Porphyrazinediols: Synthesis, Characterization, and Complexation to Group IVB Metallocenes

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The first metalated porphyrazinediols **11** have been prepared from (L)-(+)-dimethyl tartrate via conversion into the corresponding dispoke or 2,3-dimethoxy-2,3-butanediyl protected 2,3-dihydroxymaleonitrile, Linstead macrocyclization, transmetalation, and deprotection. Their stability is very dependent on the nature of the metal ion in the cavity of the porphyrazine. Reaction of these porphyrazinediols with metallocene dichlorides led to new solitaire porphyrazines **12** while DDQ oxidation followed by trapping with diaminomaleonitrile afforded new porphyrazine dinitriles **14**.

Introduction

Functional groups fused directly to the β position of the pyrrole units of porphyrazines (tetraazaporphyrines) can couple stronger to the macrocycle core than those attached to the fused benzo positions of phthalocyanines. As such, these porphyrazine systems and their metal complexes are expected to show tailorable and varied solubility and electronic, optical, magnetic, and redox properties. We have published extensively on the synthesis of diverse porphyrazines bearing 2, 4, 6, and 8 thio[1−3] or amino[4] groups as peripheral macrocyclic ring substituents and the conversion of these polydentate ligands into corresponding star,[1] solitaire,[2,5] and gemini[3] porphyrazines. The star porphyrazines derived from the octathiolate, for example, exhibited unusual coordination chemistry. Depending on the choice of the "capping" metal ion, either quadruple tridentate (*S*-*meso*-N−S) or bidentate (S−S) peripheral tetrametalation occurs. In addition, this peripheral metal ion coordination has a profound effect on the electronic structure of the porphyrazine π-system. In solitaire porphyrazines, the macrocycle is endowed with a single metal entity chelated at its peripheral site. These systems are of considerable interest for the study of indirect metal−metal interaction via the porphyrazine π-system, and indeed, strong magnetic exchange between central and peripheral metal ions in molybdocene porphyrazines has been observed.[6] We recently described the first synthesis of a free base porphyrazinoctaol derivative[7] in an enantiomerically pure form via the Ley dispoke protection procedure.[8,9] However, the preparation of star porphyrazines derived thereof proved to be difficult due to the observed instability of porphyrazinoctaol systems. Herein, we report the synthesis and characterization of related porphyrazinediols and their successful conversion into solitaire complexes. In addition, chemical oxidation and trapping studies of these new polydentate noninnocent macrocycles are also described.

Results and Discussion

Synthesis of Porphyrazinediols. The two protected 2,3-dihydroxymaleonitrile derivatives **5a**,**b**, employed in this study, were synthesized by starting from dimethyl tartrate (Scheme 1). Thus, reaction of L-(+)-dimethyl tartrate with 2,3-butanedione in methanol in the presence of trimethyl orthoformate[10] gave the dioxane derivative **3a** in a 93% yield. Similarly, reaction of excess L-(+)-dimethyl tartrate with 3,3′,4,4′-tetrahydro-6,6′-bi-2*H*-pyran (bis-DHP) (**2**) in diethyl ether in the presence of hydrogen chloride[8b] gave the dispiroketal **3b** in a 60% yield (Scheme 1). Monoiodination of both **3a**,**b** via reaction of the corresponding enolate with iodine, followed by dehydroiodination, afforded the chiral alkenes **4a**,**b** in 64 and 53%, respectively. Amide formation using saturated methanolic ammonia and dehydration with trifluoroacetic anhydride gave maleonitrile **5a**,**b** in 97 and

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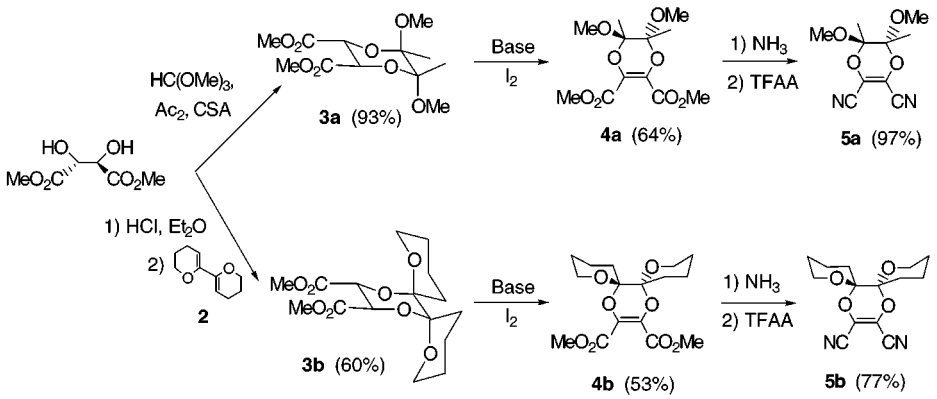
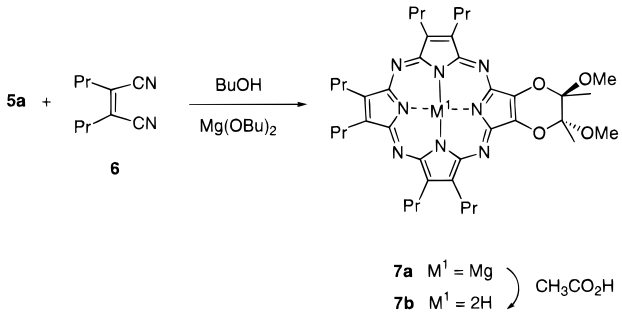
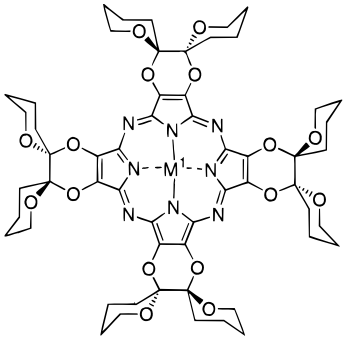
Scheme 1



Scheme 2

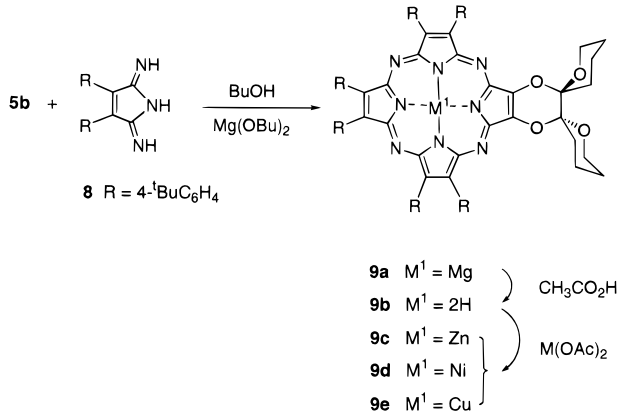




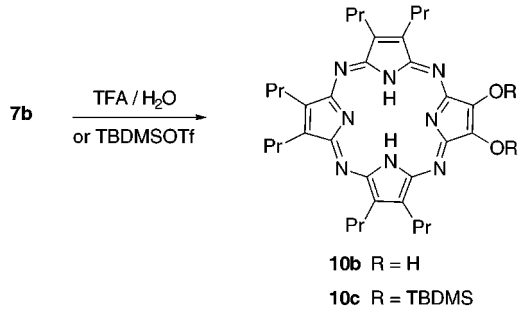
1 M^1 = 2H, Ni

Figure 1.

Scheme 3



Scheme 4



77%, respectively. Mixed Linstead macrocyclization of maleonitrile **5a** with a 7-fold excess of 2,3-dipropylmaleonitrile[11] (**6**) in the presence of magnesium butoxide gave porphyrazine **7a** (M^1 = Mg) in 60% yield (Scheme 2). Similarly, reaction of dispiromaleonitrile **5b** with an excess of pyrroline-2,5-diimine[12] **8** gave the unsymmetrical porphyrazine **9a** in 30% yield (Scheme 3). The propyl and *tert*-butyl phenyl groups in compounds **7** and **9** were selected in order to increase the solubility of the desired porphyrazines and complexes thereof. In addition, the cyclization rates of **6** and **8** matched those of the dinitriles **5a**,**b**, respectively. Porphyrazines **7a** and **9a** were best purified after demetalation of the template magnesium(II). As with the octaol derivative **1**[7] (Figure 1), removal of the Mg ion was cleanly achieved by reaction with glacial acetic acid. Thus, the free base porphyrazines **7b** and **9b** were obtained after chromatography in reasonable overall yield of 20−40%. Remetalation of **9b** with various metal(II) acetates (M^1 = Ni, Zn, Cu) at 120 °C in DMF and chlorobenzene afforded derivatives **9c**−**e** in approximatively quantitative yield. Excess metal(II) acetates were removed after evaporation of the solvent by the addition of methanolic HCl (5%).

The cleavage of the ketal unit of metal free porphyrazine **7b** was accomplished using aqueous trifluoroacetic acid (95%) at room temperature (Scheme 4). As expected, the corresponding diol **10b** was more stable than the octaol derivative obtained from **1** but decomposed easily on attempted purification. On the other hand, treatment of porphyrazine **7b** with TBDMSOTf under basic conditions gave the stable *tert*-butyldimethylsilyl derivative **10c** in 79% yield (Scheme 4). Treatment of porphyrazines **9b** (M^1 = 2H) and **9c** (M^1 = Zn) with aqueous trifluoroacetic acid (95%) led again to the unstable diols **11b**,**c** (Scheme 5). However, deprotection of metalated deriva-

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Scheme 5

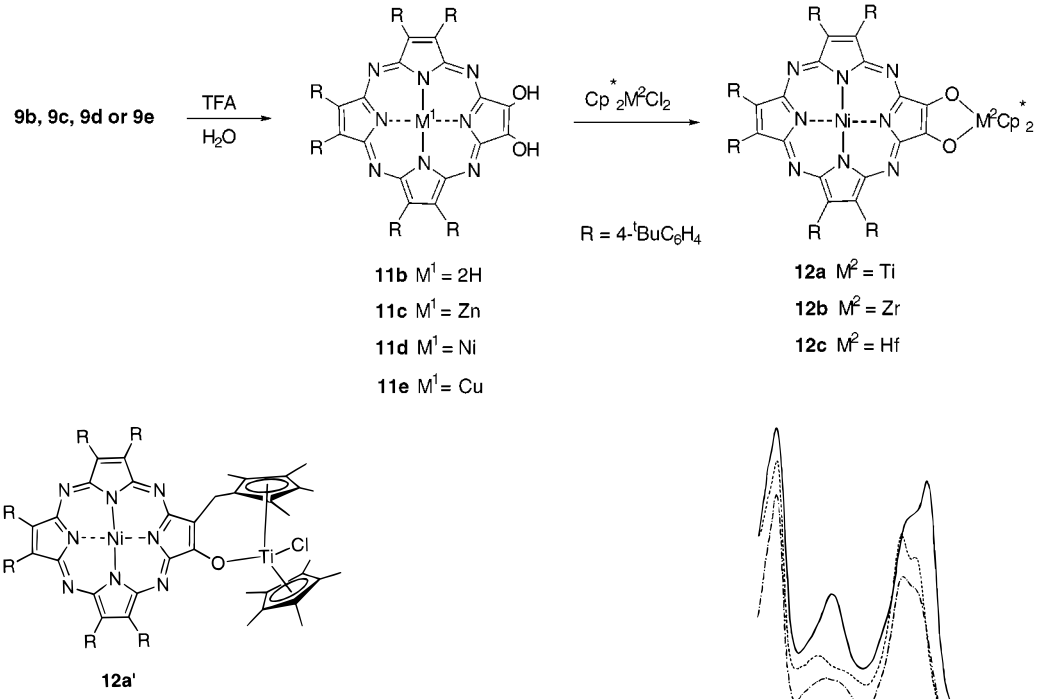

Figure 2.

Figure 3. UV−vis spectra of porphyrazines **11d** and **12a**,**c** in CH_2Cl_2.

tives **9d** (M^1 = Ni) and **9e** (M^1 = Cu) gave the isolable porphyrazinediols, **11d**,**e**, respectively, which were fully characterized, although partial decomposition in solution or in the solid state occurred upon standing. In addition, the complex cyclic voltammograms shown by diols **11d**,**e** were consistent with the nontrivial redox processes with these compounds and their attendant instability.

Peripheral Metalation. We sought to examine the coordination chemistry of the isolated Ni−porphyrazinediol **11d**. Thus, deprotonation of freshly prepared diol **11d** with potassium *tert*-butoxide and subsequent reaction with several bis(pentamethylcyclopentadienyl)-metallocene dichlorides [Cp_2*M^2Cl_2 (M^2 = Ti, Zr, Hf)] resulted in the formation of the new solitaire porphyrazines **12a**−**c** (Scheme 5). Whereas the titanium **12a** and hafnium **12c** could be purified by column chromatography, the zirconium complex **12b** was too unstable to be isolated. However, mass spectroscopy of the crude reaction mixture clearly showed the presence of the expected molecular ion. In addition, a second product was isolated from the reaction of diol **11d** with $Cp^*_2TiCl_2$. On the basis of proton NMR data, we assigned the structure **12a′** to this new compound (Figure 2). As expected for compound **12a**, with a tetrahedral geometry, the two equivalent pentamethylcyclopentadienyl moieties showed only one singlet in the ^{1}H NMR spectrum. In contrast, compound **12a′** shows six resonances associated with the Cp* ring systems of which five are singlets at δ 1.88, 2.01, 2.04, 2.08, and 2.35 ppm corresponding to 3, 3, 3, 15, and 3 protons, respectively, and one AB quartet at δ 4.62 and 4.69 (J = 18.5 Hz) corresponding to two protons. This clearly shows that the two cyclopentadienyl groups in solitaire **12a′** are not in a symmetrical environment. In addition, the downfield CH_2 clearly contained two diastereotopic protons next to the porphyrazine. Furthermore, elemental analysis and high-resolution mass ion measurement demonstrates that the fourth coordination site on titanium is occupied by a chloride ion. Unfortunately, all attempts to grow crystals suitable for an X-ray analysis failed due to decomposition of complex **12a′** in solution. Presumably, complex **12a′** arose from nucleophilic attack of one of the pentamethyl cyclopentadienyl moieties onto the keto tautomer of diol **11d**.

Optical Properties. The electronic absorption maxima of porphyrazine **11d** is shown on the representative spectra in Figure 3. The optical spectrum is typical for macrocycles of this type. It displays an intense split Q Band (C_{2v} symmetry) and an intense single peak in the Soret region. In addition, a less intense peak at around 450 nm, which we assign as the n → π* transition from the lone pairs on the peripheral oxygen atoms into a π* ring orbital, is also observed. As can be seen in Figure 3, the n → π* transition almost disappears upon peripheral metalation, thus indicating that the lone pairs on the peripheral oxygen atoms are less available for charge transfer into the porphyrazine π-system. On the other hand, the Soret and Q signals of solitaire porphyrazines **12a** and **12c** appear in a similar region as those of compound **11d**.

Oxidation. Chemical oxidation of porphyrazinediols **11d**,**e** to the corresponding porphyrazinediones **13d**,**e** was achieved in moderate yield (45%) by using DDQ in dry Et_2O at low temperature (Scheme 6). Since partial decomposition of the porphyrazinediones was observed during purification, compounds **13d**,**e** were instead trapped with diaminomaleonitrile[13] providing pyrazines

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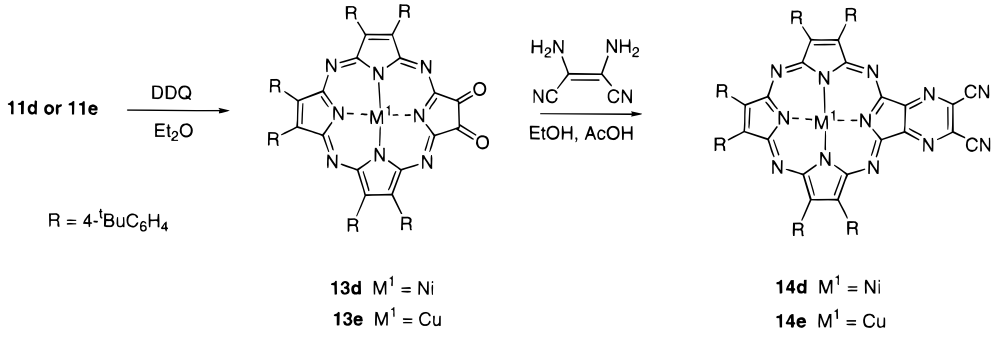
Scheme 6



14d,**e** in overall yields of 28 and 25%, respectively. These new porphyrazine dinitriles turned out to be significantly more stable than the corresponding diones and could therefore be fully characterized. In addition, porphyrazines **14** can serve as starting precursors for the preparation of novel porphyrazine heterodimers.

Conclusion

The deprotection of the unsymmetrical dispoke protected metalloporphyrazines **9d**,**e** to porphyrazinediols **11d**,**e** has been achieved successfully. Compounds **11** represent a novel class of redox-active ligands bearing a single diol chelating group directly attached at the β-positions of the macrocycle. In addition to the metal ion in the macrocyclic cavity, these new ligands are able to coordinate metals at their periphery as demonstrated with bis(pentamethylcyclopentadienyl)metallocene $Cp^*_2M^2Cl_2$, where M^2 = Ti, Zr, or Hf.

Experimental Section

General Procedures. All reactions were conducted in oven flame-dried glassware. Hexanes refers to the petroleum fraction bp 40−60 °C. Solvents used for reactions were distilled prior to use: THF, Et_2O (from sodium−benzophenone ketyl); butanol (from Mg); dichloromethane (from CaH_2). All other reagents were purchased from commercial sources and were used without further purification. TLC was performed on E. Merck precoated silica gel 60 F_{254} plates. Chromatography refers to flash chromatography on E. Merck silica gel 60, 40−60 μm (eluants are given in parentheses). 2,3-Dipropylmaleonitrile (**5**),[11] pyrroline-2,5-diimine (**7**),[12] and 3,3′,4,4′-tetrahydro-6,6′-bi-2*H*-pyran (**2**)[6b] were prepared according to literature procedures.

(2*R*,3*R*,5*R*,6*R*)-Dimethyl 5,6-Dimethoxy-5,6-dimethyl-1,4-dioxane-2,3-dicarboxylate (3a). $HC(OMe)_3$ (2.2 mL) and 2,3-butanedione (0.53 mL, 6.04 mmol) were added to (L)-(+)-dimethyl tartrate (891 mg, 5.0 mmol) and camphorsulfonic acid (58 mg, 0.25 mmol) in MeOH (10 mL). The solution was heated under reflux for 24 h and allowed to cool to room temperature and was neutralized by addition of solid $NaHCO_3$. Rotary evaporation and chromatography (5:1 hexane/EtOAc) afforded **3a** (1.36 g, 93%) as a white solid: R_f 0.23 (5:1 hexane/EtOAc); mp 106−108 °C (hexane/EtOAc); $[\alpha]^{24}_D$ −139.6° (c = 1.0, $CHCl_3$); IR (neat) ν_{max} 1745, 1174, 1142, 1115 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.54 (s, 2H), 3.78 (s, 6H), 3.34 (s, 6H), 1.37 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.4, 99.2, 68.8, 52.5, 48.5, 17.3; HRMS (FAB) calcd for $C_{11}H_{17}O_7$ (M-OCH_3)$^+$, 261.0974, found (M − OCH_3)$^+$, 261.0993. Anal. Calcd for $C_{12}H_{20}O_8$: C, 49.31; H, 6.90. Found: C, 49.30; H, 6.67.

(6*R*,7*R*,14*R*,15*R*)-Dimethyl 1,8,13,16-Tetraoxadispiro-[5.0.5.4]hexadecane-14,15-dicarboxylate (3b). HCl was bubbled through (L)-(+)-dimethyl tartrate (1.40 g, 7.83 mmol) in dry Et_2O (200 mL) for 20 min at 0 °C. Bis(dihydropyran) (**2**) (1.43 g, 8.6 mmol) in dry THF (20 mL) was added, and the mixture was allowed to warm to 10 °C over 6 h. The mixture was neutralized with 10% NaOH and extracted with EtOAc, and the combined organic layers were washed with saturated $NaHCO_3$ (3 × 50 mL), H_2O (3 × 100 mL), and brine (3 × 50 mL). Rotary evaporation and chromatography (7:1 hexane/EtOAc) afforded **3b** (1.62 g, 60%) as a white crystalline product: R_f 0.31 (7:1 hexane/EtOAc); mp 131−133 °C; $[\alpha]^{24}_D$ −8.8° (c = 1.0, $CHCl_3$); IR (KBr, DRIFTS) ν_{max} 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.57 (s, 2H), 3.76 (s, 6H), 3.74−3.70 (m, 4H), 1.84−1.78 (m, 4H), 1.61−1.50 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.7, 96.5, 68.2, 61.2, 52.4, 28.0, 24.7, 17.8; HRMS (CI) calcd for $C_{16}H_{25}O_8$ (M + H)$^+$, 345.1549, found (M + H)$^+$, 345.1544. Anal. Calcd for $C_{16}H_{24}O_8$: C, 55.81; H, 7.02. Found: C, 55.54; H, 7.17.

(2*R*,3*R*)-Dimethyl 5,6-Dimethoxy-5,6-dimethyl-1,4-diox-2-ene-2,3-dicarboxylate (4a). Lithium 2,2,6,6-tetramethylpiperidide, prepared from 2,2,6,6-tetramethylpyperidine (0.25 mL, 1.48 mmol) in THF (1.5 mL) and *n*-BuLi in hexane (1.6 M, 0.78 mL), was added to a solution of **3a** (110 mg, 0.376 mmol) in THF (0.4 mL) at −78 °C. The mixture was allowed to stir at −78 °C for 1.5 h, after which I_2 (114 mg, 0.45 mmol) in THF (1.0 mL) was added. Stirring was continued at −78 °C for 2.5 h, after which the mixture was allowed to warm to room temperature, Et_2O (3 mL) was added, and the solution was extracted with H_2O (2 mL) and brine (2 mL) and dried ($MgSO_4$). Rotary evaporation and chromatography (4:1 hexane/EtOAc) afforded **4a** (70 mg, 64%) as a white solid: R_f 0.21 (4:1 hexane/EtOAc); mp 89−91 °C (hexane/Et_2O); $[\alpha]^{24}_D$ −325.4° (c = 1.0, $CHCl_3$); IR (neat) ν_{max} 1734, 1653, 1215, 1153, 1105 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.83 (s, 6H), 3.38 (s, 6H), 1.56 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.9, 131.0, 98.9, 52.5, 49.5, 16.8; HRMS (FAB) calcd for $C_{12}H_{19}O_8$ (M + H)$^+$, 291.1080, found (M + H)$^+$, 291.1073. Anal. Calcd for $C_{12}H_{18}O_8$: C, 49.65; H, 6.25. Found: C, 49.55; H, 5.97.

(6*R*,7*R*)-Dimethyl 1,8,13,16-Tetraoxadispiro[5.0.5.4]-hexadec-14-ene-14,15-dicarboxylate (4b). Diester **4b** (262 mg, 53%) was prepared from **3b** (500 mg, 1.45 mmol) by a procedure identical to that used in the preparation of **4a**: R_f 0.30 (7:1 hexane/EtOAc); mp 92−95 °C; $[\alpha]^{24}_D$ −20.3° (c = 1.0, $CHCl_3$); IR (KBr, DRIFTS) ν_{max} 1733, 1654, 1179, 1143 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.91−3.84 (m, 2H), 3.82 (s, 6H), 3.75−3.71 (m, 2H), 2.02−1.92 (m, 4H), 1.75−1.67 (m, 4H), 1.65−1.57 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.2, 130.6, 96.6, 62.4, 52.5, 27.7, 24.7, 17.9; HRMS (CI) calcd for $C_{16}H_{23}O_8$ (M + H)$^+$, 343.1393, found (M + H)$^+$, 343.1384. Anal. Calcd for $C_{16}H_{22}O_8$: C, 56.14; H, 6.48. Found: C, 55.97; H, 6.32.

(2*R*,3*R*)-5,6-Dimethoxy-5,6-dimethyl-1,4-diox-2-ene-2,3-dinitrile (5a). Diester **4a** (55 mg, 0.19 mmol) in MeOH (8 mL) was saturated with NH_3 at 0 °C and stirred at room temperature for 4 days. Rotary evaporation afforded the amide (49 mg, 99%), which was used without further purification: R_f 0.18 (1:19 MeOH/EtOAc); mp 212−214 °C (EtOAc); $[\alpha]^{24}_D$ −260.0° (c = 1.0, MeOH); IR (neat) ν_{max} 3329, 3290, 1666, 1631, 1614, 1153 cm^{-1}; ^{1}H NMR (CD_3OD, 300 MHz) δ 3.35 (s, 6H), 1.56 (s, 6H); ^{13}C NMR (CD_3OD, 75 MHz) δ 165.2, 131.5, 98.6, 48.5, 15.7; HRMS (FAB) calcd for $C_{10}H_{17}N_2O_6$ (M + H)$^+$, 261.1087, found (M + H)$^+$, 261.1090. Anal. Calcd for $C_{10}H_{16}N_2O_6$: C, 46.15; H, 6.20; N, 10.76. Found: C, 46.41; H, 6.11; N, 10.67.

Trifluoroacetic anhydride (140 μL, 0.99 mmol) was slowly added to the amide (98 mg, 0.38 mmol) in pyridine (4 mL) at −30 °C over 1 h, and the solution was allowed to warm to room temperature over 2 h. Rotary evaporation and chromatography (5:1 hexane/EtOAc) afforded dinitrile **5a** (83 mg, 97%) as white crystals: R_f 0.31 (5:1 hexane/EtOAc); mp 102−103 °C (hexane); $[\alpha]^{24}_D$ −349.9° (c = 1.0, $CHCl_3$); IR ($CDCl_3$) ν_{max} 2235, 1630, 1165 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.38 (s, 6H), 1.55 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 121.7, 111.4, 101.2, 50.2, 16.6; MS (CI) 242 $(M + NH_4)^+$. Anal. Calcd for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.39; N, 12.49. Found: C, 53.89; H, 5.10; N, 12.46.

(6*R*,7*R*)-1,8,13,16-Tetraoxadispiro[5.0.5.4]hexadec-14-ene-14,15-dinitrile (5b). Dinitrile **5b** (28 mg, 77%) was prepared from **4b** (48 mg, 0.14 mmol) via the corresponding amide [mp 282−283 °C; $[\alpha]^{24}_D$ −16.0° (c = 1.0, MeOH); IR (KBr, DRIFTS) ν_{max} 3321, 3168, 1697, 1681, 1657, 1171 cm^{-1}; ^1H NMR (CD_3OD, 300 MHz) δ 3.88−3.69 (m, 4H), 2.07−1.92 (m, 4H), 1.84−1.73 (m, 4H), 1.68−1.62 (m, 4H); ^{13}C NMR (CD_3OD, 75 MHz) δ 165.4, 130.9, 96.4, 62.0, 27.4, 24.4, 17.7; HRMS (CI) calcd for $C_{14}H_{21}N_2O_6$ $(M + H)^+$, 313.1400, found $(M + H)^+$, 313.1420] by an identical procedure to that used in the preparation of dinitrile **5a**: R_f 0.25 (6:1 hexane/EtOAc); mp 172−173 °C; $[\alpha]^{24}_D$ −25.4° (c = 1.0, $CHCl_3$); IR ($CHCl_3$) ν_{max} 2234, 1633 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.86−3.67 (m, 4H), 2.07−1.59 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 121.6, 111.6, 99.2, 63.1, 27.5, 24.1, 17.5; HRMS (CI) calcd for $C_{14}H_{20}N_3O_4$ $(M + NH_4)^+$, 294.1454, found $(M + NH_4)^+$, 294.1440. Anal. Calcd for $C_{14}H_{16}N_2O_4$: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.92; H, 5.91; N, 10.00.

H_2[pz(OR)$_2$Pr$_6$] (7b). A small crystal of iodine, Mg (5.0 mg, 0.21 mmol), and *n*-BuOH (4 mL) were heated to reflux for 3 h and allowed to cool to room temperature when dinitriles **5a** (41 mg, 0.18 mmol) and **6** (240 mg, 1.48 mmol) were added neat under N_2. The mixture was heated under reflux for 14 h, after which the cooled solution was diluted with CH_2Cl_2 (5 mL) and filtered through Celite. Rotary evaporation and chromatography (4:1 hexane/EtOAc) gave Mg−porphyrazine **7a** (79 mg, 60%). Demetalation was effected by stirring complex **7a** (77 mg, 0.11 mmol) in AcOH (2 mL) for 10 min at room temperature. This solution was poured onto ice (ca. 30 g), neutralized with 1 M NaOH, and filtered. The solid material was taken up in CH_2Cl_2 (10 mL), extracted with H_2O (2 mL), dried ($MgSO_4$), rotary evaporated, and chromatographed (8:1 hexane:EtOAc) to give porphyrazine **7b** (53 mg, 0.074 mmol, 41% overall) as a deep purple solid: R_f 0.46 (8:1 hexane/EtOAc); mp 201−204 °C; IR (neat) ν_{max} 3305, 1622, 1487, 1379, 1153 cm^{-1}; UV−vis (CH_2Cl_2, log ϵ) λ_{max} 341 (5.09), 557 (4.74), 627 (4.99) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.09−3.95 (m, 8H), 3.91−3.86 (m, 4H), 3.60 (s, 6H), 2.43−2.32 (m, 12H), 2.13 (s, 6H), 1.33−1.25 (m, 18H), −2.56 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.2, 148.9, 148.3, 144.8, 142.2, 138.5, 101.9, 49.7, 28.3, 28.2, 27.9, 25.6, 25.4, 18.0, 14.8, 14.6; HRMS (FAB) calcd for $C_{40}H_{57}N_8O_4$ $(M + H)^+$, 713.4503, found $(M + H)^+$, 713.4492.

H_2[pz(OR)$_2$(*t*-butylphenyl)$_6$] (9b). A small crystal of iodine, Mg (100 mg, 4.1 mmol), and *n*-BuOH (40 mL) were heated to reflux for 5h under N_2 and then cooled to room temperature when dinitrile **5b** (380 mg, 1.38 mmol) and pyrroline **8** (3.6 g, 10 mmol) were added and the mixture heated to reflux for 24 h. Rotary evaporation gave the crude magnesium porphyrazine **9a**: FAB-MS 1327 $(M + H)^+$. This was allowed to react with AcOH (10 mL) in CH_2Cl_2 (40 mL) overnight at room temperature. The solution was poured onto ice (100 mL), and the metal-free porphyrazine **9b** was extracted with CH_2Cl_2, followed by Et_2O. The combined extracts were washed with H_2O and dried ($MgSO_4$). Rotary evaporation and chromatography (3:1 hexane/EtOAc) followed by precipitation in MeOH gave porphyrazine **9b** (380 mg, 21%) as a green solid: R_f 0.58 (3:1 hexane/EtOAc); mp 246−247 °C (MeOH); IR (neat) ν_{max} 3292, 1633, 1484, 1362, 1188, 1106 cm^{-1}; UV−vis (CH_2Cl_2, log ϵ) λ_{max} 362 (4.87), 458 (4.50), 610 (4.61), 652 (4.64), 675 (4.60) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.41 (d, 4H, J = 8.2), 8.36 (d, 4H, J = 8.2), 8.30 (d, 4H, J = 8.2), 7.69 (d, 4H, J = 8.2), 7.56 (d, 4H, J = 8.2), 7.52 (d, 4H, J = 8.2), 4.35−4.20 (m, 2H), 3.76 (d, 2H, J = 10.2), 2.70−2.50 (m, 4H), 2.20−2.00 (m, 4H), 1.90−1.75 (m, 4H), 1.54 (s, 18H), 1.49 (s, 18H), 1.45 (s, 18H), −1.78 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.5, 151.4, 151.3, 141.3, 140.9, 138.7, 133.4, 133.2, 131.6, 131.4, 125.8, 100.8, 63.4, 35.5, 35.45, 35.42, 32.2, 29.5, 25.7, 19.0; HRMS (FAB) calcd for $C_{86}H_{98}N_8O_4$ $(M + 2H)^+$, 1306.7711, found $(M + 2H)^+$, 1306.7748. Anal. Calcd for $C_{86}H_{96}N_8O_4$: C, 79.11; H, 7.41; N, 8.58. Found: C, 79.08; H, 7.59; N, 8.46.

Zn[pz(OR)$_2$(*t*-butylphenyl)$_6$] (9c). Porphyrazine **9b** (33 mg, 0.025 mmol), anhydrous $Zn(OAc)_2$ (45 mg, 0.25 mmol), PhCl (10 mL) and DMF (5 mL) were heated at 110 °C under N_2 for 24 h. The mixture was rotary evaporated, and methanolic HCl (5%) (15 mL) was added to the residue. The resultant solid was filtered off, washed with MeOH, and dried under vacuum to afford Zn−porphyrazine **9c** (30 mg, 89%) as a green solid: R_f 0.33 (3:1 hexane/EtOAc); mp >350 °C (MeOH); IR (neat) ν_{max} 1648, 1470, 1364, 1203, 1104 cm^{-1}; UV−vis (CH_2Cl_2, log ϵ) λ_{max} 359 (4.89), 432 (4.30), 466 (4.26), 625 (4.81), 640 (4.88) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.44−8.12 (m, 8H), 7.91−7.82 (m, 4H), 7.77−7.52 (m, 12H), 4.54−4.42 (m, 2H), 4.05−3.80 (m, 2H), 2.65−2.53 (m, 4H), 2.19−2.00 (m, 4H), 1.95−1.85 (m, 4H), 1.54 (s, 18H), 1.53 (s, 18H), 1.50 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.2, 157.2, 156.9, 150.8, 150.7, 149.7, 141.8, 133.2, 132.2, 132.1, 125.5, 100.3, 63.1, 35.4, 32.6, 29.4, 25.9, 18.8; HRMS (FAB) calcd for $C_{86}H_{96}N_8O_4Zn$ $(M + 2H)^+$, 1368.6846, found $(M + 2H)^+$, 1368.6848. Anal. Calcd for $C_{86}H_{94}N_8O_4Zn$: C, 75.45; H, 6.92; N, 8.18. Found: C, 75.36; H, 6.95; N, 7.94.

Ni[pz(OR)$_2$(*t*-butylphenyl)$_6$] (9d). Porphyrazine **9d** (29 mg, 85%) was prepared from porphyrazine **9b** (33 mg, 0.025 mmol) by a procedure identical to that used in the preparation of complex **9c** and was obtained as a green solid: R_f 0.59 (3:1 hexane/EtOAc); mp 250−251 °C (MeOH); IR (neat) ν_{max} 1675, 1460, 1377, 1215, 1104 cm^{-1}; UV−vis (CH_2Cl_2, log ϵ) λ_{max} 342 (4.87), 446 (4.51), 614 (4.75), 632 (4.78) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.31 (d, 4H, J = 8.6), 8.22 (d, 4H, J = 8.6), 8.16 (d, 4H, J = 8.2), 7.66 (d, 4H, J = 8.2), 7.49 (d, 4H, J = 8.9), 7.45 (d, 4H, J = 8.9), 4.33−4.20 (m, 2H), 3.76 (d, 2H, J = 9.9), 2.65−2.48 (m, 4H), 2.18−2.00 (m, 4H), 1.90−1.77 (m, 4H), 1.53 (s, 18H), 1.44 (s, 18H), 1.41 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.3, 151.1, 151.0, 149.8, 149.5, 142.7, 142.2, 141.9, 138.8, 133.3, 133.1, 132.9, 131.5, 131.4, 131.3, 125.7, 100.9, 63.4, 35.5, 35.3, 32.2, 32.17, 32.1, 29.4, 25.8, 18.9; HRMS (FAB) calcd for $C_{86}H_{95}N_8NiO_4$ $(M + H)^+$, 1361.6830, found $(M + H)^+$, 1361.6842. Anal. Calcd for $C_{86}H_{94}N_8NiO_4$: C, 75.82; H, 6.95; N, 8.22. Found: C, 75.59; H, 6.82; N, 8.08.

Cu[pz(OR)$_2$(*t*-butylphenyl)$_6$] (9e). Porphyrazine **9e** (30 mg, 85%), prepared from porphyrazine **9b** (33 mg, 0.026 mmol) by a procedure identical to that used in the preparation of complex **9d**, was obtained as a green solid: R_f 0.51 (3:1 hexane/EtOAc); mp 253−254 °C (MeOH); IR (neat) ν_{max} 1656, 1488, 1374, 1213, 1104 cm^{-1}; UV−vis (CH_2Cl_2, log ϵ) λ_{max} 357 (5.03), 456 (4.56), 615 (4.95), 634 (5.03) nm; HRMS (FAB) calcd for $C_{86}H_{96}CuN_8O_4$ $(M + 2H)^+$, 1367.6851, found $(M + 2H)^+$, 1367.6872. Anal. Calcd for $C_{86}H_{94}CuN_8O_4$: C, 75.55; H, 6.93; N, 8.20. Found: C, 75.73; H, 7.09; N, 8.14.

H_2[pz(OTBDMS)$_2$Pr$_6$] (10c). *t*-$BuMe_2SiO_3SCF_3$ (0.20 mL, 0.83 mmol) was added to porphyrazine **7b** (32 mg, 0.045 mmol) in CH_2Cl_2 (10 mL) at −78 °C, and the solution was allowed to warm to room temperature during 18 h. Et_3N (0.5 mL) was added, and the stirring was continued for a further 3 h. Rotary evaporation and chromatography (1:99 EtOAc/hexane) followed by extraction of the solid residue with Me_2CO (2 × 20 mL) gave porphyrazine **10c** (29 mg, 79%) as a green solid: R_f 0.12 (1:99 EtOAc/hexane); mp 178−181 °C; IR (neat) ν_{max} 1645, 1486, 1363, 1172 cm^{-1}; UV−vis (CH_2Cl_2, log ϵ) λ_{max} 342 (4.90), 558 (4.56), 601 (4.01), 629 (4.80), 657 (3.85), 761 (3.08) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.01 (t, 8H, J = 7.8), 3.89 (t, 4H, J = 7.5), 2.44−2.27 (m, 12H), 1.38 (s, 18H), 1.36−1.26 (m, 18H), 0.56 (s, 12H), −2.45 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.5, 153.2, 148.9, 148.7, 144.6, 142.5, 142.3, 141.6, 28.3, 28.1, 26.1, 25.9, 25.6, 18.8, 14.8, −3.5; HRMS (FAB) calcd for $C_{46}H_{75}N_8O_2Si_2$ $(M + H)^+$, 827.5552, found $(M + H)^+$, 827.5545.

Ni[pz(OH)$_2$(*t*-butylphenyl)$_6$] (11d). Trifluoroacetic acid and H_2O (19:1) (1 mL) were added to porphyrazine **9d** (10 mg, 7.3 μmol) under N_2 when the solution turned purple immediately. The mixture was stirred overnight at room tem-

perature and rotary evaporated, and the residue was precipitated using MeOH and filtered. The residue was washed with MeOH and dried under vacuum to afford the porphyrazine diol **11d** (6.0 mg, 69%) as a green solid: R_f 0.43 (99:1 CH_2Cl_2/EtOAc); mp 176−178 °C (MeOH); IR (neat) ν_{max} 3492, 1608, 1462, 1363, 1270 cm^{-1}; UV−vis (CH_2Cl_2, log ϵ) λ_{max} 337 (4.79), 448 (4.43), 607 (4.63), 642 (4.70) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.07 (d, 4H, J = 9.5), 7.96 (d, 4H, J = 9.5), 7.60−7.53 (m, 4H), 7.50−7.45 (m, 12H), 1.59 (s, 18H), 1.57 (s, 18H), 1.52 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.4, 151.3, 151.0, 148.3, 147.8, 147.5, 142.6, 141.7, 141.5, 140.0, 134.7, 133.5, 133.3, 132.9, 131.2, 131.1, 130.5, 125.6, 125.5, 125.4, 35.6, 35.52, 35.48, 32.5, 32.3; HRMS (FAB) calcd for $C_{76}H_{81}N_8NiO_2$ (M + H)$^+$, 1195.5836, found (M + H)$^+$, 1195.5888. Anal. Calcd for $C_{76}H_{80}N_8NiO_2$: C, 76.31; H, 6.74; N, 9.37. Found: C, 76.17; H, 6.85; N, 9.24.

Cu[pz(OH)$_2$(*t*-butylphenyl)$_6$] (11e). Diol **11e** (6.6 mg, 75%) was prepared from porphyrazine **9e** (10 mg, 7.3 μmol) by a procedure identical to that used in the preparation of diol **11d**: R_f 0.24 (99:1 CH_2Cl_2/EtOAc); mp 185−187 °C (MeOH); IR (neat) ν_{max} 3474, 1740, 1463, 1364, 1270 cm^{-1}; UV−vis (CH_2Cl_2, log ϵ) λ_{max} 354 (4.87), 458 (4.43), 610 (4.75), 640 (4.98) nm; HRMS (FAB) calcd for $C_{76}H_{81}CuN_8O_2$ (M + H)$^+$, 1200.5778, found (M + H)$^+$, 1200.5797. Anal. Calcd for $C_{76}H_{80}CuN_8O_2$: C, 76.00; H, 6.71; N, 9.33. Found: C, 75.85; H, 6.89; N, 9.26.

Ni[pz(CN)$_2$(*t*-butylphenyl)$_6$] (14d). DDQ (40 mg, 0.18 mmol) was added to diol **11d** (20 mg, 0.017 mmol) in Et_2O (10 mL) at −78 °C under N_2. The solution turned immediately from green to deep purple and was allowed to warm to room temperature and rotary evaporated. The residue was chromatographed (3:1 hexane/EtOAc) to remove a blue impurity and with hexane and EtOAc (1:2) to afford the dione **13d** (10 mg, 49%) as a purple solid: FAB-MS 1195 (M + H)$^+$. Diaminomaleonitrile (29 mg, 0.27 mmol) was added to a solution of the dione **13d** in EtOH and AcOH (5:1), and the mixture was heated to reflux for 4 h. Rotary evaporation and chromatography (3:1 hexane/EtOAc) followed by precipitation using MeOH gave pyrazine **14d** (6 mg, 57%) as a purple solid: R_f 0.57 (3:1 hexane/EtOAc); mp >350 °C (MeOH); IR (neat) ν_{max} 1660, 1464, 1364, 1268 cm^{-1}; UV−vis (CH_2Cl_2, log ϵ) λ_{max} 351 (5.06), 451 (4.48), 498 (4.55), 609 (4.73), 660 (5.10) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.11−7.52 (m, 24H), 1.50 (s, 18H), 1.49 (s, 18H), 1.47 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.3, 152.2, 151.2, 150.6, 148.3, 145.1, 142.7, 142.3, 142.0, 137.0, 133.1, 132.8, 132.7, 132.5, 129.9, 129.7, 126.0, 125.9, 125.8, 114.9, 35.6, 32.4, 32.3; HRMS (FAB) calcd for $C_{80}H_{79}N_{12}Ni$ (M + H)$^+$, 1265.5904, found (M + H)$^+$, 1265.6033. Anal. Calcd for $C_{80}H_{78}N_{12}Ni$: C, 75.88; H, 6.21; N, 13.27. Found: C, 76.12; H, 6.11; N, 13.02.

Cu[pz(CN)$_2$(*t*-butylphenyl)$_6$] (14e). Pyrazine **14e** (7.5 mg, 25%), prepared from diol **11e** (30 mg, 0.025 mmol) by a procedure identical to that used in the preparation of pyrazine **14d**, was obtained as a purple solid: R_f 0.57 (3:1 hexane/EtOAc); mp >350 °C (MeOH); IR (neat) ν_{max} 1740, 1485, 1364, 1269 cm^{-1}; UV−vis (CH_2Cl_2, log ϵ) λ_{max} 370 (4.78), 501 (4.26), 609 (4.31), 660 (4.89) nm; MS (FAB) m/z 1271 (M + H)$^+$. Anal. Calcd for $C_{80}H_{78}CuN_{12}$: C, 75.59; H, 6.19; N, 13.22. Found: C, 75.72; H, 6.11; N, 13.39.

General Procedure for the Complexation. The bis(pentamethylcyclopentadienyl)metallocene derivative (M^2 = Ti, Zr, Hf) (0.01 mmol) was added to a solution of freshly prepared diol **11d** (M^1 = Ni) (12 mg, 0.01 mmol) in dry Et_2O (5 mL) under N_2. A suspension of KO^{t}Bu (5.0 mg, 0.045 mmol) in dry Et_2O (5 mL) was added, and the mixture was stirred overnight at room temperature under N_2. The crude mixture was filtered (Celite) and washed with Et_2O. The solid was dissolved in CH_2Cl_2, filtered through Celite, and chromatographed (3:1 hexane/EtOAc) to provide the solitaire porphyrazine **12**.

Ni[pz(O$^-$)$_2$(*t*-butylphenyl)$_6$]TiCp$_2$* (12a): green solid (3 mg, 20%); R_f 0.48 (3:1 hexane/EtOAc); IR (neat) ν_{max} 3653, 1623, 1360, 1154 cm^{-1}; UV−vis (CH_2Cl_2, log ϵ) λ_{max} 273 (4.77), 342 (4.77), 427 (4.34), 594 (4.65), 624 (4.61) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.35−8.23 (m, 10H), 7.98 (d, 2H, J = 7.9), 7.68−7.52 (m, 12H), 2.02 (s, 30H), 1.57−1.49 (m, 54H); MS (FAB) m/z 1512 (M)$^{+\bullet}$; HRMS (FT-ICR) calcd for $C_{96}H_{109}N_8NiO_2Ti$ (M + H)$^+$, 1512.7536, found (M + H)$^+$, 1512.7696.

Ni[pz(O$^-$)Cp*(*t*-butylphenyl)$_6$]Cp*TiCl (12a′): green solid (8.5 mg, 55%); R_f 0.46 (3:1 hexane/EtOAc); IR (neat) ν_{max} 3647, 1615, 1447, 1404, 1287 cm^{-1}; UV−vis (CH_2Cl_2, log ϵ) λ_{max} 269 (4.71) 342 (4.70), 435 (4.31), 625 (4.49), 667 (4.42) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.34−8.20 (m, 10H), 7.93 (d, 2H, J = 8.2), 7.65−7.50 (m, 12H), 4.69 and 4.62 (ABq, 2H, J = 18.5), 2.35 (s, 3H), 2.08 (s, 15H), 2.04 (s, 3H), 2.01 (s, 3H), 1.88 (s, 3H), 1.51−1.47 (m, 54H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.7, 154.9, 151.2, 150.9, 150.8, 150.7, 150.6, 149.3, 148.7, 148.6, 147.4, 143.0, 142.9, 142.6, 141.5, 141.4, 141.3, 133.2, 133.0, 132.8, 132.0, 131.97, 131.8, 131.6, 126.0, 125.8, 125.7, 125.5, 125.4, 123.2, 122.3, 121.9, 120.6, 115.3, 35.5, 32.4, 12.9, 12.87, 12.6, 11.9, 11.7; MS (FAB) m/z 1496 (M − Cl)$^+$. HRMS (FT-ICR) calcd for $C_{96}H_{107}ClN_8NiOTi$ ($M^{+\bullet}$), 1530.7104, found ($M^{+\bullet}$), 1530.7182. Anal. Calcd for $C_{96}H_{107}ClN_8NiOTi$: C, 75.31; H, 7.04; N, 7.32. Found: C, 75.30; H, 7.04; N, 6.88.

Ni[pz(O$^-$)$_2$(*t*-butylphenyl)$_6$]ZrCp$_2$* (12b): green solid (7 mg, 45%); R_f 0.35 (3:1 hexane/EtOAc); UV−vis (CH_2Cl_2, log ϵ) λ_{max} 342 (4.70), 440 (4.24), 597 (4.62), 617 (4.60) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.35−8.10 (m, 10H), 7.84 (d, 2H, J = 8.3), 7.72−7.45 (m, 12H), 2.08 (s, 30H), 1.68−1.61 (m, 54H); MS (FAB) m/z 1555 (M)$^{+\bullet}$; HRMS (FT-ICR) calcd for $C_{96}H_{109}N_8NiO_2Zr$ (M + H)$^+$, 1555.7091, found (M + H)$^+$, 1555.7066.

Ni[pz(O$^-$)$_2$(*t*-butylphenyl)$_6$]HfCp$_2$* (12c): purple solid (3.3 mg, 21%); R_f 0.58 (3:1 hexane/EtOAc); IR (neat) ν_{max} 1638, 1362, 1153 cm^{-1}; UV−vis (CH_2Cl_2, log ϵ) λ_{max} 339 (4.71), 432 (4.22), 458 (4.25), 594 (4.52), 624 (4.49) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.41−8.28 (m, 10H), 8.10 (d, 2H, J = 6.4), 7.70−7.57 (m, 12H), 2.10 (s, 30H), 1.60−1.50 (m, 54H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.4, 150.3, 150.25, 150.19, 149.8, 149.4, 149.2, 148.2, 147.8, 147.5, 147.3, 146.4, 143.9, 142.3, 141.5, 141.3, 141.1, 140.0, 138.8, 132.6, 132.1, 131.3, 131.2, 131.1, 131.0, 125.3, 125.0, 120.4, 34.8, 34.78, 31.7, 31.6, 11.0; MS (FAB) m/z 1644 (M + H)$^+$; HRMS (FT-ICR) calcd for $C_{96}H_{109}HfN_8NiO_2$ (M + H)$^+$, 1643.7488, found (M + H)$^+$, 1643.7439.

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Supporting Information Available: Copies of ^1H NMR spectra of **12a**,**a′**,**b**,**c** and ^{13}C NMR spectra of **12a′**,**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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