridyl donor group. The ¹H and ¹⁹F NMR spectra of the previously reported⁵¹ anion $[PhCH_2B(C_6F_5)_3]$ in 11a, 11b suggest that there is no significant interaction between it and the cation.⁵² The ¹³C 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 CH₂Ph 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- $(CH_2Ph)(THF)(O_2NN'^R)]^+$ cations of **11a**, **11b**. Since it is only the cis-positioned benzyl groups in both 10a, 10b that exhibit a $Zr \cdots C_{ipso}$ 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 $H_2O_2NN'^R$ (**1a**, **1b**) and $Na_2O_2-NN'^R$ (**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 $O_2NN'^R$ 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.

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