Organometallics **1998,** *17,* 3656−3660

Synthesis of 1,2-Cyclopentadienyl Diimine Anions and Their Zirconium Complexes

Nola Etkin,[†] Christopher M. Ong, and Douglas W. Stephan*

Department of Chemistry and Biochemistry, University of Windsor,
Windsor, Ontario, Canada N9B 3P4

Received May 21, 1998

1,2-disubstituted cyclopentadienyl diimine anions are examples of extended π-systems that bind metals through the nitrogen atoms. Reaction of Cp_2Mg with benzonitrile gives the product $(1,2\text{-}C_5H_3(C(Ph)NH)_2)CpMg(NCPh)$ (**1**) in 98% yield. In an analogous manner, the related complexes $(1,2\text{-}C_5H_3(C(Ph)NH)_2)CpMg(OEt_2)$ (**2**) and $((4\text{-}Me_3SiC_5H_2)(1,2\text{-}(C(Ph)NH)_2)(Me_3SiC_5H_4)Mg(OEt_2)$ (**3**) were prepared in situ. Demetalation of these complexes **1**−**3** yields the corresponding free diimine ligands of formulation $H[(1,2\text{-}C_5H_3(C(Ph)NH)_2)]$ (**4**) and $H[4\text{-}Me_3SiC_5H_2\text{-}1,2\text{-}(C(Ph)NH)_2]$ (**5**). Hydrolysis of compound **4** leads to the fulvene derivative $1\text{-}(C(OH)Ph)\text{-}2\text{-}(O{=}C(Ph))C_5H_3$ (**6**). The zirconium complexes $(C_5H_3\text{-}1,2\text{-}(C(Ph)NH)_2)ZrCl_3(THF)$ (**7**) and $(C_5H_3\text{-}1,2\text{-}(C(Ph)NH)_2)_3ZrCl$ (**8**) were isolated from reactions of **4** with $ZrCl_4(THF)_2$. X-ray crystallographic studies of **1**, **7**, and **8** are reported. Evidence suggests that these new 1,2-disubstituted cyclopentadienyl diimine anions impart some charge delocalization, thus offering a new approach to electrophilic metal centers. This view is supported by EHMO calculations.

Introduction

The chemical landscape of early-transition-metal chemistry has undergone dramatic growth over the past few years. Much effort has focused on metallocenes and on the preparation of various related species. For example, a large variety of substituted cyclopentadienyl ligands have been utilized to mediate the steric or electronic character of the resulting metal complexes.[1,2] A second approach to controlling metal atom environments involves the development of systems incorporating alternative ancillary ligands. Early-metal systems using ligands traditionally reserved for later transition metals, such as bulky aryloxide,[3] amide,[4,5] or carbodiiminate ligands,[6] porphyrins,[7−14] or calixarenes,[15,16] are among those recently explored. In our own efforts to develop new early-metal systems, we have uncovered a convenient synthesis of 1,2-disubstituted cyclopentadienyl derivatives, an elusive class of cyclopentadienyl ligands.[17−21] Specifically, the synthesis of 1,2-disubstituted cyclopentadienyl diimine ligands and the Zr complexes thereof are described. These ligands, which bind via the imine nitrogen atoms, are anionic analogues of classic, chelating Schiff bases. Whereas related ligands have a rich, well-established late-transition-metal chemistry, the use of such ligands in early-transition-metal chemistry has only received limited attention.[22]

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing either Schlenk line techniques or a Vacuum Atmospheres or Innovative Technologies inert-atmosphere glovebox. Solvents were reagent grade, distilled from the appropriate drying agents under N_2 and degassed by the freeze−thaw method at least three times prior to use. All organic reagents were purified by conventional methods. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance 300 and 500 MHz spectrometers. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. Combustion analyses were performed by E+R Microanalytical Labor-

---

[†] Present address: Department of Chemistry, University of Prince Edward Island, Charlottetown, PEI, Canada C1A 4P3.

(1) Okuda, J. *Top. Curr. Chem.* **1992**, *160*, 97.

(2) Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291.

(3) Firth, A. V.; Stephan, D. W. *Organometallics* **1997**, *16*, 2183.

(4) Tayebani, M.; Feghali, K.; Gambarotta, S.; Bensimon, C. *Organometallics* **1997**, *16*, 5084.

(5) Moore, M.; Gambarotta, S.; Bensimon, C. *Organometallics* **1997**, *16*, 1086.

(6) Dawson, D. Y.; Arnold, J. *Organometallics* **1997**, *16*, 1111.

(7) Arnold, J. *J. Chem. Soc., Chem. Commun.* **1990**, 976.

(8) Berreau, L. M.; Hays, A.; Young, J. V. G.; Woo, L. K. *Inorg. Chem.* **1994**, *33*, 105.

(9) Berreau, L. M.; Young, J. V. G.; Woo, L. K. *Inorg. Chem.* **1995**, *34*, 527.

(10) Brand, H.; Arnold, J. *Organometallics* **1993**, *12*, 3655.

(11) Brand, H.; Capriotti, J. A.; Arnold, J. *Organometallics* **1994**, *13*, 4469.

(12) Jacoby, D.; Isoz, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 2793.

(13) Jacoby, D. I. S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 2805.

(14) Woo, L. K.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102.

(15) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 998.

(16) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Cheisi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 9709.

(17) Hughes, R. P.; Kowalski, A. S.; Lomprey, J. R. *Organometallics* **1994**, *13*, 2691.

(18) Hughes, R. P.; Lomprey, J. R.; Rheingold, A. L.; Yap, G. *J. Organomet. Chem.* **1996**, *517*, 63.

(19) Hughes, R. P.; Lomprey, J. R.; Rheingold, A. L.; Haggerty, B. S.; Yap, G. *J. Organomet. Chem.* **1996**, *517*, 89.

(20) Little, W., F.; Koestler, R. C. *J. Chem. Soc.* **1961**, 3245.

(21) Lappert, M. F.; Liu, D. S. *J. Organomet. Chem.* **1995**, *500*, 203.

(22) Martin, A.; Uhrhammer, R.; Gardner, T. G.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1998**, *17*, 382.

S0276-7333(98)00409-9 CCC: $15.00
Publication on Web 07/21/1998

Table 1. Crystallographic Parameters

	1	**4**	**7**	**8**
formula	$C_{37}H_{31}MgN_3$	$C_{19}H_{16}N_2$	$C_{23}H_{23}Cl_3ON_2Zr$	$C_{57}H_{45}ClN_6Zr$
fw	541.96	272.34	541.03	940.66
cryst size	0.50 × 0.30 × 0.30	0.40 × 0.40 × 0.30	0.30 × 0.25 × 0.18	0.20 × 0.18 × 0.16
a (Å)	8.0498(13)	13.258 70(10)	10.316(3)	16.1031(4)
b (Å)	13.014(3)		13.812(2)	12.3010(3)
c (Å)	16.376(4)	16.8857(2)	8.805(2)	23.9529(5)
α (deg)	111.81(2)		97.29(2)	
β (deg)	101.55(2)		94.54(2)	92.4690(10)
γ (deg)	91.15(2)		97.02(2)	
cryst syst	triclinic	tetragonal	triclinic	monoclinic
space group	$P\bar{1}$	$I4_1cd$	$P\bar{1}$	$P2_1/n$
V (Å^3)	1552.1(6)	2968.39(5)	1229.4(5)	4740.3(2)
D_{calcd} (g cm^{-1})	1.16	1.22	1.46	1.32
Z	2	8	2	4
abs coeff, μ, cm^{-1}	0.860	0.072	7.89	3.33
no. of data collected	6803	4847	4700	6970
no. of data $F_o^2 > 3\sigma(F_o^2)$	5904	763	2643	5092
no. of variables	415	96	271	586
transmissn factors	0.966−1.255	n/a	n/a	0.850−1.120
R (%)	5.80	8.95	5.80	5.34
R_w (%)	16.15	26.70	5.90	10.51
goodness of fit	1.132	1.081	2.710	1,101

atory Inc., Corona, NY. Cp_2Mg was prepared via literature methods. All other reagents were purchased from the Aldrich Chemical Co.

Synthesis of (1,2-C_5H_3(C(Ph)NH)$_2$)CpMg(NCPh) (1). To a solution of Cp_2Mg (0.930 g, 0.60 mmol) in 4 mL of ether was added benzonitrile (0.252 g, 2.45 mmol). The reaction mixture was stirred for 10 h, and the solvent was removed under vacuum. Recrystallization of the product from benzene afforded **1** as orange crystals (yield 98%). ^{1}H NMR (C_6D_6, 25 °C): δ 7.47 (2H, s), 7.44 (4H, d, $|J_{H-H}| = 1.7$ Hz), 7.07−7.00 (6H, m), 6.74−6.68 (5H, m), 6.64 (2H, d, $|J_{H-H}| = 3.8$ Hz), 6.62 (5H, s), 6.35 (1H, t, $|J_{H-H}| = 3.7$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 178.1, 146.8, 133.5, 133.0, 129.3, 128.9, 128.6, 121.1, 120.2, 118.8, 113.7, 109.8, 105.8. Anal. Calcd for $C_{31}H_{24}MgN_3$: C, 80.44; H, 5.23; N, 9.08. Found: C, 79.99; H, 5.69; N, 8.78.

Synthesis of (1,2-C_5H_3(C(Ph)NH)$_2$)CpMg(OEt_2) (2). This compound was prepared as for **1** using a benzonitrile:Cp_2Mg ratio of 2.5:1. Yield: 95%. ^{1}H NMR (C_6D_6, 25 °C): δ 7.44−7.41 (6H, m), 7.12−7.08 (6H, m), 6.61 (2H, d, $|J_{H-H}| = 3.8$ Hz), 6.38−6.34 (6H, m), 3.10 (4H, q, $|J_{H-H}| = 7.02$), 0.77 (6H, t, $|J_{H-H}| = 6.3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 77.8, 146.7, 134.1, 129.3, 128.8, 120.8, 119.5, 114.4, 105.5, 64.7, 14.1. Anal. Calcd for $C_{28}H_{28}MgON_2$: C, 77.70; H, 6.52; N, 6.47. Found: C, 77.14; H, 6.74; N, 6.77.

Synthesis of H[1,2-C_5H_3(C(Ph)NH)$_2$] (4). (i) Compound **1** (0.800 g, 0.17 mmol) was dissolved in benzene and chromatographed on an neutral alumina column with benzene elution. This afforded **4** in 92% yield.

(ii) Compound **2** (0.40 g, 0.09 mmol) was dissolved in 5 mL of ether, and methanol was added (0.17 g, 0.55 mmol). The mixture was stirred for 1 h. Addition of ether, filtration, and solvent removal afforded the white solid **4** in 89% yield. ^{1}H NMR (C_6D_6, 25 °C): δ 14.96 (1H, s), 7.30 (4H, d, $|J_{H-H}| = 7.0$ Hz), 7.01−7.07 (6H, m), 6.84 (2H, d, $|J_{H-H}| = 3.7$ Hz), 6.71 (2H, s), 6.47 (1H, t, $|J_{H-H}| = 3.7$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 69.8, 142.4, 135.1, 128.4, 128.1, 122.3, 120.1, 118.7. Anal. Calcd for $C_{19}H_{15}N_2$: C, 84.10; H, 5.57; N,10.32. Found: C, 84.01; H, 5.96; N, 10.57.

Synthesis of H[4-$Me_3SiC_5H_2$-1,2-(C(Ph)NH)$_2$] (5). This compound was prepared following methods used to prepare **4** with the use of ($Me_3SiC_5H_4$)$_2$Mg as the starting material. ^{1}H NMR (C_6D_6, 25 °C): δ 15.0 (1H, s), 7.75 (4H, d, $|J_{H-H}| = 29.4$ Hz), 7.42 (2H, s), 6.78−6.92 (6H, m), 6.56 (2H, s), 0.40 (9H, s). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 173.6, 146.1, 138.8, 135.7, 133.5, 132.9, 126.0, 122.3, 5.2. Anal. Calcd for $C_{22}H_{23}N_2Si$: C, 76.92; H, 6.75; N, 8.15. Found: C, 76.89; H, 6.70; N, 8.11.

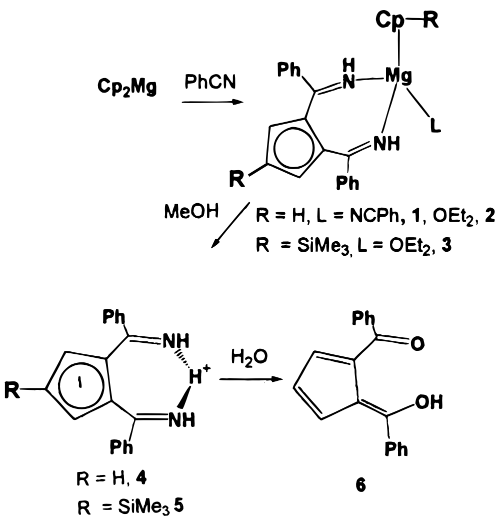
Synthesis of 1-(C(OH)Ph)-2-(O═C(Ph))C_5H_3) (6).[20] To a solution of compound **4** (0.126 g, 0.46 mmol) in THF (5 mL) was added 5 mL of 10% aqueous HCl under nitrogen. The solution was stirred for 1 h. Addition of THF was followed by separation of the organic layer, which was dried over $MgSO_4$ overnight. The mixture was filtered and the solvent removed, giving **6** in 62% yield. Spectroscopic data were in agreement with literature data. ^{1}H NMR (C_6D_6, 25 °C): δ 7.70 (4H, d, $|J_{H-H}| = 4.6$ Hz), 7.61 (4H, t, $|J_{H-H}| = 4.4$ Hz), 7.48 (2H, t, $|J_{H-H}| = 4.4$ Hz), 6.89 (2H, d, $|J_{H-H}| = 2.2$ Hz), 6.27 (1H, t, $|J_{H-H}| = 2.2$ Hz), 5.58 (1h, br s). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 171.5, 138.6, 135.9, 133.7, 131.9, 128.5, 121.1, 120.5.

Generation of (C_5H_3(1,2-C(Ph)NH)$_2$)$ZrCl_3$(THF) (7) and (1,2-C_5H_3(C(Ph)NH)$_2$)$_3$ZrCl (8). To solutions of varying amounts of **4** in benzene (5 mL) was added sodamide, and the mixture was stirred for 3 h. $ZrCl_4(THF)_2$ was added and stirring continued for an additional 10 h. NMR data revealed a mixture of species dependent on stoichiometry. Use of **4** (0.100 g, 0.367 mmol) and $ZrCl_4(THF)_2$ (0.198 g, 0.525 mmol) gave predominantly **7** in solution, whereas use of **4** (0.050 g, 0.183 mmol) and $ZrCl_4(THF)_2$ (0.198 g, 0.525 mmol) gave predominantly **8** in solution. Attempts to isolate material led to an inseparable mixture of products; nonetheless, X-ray-quality crystals of **7** and **8** were obtained from these mixtures. **7**: ^{1}H NMR (C_6D_6, 25 °C) δ 8.32 (2H,s), 7.37 (4H, d, $|J_{H-H}| = 4.5$ Hz), 7.02−7.06 (4H, m), 6.95 (2H, t, $|J_{H-H}| = 4.5$ Hz), 6.69 (2H, d, $|J_{H-H}| = 2.2$ Hz), 6.28 (1H, t, $|J_{H-H}| = 2.2$ Hz), 3.86 (4H, br m), 0.76 (4H, br m); $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ 175.9, 143.0, 140.0, 130.4, 129.6, 123.8, 119.6, 119.4, 69.2, 25.2. **8**: orange crystals, yield 76%; ^{1}H NMR (C_6D_6, 25 °C) δ 9.58 (2H, s), 7.30 (4H, d, $|J_{H-H}| = 7.4$ Hz), 6.85−7.00 (6H, m), 6.77 (2H, d, $|J_{H-H}| = 3.5$ Hz), 6.39 (1H, t, $|J_{H-H}| = 3.5$ Hz); $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ 175.3, 144.1, 138.8, 130.0, 129.6, 122.9, 120.2, 119.6.

Molecular Orbital Calculations. Extended Huckel calculations were performed and visualized employing the Personal Cache Software Package operating on a Pentium 166 computer. Initial coordinates and geometric parameters were derived from a molecular mechanics optimization of the geometry.

X-ray Data Collection and Reduction. X-ray-quality crystals of **1**, **4**, **7**, and **8** were obtained directly from the preparation as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer collecting a hemisphere of data in 1329

Scheme 1



frames with 10 s exposure times. Crystal data are summarized in Table 1. The observed extinctions were consistent with the space groups in each case. The data sets were collected (4.5° $< 2\theta <$ 50.0°). A measure of decay was obtained by recollecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package operating on a SGI Indy computer. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in the refinements.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations. The heavy-atom positions were determined using direct methods, employing the SHELXTL direct methods routines. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they were bonded, assuming a C−H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they were bonded. The hydrogen atom contributions were calculated but not refined. The final values of R, R_w, and the goodness of fit in the final cycles of the refinements are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information.

Results and Discussion

Reaction of Cp_2Mg with 4−5 equiv of benzonitrile proceeds rapidly and easily in benzene to yield an orange solution. Upon concentration of the solution and standing, orange crystals of the product **1** were obtained in 98% yield. NMR data for **1** were consistent with the incorporation of 3 equiv of benzonitrile (Scheme 1). Integration data suggested that one cyclopentadienyl group remains unaltered, while the other is 1,2-disubstituted. The ^1H NMR resonance at 6.1 ppm infer nitrile reduction to imino-NH groups. The formulation of complex **1** was unambiguously determined to be $(1,2\text{-}C_5H_3(C(Ph)NH)_2)CpMg(NCPh)$ via X-ray crystallography (Figure 1). The pseudo-tetrahedral coordination sphere about Mg in **1** is comprised of an η^5-cyclopentadienyl group, two nitrogen donors of the newly formed monoanionic 1,2-cyclopentadienyl diimine ligand, and a coordinated molecule of benzonitrile. Within the diimine anionic ligand, the cyclopentadienyl ring and the CN moieties are essentially planar. The extended π-system is consistent with C−N distances of 1.304(2) Å and C(Cp)−C(CN) distances of 1.436(2) Å. Some degree of C−N bond order reduction, as well as steric crowding, accounts for the pseudo-pyramidal geometry about N. The phenyl groups on the imino carbon are approximately orthogonal to the plane of the ligand, presumably a further consequence of steric demands.

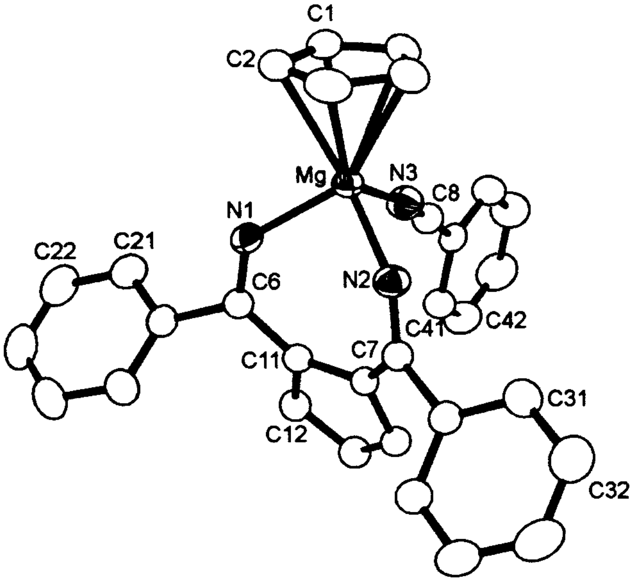


Figure 1. ORTEP drawing of **1**; 30% thermal ellipsoids are shown. Bond distances and angles are as follows: Mg−N(1) = 2.055(2) Å, Mg−N(2) = 2.046(2) Å, Mg−N(3) = 2.152(2) Å, Mg−C(1) = 2.384(2) Å, Mg−C(2) = 2.433(2) Å, Mg−C(3) = 2.483(2) Å, Mg−C(4) = 2.479(2) Å, Mg−C(5) = 2.423(2) Å, N(1)−C(6) = 1.302(2) Å, N(2)−C(7) = 1.306(2) Å, N(3)−C(8) = 1.133(3) Å; N(2)−Mg−N(1) = 94.97(7)°, N(2)−Mg−N(3) = 97.07(8)°, N(1)−Mg−N(3) = 96.25(8)°, C(6)−N(1)−Mg = 129.74(13)°, C(7)−N(2)−Mg = 130.27(13)°, C(8)−N(3)−Mg = 172.4(2)°.

In an analogous manner, the related complex $(1,2\text{-}C_5H_3(C(Ph)NH)_2)CpMg(OEt_2)$ (**2**) is readily obtained via reaction of Cp_2Mg and 2 equiv of benzonitrile in diethyl ether (Scheme 1). Demetalation of the complexes **1** and **2** and isolation of the corresponding free diimine ligands is readily accomplished via chromatography on alumina with benzene elution. Alternatively, treatment of **1** with 6 equiv of methanol in benzene solution affords **4**. This species exhibits ^1H NMR resonances, including peaks at 6.1 and 14.9 ppm, attributed to imino NH hydrogens. The lower field resonance infers N−H−N hydrogen bonding. This and the cyclopentadienyl proton resonances suggest the zwitterionic formulation $H[1,2\text{-}C_5H_3(C(Ph)NH)_2]$ for **4**. This notion was confirmed crystallographically. The molecule **4** is planar and 2-fold

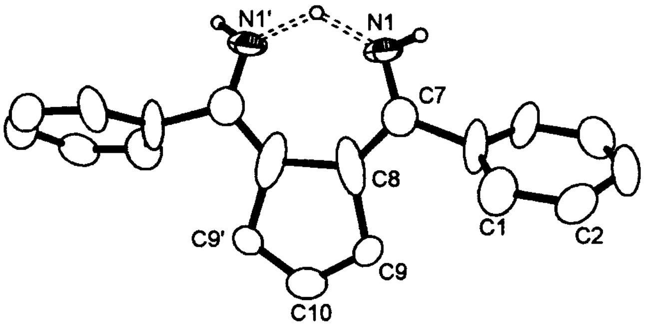
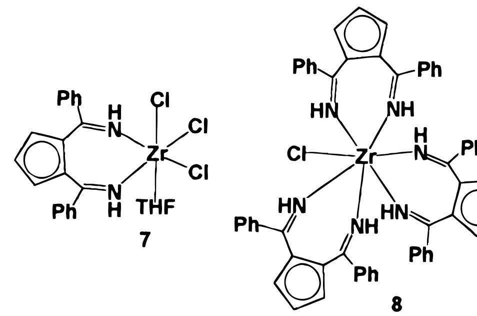


Figure 2. ORTEP drawing of **4**; 30% thermal ellipsoids are shown.

Chart 1



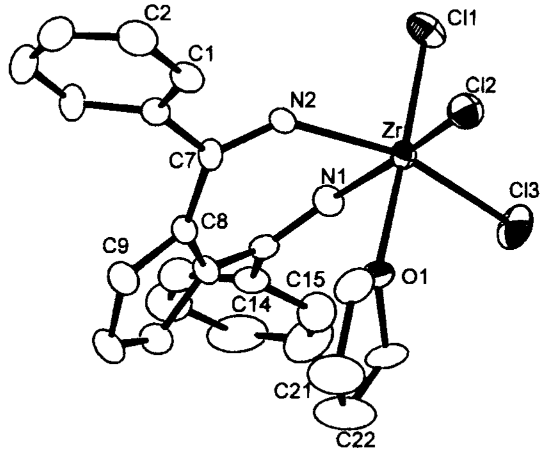


Figure 3. ORTEP drawing of **7**; 30% thermal ellipsoids are shown. Bond distances and angles are as follows: Zr(1)−Cl(2) = 2.425(3) Å, Zr(1)−Cl(3) = 2.429(3) Å, Zr(1)−Cl(5) = 2.379(3) Å, Zr(1)−O(1) = 2.237(7) Å, Zr(1)−N(1) = 2.198(9) Å, Zr(1)−N(2) = 2.182(7) Å; Cl(2)−Zr(1)−Cl(3) = 99.8(1)°, Cl(2)−Zr(1)−Cl(5) = 94.8(1)°, Cl(2)−Zr(1)−O(1) = 84.6(2)°, Cl(2)−Zr(1)−N(1) = 87.0(2)°, Cl(2)−Zr(1)−N(2) = 164.3(2)°, Cl(3)−Zr(1)−Cl(5) = 96.6(1)°, Cl(3)−Zr(1)−O(1) = 87.7(2)°, Cl(3)−Zr(1)−N(1) = 170.2(2)°, Cl(3)−Zr(1)−N(2) = 90.4(2)°, Cl(5)−Zr(1)−O(1) = 175.6(2)°, Cl(5)−Zr(1)−N(1) = 89.8(2)°, Cl(5)−Zr(1)−N(2) = 95.8(2)°, O(1)−Zr(1)−N(1) = 85.9(3)°, O(1)−Zr(1)−N(2) = 84.0(3)°, N(1)−Zr(1)−N(2) = 81.6(3)°.

symmetric in the solid state, with one hydrogen atom bridging the two nitrogen atoms (Figure 2). Metric parameters within **4** are unexceptional.

The similar reaction of $(Me_3SiC_5H_4)_2Mg$ with 2 equiv of benzonitrile in diethyl ether generates $((4\text{-}Me_3SiC_5H_2)(1,2\text{-}(C(Ph)NH)_2)(Me_3SiC_5H_4)Mg(OEt_2)$ (**3**) in situ. Subsequent methanolysis of **3** affords the species $H[4\text{-}Me_3SiC_5H_2\text{-}1,2\text{-}(C(Ph)NH)_2]$ (**5**) in 80% yield. Mechanistically, the formation of these complexes **1**−**3** is thought to be initiated via coordination of nitrile to magnesium with subsequent attack of the nitrile carbon by a cyclopentadienyl ligand and H atom migration to nitrogen. It is presumably the template effect of the Mg center that mediates or encourages 1,2-substitution, although the mechanistic details of these reactions have not been investigated as yet.

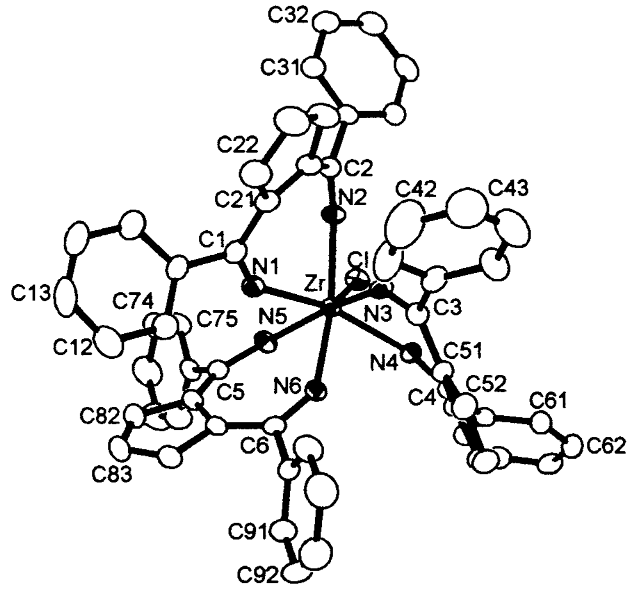


Figure 4. ORTEP drawing of **8**; 30% thermal ellipsoids are shown. Bond distances and angles are as follows: Zr−N(1) = 2.257(3) Å, Zr−N(2) = 2.218(3) Å, Zr−N(3) = 2.237(3) Å, Zr−N(4) = 2.225(3) Å, Zr−N(5) = 2.218(3) Å, Zr−N(6) = 2.235(3) Å, Zr−Cl = 2.6163(11) Å, N(1)−C(1) = 1.327(5) Å, N(2)−C(2) = 1.325(5) Å, N(3)−C(3) = 1.312(5) Å, N(4)−C(4) = 1.320(5) Å, N(5)−C(5) = 1.338(5) Å, N(6)−C(6) = 1.317(5) Å; N(2)−Zr−N(5) = 113.52(12)°, N(2)−Zr−N(4) = 118.01(12)°, N(5)−Zr−N(4) = 108.48(12)°, N(2)−Zr−N(6) = 150.70(12)°, N(5)−Zr−N(6) = 80.15(12)°, N(4)−Zr−N(6) = 78.16(12)°, N(2)−Zr−N(3) = 78.27(12)°, N(5)−Zr−N(3) = 157.42(12)°, N(4)−Zr−N(3) = 79.88(12)°, N(6)−Zr−N(3) = 81.22(12)°, N(2)−Zr−N(1) = 78.81(12)°, N(5)−Zr−N(1) = 80.51(12)°, N(4)−Zr−N(1) = 152.74(12)°, N(6)−Zr−N(1) = 78.20(12)°, N(3)−Zr−N(1) = 83.28(12)°, N(2)−Zr−Cl 74.14(9)°, N(5)−Zr−Cl = 74.92(9)°, N(4)−Zr−Cl = 75.32(9)°, N(6)−Zr−Cl = 135.15(9)°, N(3)−Zr−Cl = 127.64(9)°, N(1)−Zr−Cl = 131.74(9)°, C(1)−N(1)−Zr = 140.8(3)°, C(2)−N(2)−Zr = 143.6(3)°, C(3)−N(3)−Zr = 141.5(3)°, C(4)−N(4)−Zr = 142.3(3)°, C(5)−N(5)−Zr = 143.9(3)°, C(6)−N(6)−Zr = 142.5(3)°.

Hydrolysis of compound **4** leads to the fulvene derivative $1\text{-}(C(OH)Ph)\text{-}2\text{-}(O{=}C(Ph))C_5H_3$ (**6**)[20] (Scheme 1). This is achieved via addition of 10% aqueous HCl to a THF solution of **4** or **5** followed by typical organic extraction and drying over $MgSO_4$, filtration, and solvent removal. Compounds **4**−**6** represent rare examples of 1,2-disubstituted cyclopentadienyl derivatives. Certainly, the ease of these preparations is unprecedented, as the syntheses of related 1,2-disubstituted species are more arduous.[17,20]

Zirconium complexes of **4** were targeted in reactions of the diimine with 3 equiv of sodamide and varying stoichiometric amounts of $ZrCl_4(THF)_2$ in benzene. Monitoring these reactions via NMR spectroscopy inferred the presence of mixtures of products, presumably arising from varying degrees of ligand substitution. In the presence of 1.5 equiv of $ZrCl_4(THF)_2$, NMR data showed the preponderance of a species characterized by

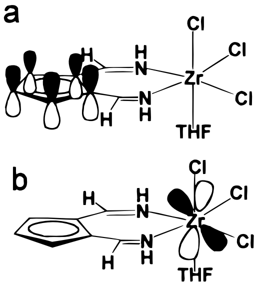


Figure 5. (a) HOMO and (b) LUMO of the model compound (1,2-$C_5H_3(C(H)NH)_2)ZrCl_3(THF)$.

a single ^1H NMR resonance at 8.32 ppm attributable to the imino NH protons, while the 1:1 integral ratio of diimine ligand and coordinated THF were consistent with the formulation of **7** as (1,2-$C_5H_3(C(Ph)NH)_2)ZrCl_3$-(THF) (**7**) (Chart 1). X-ray-quality orange crystals of **7** were separated from the mixture of solid products. Crystallographic data affirm that **7** is a pseudo-octahedral complex in which the diimine ligand binds to Zr through the N atoms (Figure 3). The chlorides form a facial array, two of which are trans to the N atoms. A coordinated molecule of THF completes the Zr coordination sphere. The structural parameters within the ligand are similar to those seen in **1**.

A second Zr species was isolable in the presence of greater than 3 equiv of the diimine ligand. Under these conditions the product **8** was predominant in solution. NMR data were characterized by a single ^1H NMR resonance at 9.57 ppm attributable to the imino NH protons. An X-ray crystallographic study unambiguously confirmed **8** to be (1,2-$C_5H_3((Ph)CNH)_2)_3)ZrCl$ (Chart 1, Figure 4). The interaction of the three anionic diimine ligands with Zr is similar to that seen in **1** and **7**, in that coordination occurs through nitrogen, forming a chelate complex. The result is a seven-coordinate Zr center in which the coordination sphere is comprised of six nitrogen atoms of the diimine ligands and a single chloride atom. The Zr−N distances in **8** range from 2.218(3) to 2.257(3) Å, slightly longer than the Zr−N distances of 2.190(9) Å seen in **7**. Also, the N−Zr−N bite angles for the three chelating diimines in **8** average 79.68(12)°, which is slightly smaller than the N−Zr−N angle of 81.6(3)° seen in **7**. These metric differences are presumably associated with the steric congestion within **8**. Each of these diimine chelates in **8** offers one nitrogen donor that forms Cl−Zr−N angles of 74.14(9)−75.32(9)° while the remaining nitrogen atoms give rise to N−Zr−Cl angles of 127.64(9)−135.15(9)°. The Zr−Cl distance of 2.6163(11) Å in **8** is dramatically longer than the typical values seen in **7** (Zr−Cl = 2.427-(3) Å), also consistent with the steric congestion of the seven-coordinate Zr center. It is noteworthy that efforts to specifically prepare the L_2ZrCl_2 complex were unsuccessful. Rather, mixtures of **7** and **8** were observed at all intermediate stoichiometries of ligand to metal. It may be that the lack of substitution on N facilitates ligand redistribution. Related monoanions which present a sterically encumbering coordination sphere are the subject of current synthetic efforts.

The 1,2-disubstituted cyclopentadienyl diimine anions are extended planar π-systems, which bind to a metal center via the nitrogen atoms. Computation of the frontier orbitals of the model (1,2-$C_5H_3(C(H)NH)_2)ZrCl_3$-(THF) by extended Huckel methods reveal that the HOMO is essentially π-orbitals centered on the cyclopentadienyl group, while the LUMO is largely a vacant metal-based d orbital (Figure 5). Thus, the bonding mode provides an avenue for formal charge separation and thus imparts electrophilic character to the zirconium. Such Lewis acidity is further exemplified by the seven-coordinate metal center in **8**.

Summary

The reactions of Cp_2Mg with benzonitrile provide a facile synthetic route to the otherwise illusive 1,2-difunctionalized cyclopentadienyl ligands. Use of these extended π-ligand systems imparts some formal charge separation to the complex and thus offers a unique approach to enhancing the electrophilic character of the metal center. The ramification of such electrophilicity on the resulting chemistry is the subject of current investigations.

Acknowledgment. Financial support from the NSERC of Canada is gratefully acknowledged.

Supporting Information Available: Crystallographic parameters, in CIF format, are available. Access information is given on any current masthead page.

OM980409L