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Cyclooctatetraene Poly(azolyl)borate Complexes of Zirconium: $[Zr(\kappa^2\text{-}L)Cl(\eta\text{-}C_8H_8)]$ ($L = H_2B(pz)_2$, $HB(pzMe_2)_3$, $H_2B(mt)_2$; pz = Pyrazolyl, mt = Methimazolyl)

Anthony F. Hill* and Matthew K. Smith

Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra, Australian Capital Territory, Australia

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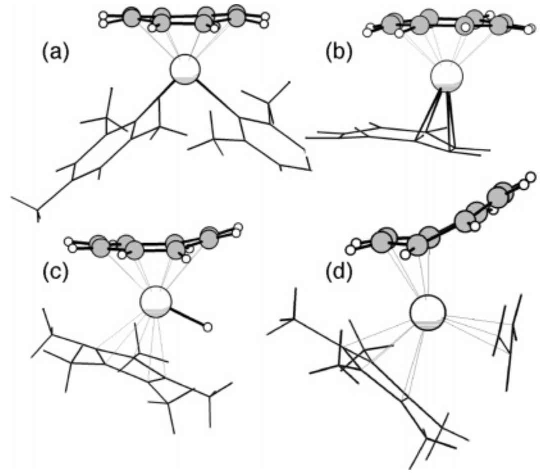
Summary: The reactions of $[ZrCl_2(thf)(\eta\text{-}C_8H_8)]$ *with* $K[H_2B(pz)_2]$, $K[HB(pzMe_2)_3]$, *and* $Na[H_2B(mt)_2]$ *(pz = pyrazolyl, mt = methimazolyl) provide the complexes* $[Zr(\kappa^2\text{-}L)Cl(\eta\text{-}C_8H_8)]$ *(*$L = H_2B(pz)_2$, $HB(pzMe_2)_3$, $H_2B(mt)_2$*). In each case the metal is electronically unsaturated (16 electrons), despite the capability, in principle, of each of the ligands "L" to increase the metal coordination number. The only product isolated so far from the corresponding reaction with* $K[H_2B(pzMe_2)_2]$ *is, however, the organometallic oxide cluster* $[Zr_4(\mu\text{-}O)_4(\mu\text{-}Cl)_2Cl_2(\eta\text{-}C_8H_8)_4]$.

Since the isolation of the first cyclooctatetraene complex by Stone,[1] this hydrocarbon has proven to be an intriguing ligand in organometallic chemistry. This exceptional versatility of C_8H_8 may be traced, in part, to variable hapticity such that it may provide, as an aromatic dianion (charged formalism), up to 10 valence electrons to a suitably receptive metal center (Chart 1). In practice, it is only metal centers with sufficiently low (ideally nil) d configurations that are capable of accepting so many valence electrons to one face of a coordination polyhedron. Thus, structurally authenticated[3] η^8 coordination to transition metals is commonly encountered in group 4,[4] is rare in group 5,[5] and is unheard of for metals from other groups. Within the chemistry of zirconium,[4] a range of hapticities has been observed, depending on the number of valence electrons provided by the remaining coligands. Thus, for exemplary zirconium complexes (Chart 1) in which the remaining coligands may contribute two, four, six, or eight electrons, the C_8H_8 hapticity progressively decreases.

Chart 1. Variations in Cyclooctatetraene Hapticity: (a) $[Zr(C_6H_2Me_3\text{-}2,4,6)_2(C_8H_8)]$;[4q] (b) $[Zr(C_8H_8)_2]$;[4p] (c) $[ZrH(C_5Me_5)(C_8H_8)]$;[4s] (d) $[Zr(C_3H_5)(C_5Me_5)(C_8H_8)]$[4s]



We have recently been concerned with the organometallic chemistry of poly(methimazolyl)borates[6] and poly(methimazolyl)boranes ("metallaboratranes")[7] and have noted a recurrent tendency for the dihydrobis(methimazolyl)borate ligand ($H_2B(mt)_2$, mt = methimazolyl) to enter into three-center, two-electron (3c−2e) B−H−M bonding with a range of metals. Within poly(pyrazolyl)borate chemistry such interactions were first encountered[8] for the complex $[Mo(\eta\text{-}C_3H_8)(CO)_2\{H_2B(pzMe_2)_2\}]$ (pz = pyrazolyl), discovered by Trofimenko.[9] We are accumulating a body of circumstantial evidence which suggests that the $H_2B(mt)_2$ ligand shows a greater propensity for such interactions than do the more familiar $H_2B(pz)_2$ or $H_2B(pzMe_2)_2$ ligands but sought a means of assessing this. Given the apparent ability of cyclooctatetraene to act as a "reporter ligand" for the electronic requirements of a metal center, we have now turned our attention to the synthesis of poly(azolyl)borate complexes of the "$Zr(C_8H_8)$" fragment. The study has

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* To whom correspondence should be addressed. E-mail: a.hill@anu.edu.au.

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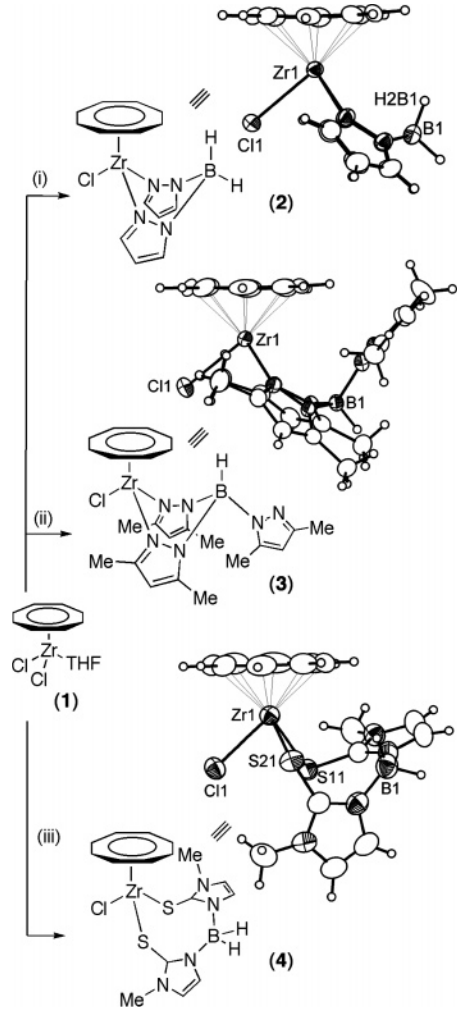
provided the first zirconium complex of a dihydrobis(methimazolyl)borate ligand. Although this class of ligand is more commonly associated with later "soft" transition-metal centers,[10−14] a small number of reports of poly(methimazolyl)borate complexes of selected early transition metals have appeared.[15] Of particular relevance is the very recent report by Parkin of the first zirconium complex bearing a HB(mt)$_3$ ligand: viz., [ZrCl$_2$(η-C$_5$H$_5$){HB(mt)$_3$}].[16]

Scheme 1. Cyclooctatetraene Poly(azolyl)borato Complexes of Zirconium: (a) K[H$_2$B(pz)$_2$]; (b) K[HB(pzMe$_2$)$_3$]; (c) Na[H$_2$B(mt)$_2$]



Though not isolated therein, the formation of Wilke's complex [ZrCl$_2$(thf)(η-C$_8$H$_8$)] (**1**)[17] is implicit in Spencer's one-pot synthesis of [ZrCl(C$_5$Me$_5$)(η-C$_8$H$_8$)].[4s] Although **1** prepared in this manner is somewhat difficult to completely separate from residual traces of KCl, this does not interfere with the subsequent chemistry. Reger has reported that the reaction of [ZrCl$_3$(dme)(η-C$_5$H$_5$)] with K[H$_2$B(pz)$_2$] provides the complex [ZrCl$_2$(η-C$_5$H$_5$){H$_2$B(pz)$_2$}], which features a 3c−2e B−H−Zr interaction (Zr−H = 2.273 Å, Zr−B = 2.958 Å).[18] We find that the reaction of **1** with Na[H$_2$B(pz)$_2$] provides an orange complex with the composition [ZrCl{H$_2$B(pz)$_2$}(C$_8$H$_8$)] (**2**) (Scheme 1), the connectivity of which does not, however, follow unequivocally from spectroscopic data alone.[3,19] Thus, the appearance

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(19) **2**: a suspension of [ZrCl$_2$(thf)(η-C$_8$H$_8$) (0.100 g, 0.30 mmol) in thf (10 mL) was cooled (dry ice/propanone) and treated with K[H$_2$B(pz)$_2$] (0.056 g, 0.30 mmol), and then this mixture was warmed to room temperature and stirred for 12 h. The orange suspension was freed of volatiles and the residue extracted with CH$_2$Cl$_2$. The combined filtered extracts were concentrated and cooled to −20 °C to provide orange crystals. Yield: 0.066 g (58%). NMR (CD$_2$Cl$_2$, 25 °C): ^{1}H, δ_H 3.5 (s v br , ∼2H, BH$_2$, $^1J_{BH}$ = 210 Hz), 6.09 (dd, 2H, H^4(pz), $^3J_{HH}$ = 2.3 Hz), 6.99 (s, 8H, C$_8$H$_8$), 7.37, 7.65 (d × 2, 2H × 2, H^{3,5}(pz), $^3J_{HH}$ = 2.1 Hz); ^{13}C{^{1}H}, δ_C 100.0 (C$_8$H$_8$), 104.2 (C^4(pz)), 135.6, 141.4 (C^{3,5}(pz)). Anal. Found: C, 44.03; H, 4.58; N, 14.52. Calcd for $C_{14}H_{16}BClN_4Zr$: C, 44.51; H, 4.27; N, 14.83%. Crystal data for **2**: $C_{14}H_{16}BClN_4Zr$, M_w = 377.79, monoclinic, $P2_1/c$, a = 11.512(2) Å, b = 9.5680(19) Å, c = 14.109(3) Å, β = 97.74(3)°, V = 1539.9(5) Å^3, Z = 4, D_x = 1.630 Mg m^{-3}, μ(Mo Kα) = 0.884 mm^{-1}, T = 200(2) K, 3534 independent reflections. F^2 refinement, R = 0.032, R_w = 0.078 for 2830 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 55°), 197 parameters (CCDC 285124).

of a single C_8H_8 resonance in the ^1H NMR spectrum (δ_H 6.99) does not necessarily signify η^8 coordination. In contrast to $[ZrCl_2\{H_2B(pz)_2\}(\eta\text{-}C_5H_5)]$, which is unstable in solution,[15] **2** appears robust under ambient, strictly anaerobic conditions. The ground-state structure of **2** was established by a crystallographic study, the results of which are summarized in Scheme 1 and Figure S1 (Supporting Information), from which it is apparent that, despite the 16-electron zirconium center being coordinatively unsaturated, the borohydride group remains beyond what would be considered an appropriate distance for invoking B−H−Zr 3c−2e bonding (Zr1−H2B1 = 3.47(7) Å, Zr1−B1 = 3.56(6) Å). In the absence of such an interaction, the $Zr(pz)_2B$ unit adopts a shallow boat conformation.

The reaction of the potentially tridentate proligand salt $K[HB(pzMe_2)_3]$ also proceeded by simple halide metathesis to provide $[ZrCl\{HB(pzMe_2)_3\}(C_8H_8)]$ (**3**),[20] the ^1H NMR spectrum of which indicates the presence of two $pzMe_2$ environments (in a 2:1 ratio) in addition to a single C_8H_8 resonance (δ_H 6.57). These data would be consistent with either a tridentate $HB(pzMe_2)_3$ ligand straddling a molecular plane of symmetry or, alternatively, bidentate (κ^2N,N′) chelation. Bidentate coordination of tris(pyrazolyl)borates to metal centers with less than a d^8 configuration is uncommon,[8] though it is occasionally encountered.[21] The molecular geometry of **3** adopted in the solid state is depicted in Scheme 1 and Figure S2 (Supporting Information), which reveals that in fact the $HB(pzMe_2)_3$ ligand does indeed adopt a bidentate mode of coordination that leaves one pendant $pzMe_2$ donor uncoordinated and the zirconium center coordinatively unsaturated. The orientation of the three pyrazolyl groups allows (or results from) weak interligand hydrogen-bonding interactions between (a) the chloride ligand and two pyrazolyl methyl substituents (H16C⋯Cl1 = 2.65(4) Å, H26A⋯Cl1 = 2.70(4) Å) and (b) C−H⋯π($pzMe_2$) and the third (pendant) pyrazolyl ring drawing it toward the C_8H_8 ring.

The reaction of **1** with $Na[H_2B(mt)_2]$ proceeded similarly to that with $Na[H_2B(pz)_2]$ to provide the yellow-orange complex $[ZrCl\{H_2B(mt)_2\}(C_8H_8)]$ (**4**) in moderate yield.[22] One methimazolyl environment is indicated by the ^1H NMR data, which again also include only a single resonance due to the C_8H_8 ligand (δ_H 6.83). Although **4** is the first zirconium complex bearing the $H_2B(mt)_2$ ligand, we have recently isolated the titanium complex $[Ti({=}NCMe_3)\{H_2B(mt)_2\}_2]$, in which the two $H_2B(mt)_2$ ligands adopt distinct κ^2*S,S′* and κ^3*H,S,S′* coordination modes.[15a] Accordingly, tridentate κ^3*H,S,S′* coordination of the $H_2B(mt)_2$ ligand might also appear feasible for **4**; however, this proves not to be the case. The molecular structure of **4** (Scheme 1, Figure S3 (Supporting Information)) adopts, as do **2** and **3**, a three-legged piano-stool arrangement that leaves the borohydride group distal from zirconium (Zr1⋯H2B1 = 3.78(7) Å, Zr1⋯B1 = 4.20(8) Å). In contrast to the chelates in **2** and **3**, which approach local C_s-symmetric $B(pz)_2Zr$ boat geometries, the chelate in **4** appears to actually undergo quite substantial twisting to avoid interaction between zirconium and the BH_2 group, in contrast to the symmetric sigmoidal κ^2*S,S′* chelate in $[Ti({=}N^tBu)\{H_2B(mt)_2\}_2]$.[15a] A corollary of this twisting is that the molecule is chiral (racemic $P\bar{1}$ crystal), although ^1H and ^{13}C NMR data indicate that, in solution, inversion is rapid.

In each of the molecules **2**−**4**, a three-legged piano-stool geometry is adopted, leaving the zirconium center electronically unsaturated (16 electrons) despite the presence of potential, but pendant, donors (B−H or N). This is in stark contrast to the complex $[ZrH(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)]$,[4s] which accommodates the bulky C_5Me_5 ligand in a η^5 manner. This reluctance on the part of complexes **2**−**4** to attain electronic saturation by adopting a four-legged piano-stool geometry may perhaps be traced to the effect of cyclooctatetraene coordination upon the relative energies of the zirconium orbitals. A geometric consequence of $\eta^8\text{-}C_8H_8$ coordination is that the ring centroid is drawn close to the metal, affording more effective orbital overlap. This, coupled with the increase in energy and occupation of δ-symmetry orbitals of cyclo-C_nR_n ligands as "*n*" increases, means that δ bonding with the metal becomes significant. Thus, for a coordinate system where *z* is the unique axis, the d_{xy} and $d_{x^2-y^2}$ ($4e_2$) orbitals are strongly destabilized relative to the remaining three orbitals d_{z^2}, d_{xz}, and d_{yz} ($6a_1$, $5e_1$) available for bonding to *three* coligands. For the hypothetical "$[Zr(\eta^8\text{-}C_8H_8)]^{2+}$" fragment, a substantial energy gap (1.76 eV) has been estimated[23] between the $5e_1$ and $4e_2$ pairs of orbitals. Since it is the latter pair that would constitute the LUMOs of a d^0-$[ZrL_3(\eta^8\text{-}C_8H_8)]$ complex, it appears that there is little to be gained in employing one of these for bonding to either the pendant $pzMe_2$ group of **3** or the borohydride groups in **2** and **4**. Neither is the loss of δ bonding that would accompany reduced C_8H_8 hapticity apparently compensated for by increased denticity on the part of $H_2B(pz)_2$, $HB(pzMe_2)_3$, or $H_2B(mt)_2$ ligands. This again contrasts with the ground-state structure of $[Zr(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_8H_8)]$ (Chart 1d), wherein the allyl and cyclopentadienyl ligands adopt their maximum hapticity, accommodated by C_8H_8 ring slippage.[4s]

Finally, it should be noted that an obvious omission from the above set of compounds would be the derivative $[ZrCl\{H_2B(pzMe_2)_2\}(C_8H_8)]$, given the pivotal role that the $H_2B(pzMe_2)_2$ has played in the discovery of such B−H−M

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[20] **3**: a mixture of $[ZrCl_2(thf)(\eta\text{-}C_8H_8)]$ (0.150 g, 0.45 mmol) and $K[HB(pzMe_2\text{-}3,5)_3]$ (0.135 g, 0.40 mmol) in thf (5 mL) was stirred for 12 h. The solvent was removed, the residue extracted with CH_2Cl_2, and the extract filtered, concentrated, and cooled (−20 °C) to provide orange crystals of **3**. Yield: 0.097 g (41%). NMR (CD_2Cl_2, 25 °C): δ_H 1.49 (3 H), 2.29 (6 H), 2.34 (3 H), 2.66 (6 H) (s × 4, $pzCH_3$), 5.85 (2 H), 6.00 (1 H) (s × 2, H^4(pz)), 6.57 (s, 8H, C_8H_8); $^{13}C\{^1H\}$, δ_C 11.00 (1 C), 13.72 (1 C), 14.01 (2 C), 16.29 (2 C) ($pzCH_3$), 99.58 (C_8H_8), 107.7 (C^4(pz)), 143.3 (1 C), 147.9 (2 C), 148.7 (1 C), 151.4 (2 C) ($C^{3,5}$(pz)). Anal. Found: C, 52.01; H, 5.94; N, 15.45. Calcd for $C_{23}H_{30}BClN_6Zr$: C, 52.32; H, 5.73; N, 15.92. Crystal data for **3**: $C_{23}H_{30}BClN_6Zr$, $M_w = 528.01$, monoclinic, $P2_1/c$, $a = 11.077(2)$ Å, $b = 15.937(3)$ Å, $c = 27.729(6)$ Å, $\beta = 99.38(3)°$, $V = 4829.6(17)$ Å^3, $Z = 8$, $D_x = 1.452$ Mg m^{-3}, μ(Mo Kα) = 0.589 mm^{-1}, $T = 200(2)$ K, 8507 independent reflections, F^2 refinement, $R = 0.042$, $R_w = 0.093$ for 6468 reflections ($I > 2\sigma(I)$, $2\theta_{max} = 50°$), 593 parameters (CCDC 285125).

[21] Illustrative examples include: (a) Connelly, N. C.; Emslie, D. J. H.; Metz, B.; Orpen, A. G.; Quayle, M. J. *J. Chem. Soc., Chem. Commun.* **1996**, 2289. (b) Bohanna, C.; Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Martinéz, M. P. *Organometallics* **1997**, *16*, 4464. (c) Burns, I. D.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 1552. (d) Paulo, A.; Domingos, A.; Santos, I. *Inorg. Chem.* **1996**, *35*, 1798.

[22] **4**: a suspension of $[ZrCl_2(thf)(\eta\text{-}C_8H_8)]$ (0.200 g, 0.59 mmol) in thf (15 mL) was cooled (dry ice/propanone) and treated with $Na[H_2B(mt)_2]$ (0.153 g, 0.58 mmol) and stirred at that temperature for 30 min. The mixture was then warmed to room temperature and stirred for 12 h to provide a red solution and white precipitate, which was removed by filtration. The filtrate was concentrated in vacuo and then diluted with hexane and cooled (−20 °C) to provide orange-red crystals of **4**•2thf (by ^1H NMR). Yield: 0.19 g (72%). NMR (CD_2Cl_2, 25 °C): ^1H, δ_H 3.54 (s, 6H, NCH_3), 6.73, 6.81 (d × 2, 2H × 2, NCHCHN, $^3J_{HH} = 2.1$ Hz), 6.83 (s, 8H, C_8H_8); $^{13}C\{^1H\}$, δ_C 35.1, 36.0 (NCH_3), 98.9 (C_8H_8), 119.6, 124.0 (NCHCHN), 154.0 (CS). Satisfactory elemental microanalytical data could not be obtained, due to partial desolvation. Crystals suitable for diffractometry were obtained from a cooled saturated thf solution as a bis(thf) solvate. Crystal data for **4**•2thf: $C_{16}H_{20}BClN_4S_2Zr.(C_4H_8O)_2$, $M_w = 614.17$, triclinic, $P\bar{1}$ (No. 2), $a = 10.126(2)$ Å, $b = 11.608(2)$ Å, $c = 13.690(3)$ Å, $\alpha = 75.95(3)°$, $\beta = 72.01(3)°$, $\gamma = 69.47(3)°$, $V = 1416.8(56)$ Å^3, $Z = 2$, $D_x = 1.440$ Mg m^{-3}, μ(Mo Kα) = 0.658 mm^{-1}, $T = 200(2)$ K, 6528 independent reflections. F^2 refinement, $R = 0.050$, $R_w = 0.135$ for 5449 reflections ($I > 2\sigma(I)$, $2\theta_{max} = 55°$), 324 parameters (CCDC 285126).

[23] Belanzoni, P.; Rosi, M.; Sgamellotti, A. *Chem. Phys. Lett.* **2001**, *344*, 536.

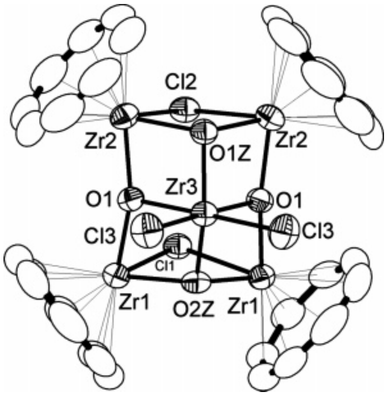

Figure 1. Molecular geometry of **5** in a crystal of **5**·MeCN·CH_2Cl_2 (40% displacement ellipsoids, Hydrogen atoms are omitted.

interactions.[9] We have not yet been successful in obtaining this compound; however, from the reaction of **1** with K[$H_2B(pzMe_2)_2$] we have isolated, in trace amounts, crystals of a novel borate-free cluster, **5**, derived presumably from adventitious moisture. Unfortunately, despite attempts at the controlled hydrolysis of **1**, we have not been able to obtain **5** in sufficient quantity for spectroscopic or elemental analysis. However, given the novelty and aesthetic appeal, we include herein the results of a crystallographic study, which are summarized in Figure 1.[24] The cluster may be most simply viewed as a $[ZrCl_2]^{2+}$ adduct of the tetrameric dianion $[Zr_4(\mu\text{-}O)_4(\mu\text{-}Cl)_2(C_8H_8)]^{2-}$ or, alternatively, as a cyclooctatetraenediyl-stabilized $[Zr_5O_4Cl_4]^{8+}$ cluster. The cluster has two distinct types of μ_3-oxo ligands: (i) the first (O1) has an approximate T-shaped geometry (angles at O1 157.55, 100.61° × 2; sum of angles 358.8°) and lies in the plane of the three zirconium atoms to which it binds; (ii) the second (O1Z, O2Z) adopts a flattened-pyramidal geometry with more similar Zr−O−Zr angles (117.99, 102.93° × 2, sum of angles 323.9°). While there exist copious structural data for organometallic oxide clusters of the form $[(\eta^n\text{-}C_nR_n)_xM_x(O)_y]^z$ ($x > 2$) with cyclopentadienyl ligands ($n = 5$), including examples based on zirconium,[25] there is only one structurally characterized cycloheptatrienyl example, the hydroxocubane $[Mo_4(\mu\text{-}OH)_4(C_7H_7)_4][Mo_2(\mu\text{-}Cl)_2(\mu\text{-}OH)(\eta\text{-}C_7H_7)_2]$,[26] and **5** represents the first such cyclooctatetraene derivative ($n = 8$). While the synthesis of **5** remains frustratingly irreproducible, its isolation and structural characterization do point to a potentially diverse new class of compounds for study.

To conclude, despite an increasingly recognized propensity for κ^3H,S,S' coordination by the $H_2B(mt)_2$ ligand and precedent for B−H−Zr bonding being provided by Reger's complex $[ZrCl_2\{H_2B(pz)_2\}(\eta\text{-}C_5H_5)]$,[17] in the present system η^8-C_8H_8 coordination is retained in preference to the formation of 3c−2e B−H−Zr associations or, indeed, tridentate coordination of the $HB(pzMe_2)_3$ ligand. Nevertheless, the isolation of **4** establishes, for the first time, the viability of bis(methimazolyl)borate ligands in organozirconium chemistry.

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Supporting Information Available: CIF files giving full details of the crystal structure determinations of **2** (CCDC 285124), **3** (CCDC 285125), **4** (CCDC 285126), and **5** (CCDC 645677) and figures giving the structures of **2**−**4**, along with selected bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] **5**: K[$H_2B(pzMe_2)_2$] (0.113 g, 0.50 mmol) and **1** (0.200 g, 0.59 mmol) were stirred in thf (15 mL) for 12 h, and the mixture was then freed of volatiles. The residue was extracted with CH_2Cl_2 (20 mL) and the extract filtered and cooled to afford a small number of red crystals, which were isolated by decantation, but in insufficient quantity to obtain spectroscopic data. Crystal data for $C_{37}H_{38}Cl_6O_6Zr_5$, $M_w = 1247.48$, monoclinic, *Cmc*2₁ (No. 36), $a = 17.415(4)$ Å, $b = 19.118(4)$ Å, $c = 13.417(3)$ Å, $V = 4467.1(2)$ Å^3, $Z = 8$, $D_x = 1.855$ Mg m^{-3}, μ(Mo Kα) = 1.528 mm^{-1}, $T = 173(2)$ K, 5071 independent reflections. F^2 refinement, $R = 0.058$, $R_w = 0.160$ for 4273 reflections ($I > 2\sigma(I)$, $2\theta_{max} = 55°$), 263 parameters (CCDC 645677).

[25] (a) Bai, G.; Roesky, H. W.; Lobinger, P.; Noltmeyer, M.; Schmidt, H.-G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2156. (b) Bai, G.; Ma, Q.; Roesky, H. W.; Vidovic, D.; Herbst-Irmer, R. *Chem. Commun.* **2003**, 898. (c) Bai, G.; Roesky, H. W.; Li, J.; Labahn, T.; Cimpoesu, F.; Magull, J. *Organometallics* **2003**, *22*, 3034. (d) Babcock, L. M.; Day, V. W.; Klemperer, W. G. *Chem. Commun.* **1988**, 519. (e) Babcock, L. M.; Day, V. W.; Klemperer, W. G. *Inorg. Chem.* **1989**, *28*, 806. (f) Hidalgo, G.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *Chem. Commun.* **1990**, 1118.

[26] Couldwell, C.; Prout, K. *Acta Crystallogr., Sect. B.: Struct. Crystallogr. Cryst. Chem.* **1978**, *34*, 2439.