Organometallics **2007,** *26,* 3516−3523

Zinc, Cadmium, and Mercury Metallocenes Incorporating 1,2-Diaza-3,5-diborolyl Ligands

Hanh V. Ly,[†] Taryn D. Forster,[†] Masood Parvez,[†] Robert McDonald,[‡] and Roland Roesler*,[†]

Departments of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4, and University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received March 9, 2007

Sandwich compounds incorporating 1,2-diaza-3,5-diborolidine ligands have been prepared by metathesis reactions between zinc, cadmium, and mercury dihalides and M[cyclo-MeC(BR)$_2$(N*i*Pr)$_2$] (M = Li, K; R = Me, Ph). The metallocenes M[cyclo-MeC(BR)$_2$(N*i*Pr)$_2$)]$_2$ (M = Zn, R = Me (**2a**), Ph (**2b**); M = Cd, R = Me (**3a**), Ph (**3b**); M = Hg, R = Me (**4a**)) have been isolated and characterized by multinuclear NMR and mass spectrometry. The molecular structures of complexes **2a**,**b**, **3a**·BrLi(THF)$_3$, **3b**, and **4a** were determined by single-crystal X-ray diffraction and displayed strong similarities to the structures of their cyclopentadienyl analogues. All molecules are monomeric in the solid state, containing nearly parallel ligands featuring an η^3 coordination mode in **2a** and η^1 coordination modes in the remaining complexes. Spectroscopic evidence indicates that the solid-state structure is maintained in solution and that Lewis basic solvents have the ability to coordinate reversibly to the metal centers. For comparison, the σ-bonded analogues [cyclo-MeC(BR)$_2$(N*i*Pr)$_2$]SiCl$_3$ (R = Me (**5a**), Ph (**5b**)) were prepared, and the structure of **5b** was determined using single-crystal X-ray diffractometry.

Introduction

Cyclopentadienyl and its derivatives form a versatile and extensively investigated class of ligands that has played a key role in organometallic chemistry.[1] Cyclopentadienyl complexes, known as sandwich compounds or metallocenes, have found numerous applications as olefin polymerization catalysts[2] and materials with special properties.[3] In comparison to the other metals, only few metallocenes of the electron-rich group 12 elements have been reported. The first structurally characterized sandwich complex of zinc, Cp$_2$Zn, displays a polymeric structure with η^1- and η^2-coordinated ligands.[4a] Five other base-free zincocenes featuring asymmetric structures with η^1:η^5-bonded cyclopentadienyls are known,[4] and also tetrahydrofuran and N-heterocyclic carbene (NHC) adducts of Cp*$_2$Zn and difluorenylzinc, respectively, have been described.[5] Even fewer cyclopentadienyl derivatives of the heavier group 12 metals, cadmium and mercury, have been reported. The crystal structures for three cadmium sandwich complexes containing Lewis bases coordinated to the metal have been reported: Cp$_2$CdPy$_2$,[6a,b] Cp$_2$Cd(TMEDA), and Cp$_2$Cd(PMDETA).[6d] The structures of the first two base-free cadmocenes, (tBu$_3$C$_5$H$_2$)$_2$Cd and (iPr$_4$C$_5$H)$_2$Cd,[6e] were recently reported, and also a dimeric half-sandwich complex of cadmium, [Cp*CdN(SiMe$_3$)$_2$]$_2$,[6c] was structurally characterized. Three sandwich compounds of mercury have been crystallographically characterized, and they all exhibit η^1 coordination modes: Cp$_2$Hg,[7b] (tBu$_3$C$_5$H$_2$)$_2$Hg,[7d] and [(tBuMe$_2$Si)C$_5$Me$_4$]$_2$Hg.[7e] The structures of η^1-bonded mercury half-sandwiches have also been determined: (Cl$_5$C$_5$)HgC$_6$H$_5$,[7a] Cp*HgCl,[7c] and [(tBuMe$_2$Si)C$_5$Me$_4$]HgCl.[7e] Dizincocenes, [(η^5-C$_5$Me$_4$R)$_2$Zn$_2$], were recently isolated, and their structures were subsequently the subject of theoretical calculations.[8] Aside from their fundamental impor-

---

* To whom correspondence should be addressed. E-mail: roesler@ucalgary.ca.

[†] University of Calgary.

[‡] University of Alberta.

(1) (a) Togni, A.; Halterman, R. L. *Metallocenes*; Wiley-VCH: Weinheim, Germany, 1998; Vols. I and II. (b) Long, N. J. *Metallocenes: An Introduction to Sandwich Complexes*; Blackwell Science: London, 1998. (c) Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969.

(2) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587. (c) Patil, A. O.; Hlatky, G. G. *Beyond Metallocenes: Next-Generation Polymerization Catalysts*; American Chemical Society: Washington, DC, 2003.

(3) (a) Rao, C. N. R.; Govindaraj, A. *Acc. Chem. Res.* **2002**, *35*, 998. (b) Wong, X.-S.; Arsenault, A.; Ozin, G. A.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 12686. (c) Wong, X.-S.; Winnik, M. A.; Manners, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 3703.

(4) (a) Budzelaar, P. H. M.; Boersma, J.; van der Kerk, G. J. M.; Spek, A. L.; Duisenberg, A. J. M. *J. Organomet. Chem.* **1985**, *281*, 123. (b) Fischer, B.; Wijkens, P.; Boersma, J.; van Koten, G.; Smeets, W. J. J.; Spek, A. L.; Budzelaar, P. H. M. *J. Organomet. Chem.* **1989**, *376*, 223. (c) Burkey, D. J.; Hanusa, T. P. *J. Organomet. Chem.* **1996**, *512*, 165. (d) Fernández, R.; Resa, I.; del Río, D.; Carmona, E. *Organometallics* **2003**, *22*, 381.

(5) (a) Fischer, B.; Boersma, J.; van Koten, G.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1989**, *8*, 667. (b) Arduengo, A. J., III; Davidson, F.; Krafczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, *17*, 3375.

(6) (a) Fischer, B.; van Mier, G. P. M.; Boersma, J.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1987**, *322*, C37. (b) Smeets, W. J. J.; Spek, A. L.; Fischer, B.; van Mier, G. P. M.; Boersma, J. *Acta Crystallogr.* **1987**, *C43*, 893. (c) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1991**, *10*, 3781. (d) Barr, D.; Edwards, A. J.; Raithby, P. R.; Rennie, M.-A.; Verhorevoort, K. L.; Wright, D. S. *J. Organomet. Chem.* **1995**, *493*, 175. (e) Bentz, D.; Wolmershäuser, G.; Sitzmann, H. *Organometallics* **2006**, *25*, 3175.

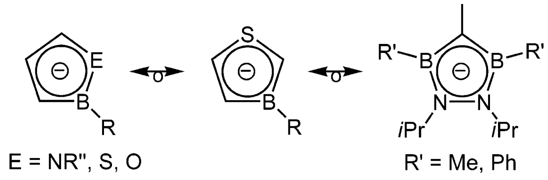
(7) (a) Davies, A. G.; Goddard, J. P.; Hursthouse, M. B.; Walker, N. P. C. *J. Chem. Soc., Dalton Trans.* **1985**, 471. (b) Fischer, B.; van Mier, G. P. M.; Boersma, J.; van Koten, G.; Smeets, W. J. J.; Spek, A. L. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 259. (c) Lorberth, J.; Berlitz, T. F.; Massa, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 611. (d) Sitzmann, H.; Wolmershäuser, G. *Z. Anorg. Allg. Chem.* **1995**, *621*, 109. (e) Hitchcock, P. B.; Keates, J. M.; Lawless, G. A. *J. Am. Chem. Soc.* **1998**, *120*, 599.

(8) (a) Resa, I.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. *Science* **2004**, *305*, 1136. (b) del Río, D.; Galindo, A.; Resa, I.; Carmona, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 1244. (c) Xie, Y.; Schaefer, H. F., III; King, R. B. *J. Am. Chem. Soc.* **2005**, *127*, 2818. (d) Grirrane, A.; Resa, I.; Rodriguez, A.; Carmona, E.; Alvarez, E.; Gutierrez-Puebla, E.; Monge, A.; Galindo, A.; del Río, D.; Andersen, R. A. *J. Am. Chem. Soc.* **2007**, *129*, 693. (e) Alvarez, E.; Grirrane, A.; Resa, I.; del Río, D.; Rodríguez, A.; Carmona, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 1296.

10.1021/om070230n CCC: $37.00

tance, group 12 metallocenes have shown potential as molecular precursors for semiconducting films.[6c,d] To our knowledge, no sandwich compounds of the group 12 metals incorporating heterocyclic cyclopentadienyl analogues have been reported.

In the search for new ancillary ligands, a series of boron-containing five-membered cyclopentadienyl analogues have been isolated through the formal substitution of cyclopentadienyl ring carbon atoms with isolobal main-group fragments. The 1,2-oxa-, thia-, and azaborolidines **A** were obtained by the replacement of two adjacent ring carbons with boron and oxygen,[9k] sulfur,[9g] or nitrogen,[9a−c,f,h−j,l] respectively, and have been coordinated to transition metals. Complexes containing the 1,3-thiaborolide ligand **B** have been described as well.[9d,e] Some of the transition-metal complexes containing these heterocyclic ligands have been investigated as catalysts.[9e,l] Continuing our investigations of boron-based heterocyclic cyclopentadienyl analogues of type **C**,[10] we report herein the synthesis and structural characterization of zinc, cadmium, and mercury sandwich complexes incorporating 1,2-diaza-3,5-diborolyl ligands. A detailed structural discussion of a recently communicated zincocene from this family, **2a**,[10a] is also presented.

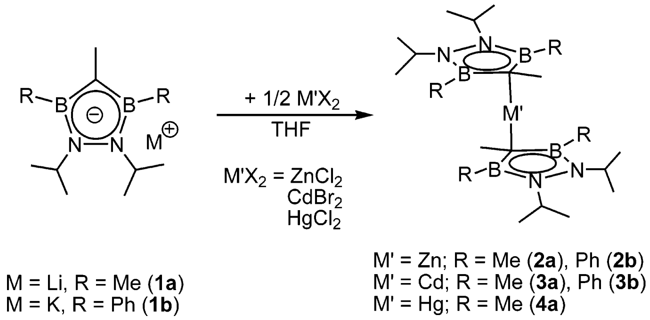


A **B** **C**

Results and Discussion

The syntheses of the ligands and their alkali-metal salts (1,2-diisopropyl-3,5-dimethyl-1,2-diaza-3,5-diborolyl)lithium (**1a**) and (1,2-diisopropyl-3,5-diphenyl-1,2-diaza-3,5-diborolyl)potassium (**1b**) have been previously described.[10] The reactions of these salts with the appropriate group 12 metal dihalides in THF produced the sandwich complexes **2**−**4** (Scheme 1).

Scheme 1



Complexes **2**−**4** were isolated as air- and moisture-sensitive colorless solids with good solubility in organic solvents. Unlike the case for the alkali-metal salts **1a**,**b**, their ^{1}H and ^{13}C{^{1}H} NMR spectra exhibit two resonances corresponding to diastereotopic methyl groups on the isopropyl substituents, indicating that the two faces of the ligand are not equivalent and, therefore, the sandwich structure is retained in solution. The presence of ^{113}Cd satellites in the ^{1}H and ^{13}C NMR spectra of **3a**,**b** and ^{199}Hg satellites in the ^{1}H and ^{13}C NMR spectra of **4a** for the singlet resonances corresponding to the methyl substituents on the ring carbon and boron ($^{3}J_{\mathrm{CdH}} = 59$ Hz, $^{4}J_{\mathrm{CdH}} = 8$ Hz, $^{2}J_{\mathrm{CdC}} = 42$ Hz, $^{3}J_{\mathrm{HgH}} = 143$ Hz, $^{4}J_{\mathrm{HgH}} = 20$ Hz, $^{2}J_{\mathrm{HgC}} = 65$ Hz) confirms that no ligand dissociation occurs in solution. A broad signal is observed for the ring carbon in the ^{13}C NMR spectra of complexes **2**−**4** between δ 69 and 78 ppm. This represents a 20 ppm upfield shift with respect to the corresponding alkali-metal salts, indicating an increased covalent character of the metal−ligand interaction in the former compounds. All complexes display only one broad signal in the ^{11}B NMR spectrum, with a chemical shift situated in a narrow δ range of 37−41 ppm, which is typical also for the alkali-metal salts of these ligands. There is little difference between the ^{1}H, ^{13}C, and ^{11}B NMR spectra recorded in C_6D_6 and those recorded in THF-d_8. However, the ^{113}Cd{^{1}H} NMR spectra of **3a**,**b** exhibit resonances at δ 256.2 and 286.1 ppm, respectively, when recorded in C_6D_6, while the resonance for **3a** appears at 397.9 ppm when recorded in THF-d_8. The large difference is likely due to the formation of **3a**·THF and **3a**·2THF adducts in the coordinating solvent, similar to adducts containing substituted cyclopentadienyls that have been crystallographically characterized for zinc[5] and cadmium.[6a,b,d] All metallocenes described herein have been prepared in a THF solution and isolated free of solvent after workup, which implies that their THF adducts are weakly bonded. The ^{199}Hg NMR spectrum of **4a** in C_6D_6 displays a single resonance at δ −2063.3 ppm. To our knowledge, no Cd NMR data are available in the literature for cadmium cyclopentadienyl compounds, and only one ^{199}Hg NMR resonance has been reported for a mercury metallocene, at δ −1112 ppm.[7e] The mass spectra of all complexes described here feature signals that were assigned to the molecular ions $[ML_2]^+$, as well as to the fragments $[ML]^+$ and $[L]^+$. No signals corresponding to CH_3CN adducts of the metallocenes were observed in the electrospray mass spectra of **2b** and **3b**, which were recorded using acetonitrile solutions.

Crystal structures have been determined for **2a**[10] as well as **2b**, **3b**, **3a**·BrLi(THF)$_3$, and **4a** (Table 1), confirming the sandwich structures predicted on the basis of the multinuclear NMR and mass spectra. The metric parameters of the CB_2N_2 ring display little variation between all structures (Table 2), showing a minor dependence on the organic substituent on boron (methyl or phenyl) or the coordinated metal. The planarity of the rings is slightly better for the phenyl derivatives **2b** and **3b** than for the methyl derivatives **2a**, **3a**·BrLi(THF)$_3$, and **4a**, with the sum of the intraannular angles ranging between 539.5 and 539.7° for the former and between 538.6 and 539.1° for the latter. The slight deviation from planarity results in an envelope conformation, which can be described as either a folding along the B···B axis, with the ring carbon pointing toward the metal, or a folding along a C···N axis, with one boron atom pointing away from the metal (Figure 1). In all cases, the latter model offers a slightly better description of the structure, with the CBN_2/CBN folding angle measuring 9.6−11.3° for the methyl derivatives and 5.1−6.5° for the phenyl derivatives.

---

(9) (a) Schulze, J.; Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 54. (b) Schulze, J.; Boese, R.; Schmid, G. *Chem. Ber.* **1980**, *113*, 2348. (c) Schmid, G. *Comments Inorg. Chem.* **1985**, *4*, 17. (d) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1998**, *17*, 2379. (e) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 1821. (f) Ashe, A. J., III; Fang, X. *Org. Lett.* **2000**, *2*, 2089. (g) Ashe, A. J., III; Kampf, J. W.; Schiesher, M. *Organometallics* **2000**, *19*, 4681. (h) Liu, S.-Y.; Hills, I. D.; Fu, G. C. *Organometallics* **2002**, *21*, 4323. (i) Liu, S.-Y.; Lo, M. M.-C.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 174. (j) Ashe, A. J., III; Yang, H.; Fang, X.; Kampf, J. W. *Organometallics* **2002**, *21*, 4578. (k) Chen, J.; Fang, X.; Bajko, Z.; Kampf, J. W.; Ashe, A. J., III. *Organometallics* **2004**, *23*, 5088. (l) Liu, S.-Y.; Hills, I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 15352.

(10) (a) Ly, H. V.; Forster, T. D.; Maley, D.; Parvez, M.; Roesler, R. *Chem. Commun.* **2005**, 4468. (b) Ly, H. V.; Forster, T. D.; Corrente, A. M.; Eisler, D. J.; Konu, J.; Parvez, M.; Roesler, R. *Organometallics* **2007**, *26*, 1750.

Table 1. Selected Data and Structure Refinement Details for 2b, 3a·BrLi(THF)$_3$, 3b, 4a, and 5b·0.25C$_5$H$_{12}$

	2b	**3a**·BrLi(THF)$_3$	**3b**	**4a**	**5b**·0.25C$_5$H$_{12}$
empirical formula	$C_{40}H_{54}B_4N_4Zn$	$C_{32}H_{68}B_4BrCdLiN_4O_3$	$C_{40}H_{54}B_4CdN_4$	$C_{20}H_{46}B_4HgN_4$	$C_{20}H_{27}B_2Cl_3N_2Si \cdot 0.25C_5H_{12}$
formula wt	699.48	799.40	746.51	586.44	469.53
cryst syst	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$I2/m$	$P2_1/n$
a (Å)	10.681(3)	9.396(2)	10.940(3)	16.095(2)	6.755(6)
b (Å)	12.141(4)	21.241(7)	12.001(4)	15.295(2)	19.491(9)
c (Å)	17.176(4)	21.107(7)	16.987(5)	11.350(1)	20.603(10)
α (deg)	75.483(14)	90	76.011(16)	90	90
β (deg)	80.656(15)	96.85(2)	80.947(16)	101.249(1)	93.47(4)
γ (deg)	66.124(13)	90	66.866(16)	90	90
V (Å^3)	1967.0(10)	4182(2)	1985.2(10)	2740.6(5)	2708(3)
Z	2	4	2	4	4
d_{calcd} (g cm^{-3})	1.181	1.270	1.249	1.421	1.152
$2\theta_{max}$ (deg)	55.0	50.2	55.0	52.8	50
μ(Mo Kα) (mm^{-1})	0.657	1.511	0.582	5.629	0.393
no. of indep rflns	8921 ($R_{int} = 0.029$)	7345 ($R_{int} = 0.024$)	9039 ($R_{int} = 0.038$)	2918 ($R_{int} = 0.031$)	4738 ($R_{int} = 0.049$)
no. of data/restraints/params	8921/0/451	7345/0/425	9039/0/442	2918/0/240	4738/0/267
GOF on F^2	1.02	1.04	1.12	1.08	1.11
R1(F) ($I > 2\sigma(I)$)	0.042	0.038	0.061	0.020	0.066
wR2(F^2) (all data)	0.109	0.097	0.189	0.050	0.189

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Metallocenes 2−5

	2a (M = Zn)	**2b** (M = Zn)	**3a**·BrLi(THF)$_3$ (M = Cd)	**3b** (M = Cd)	**4a** (M = Hg)[b]	**5b**·0.25C$_5$H$_{12}$ (M = Si)
M−C	2.001(3)−2.004(4)	1.999(2), 2.004(2)	2.248(3), 2.255(3)	2.201(5), 2.206(5)	2.168(6), 2.177(6)	1.829(5)
M···B	2.443(4)−2.546(5)	2.564(2)−2.626(2)	2.796(4)−2.872(4)	2.706(6)−2.758(6)	2.729(7)−2.780(6)	2.755(6), 2.774(6)
B−C$_{intra}$[a]	1.507(6)−1.541(7)	1.537(3)−1.556(3)	1.519(5)−1.529(6)	1.535(8)−1.555(7)	1.546(10)−1.557(9)	1.585(7), 1.592(7)
N−B	1.406(5)−1.442(5)	1.424(3)−1.433(3)	1.426(5)−1.442(5)	1.423(7)−1.444(7)	1.390(12)−1.416(11)	1.382(6), 1.404(6)
N−N	1.424(4)−1.443(4)	1.443(2), 1.446(2)	1.438(5), 1.457(4)	1.445(6), 1.450(6)	1.454(7), 1.486(12)	1.454(5)
C$_{extra}$−C$_{intra}$	1.527(5)−1.56(3)	1.527(3), 1.534(3)	1.531(5), 1.533(5)	1.517(7), 1.535(7)	1.524(9), 1.536(11)	1.568(6)
B−C$_{extra}$	1.578(6)−1.59(2)	1.574(3)−1.581(3)	1.589(6)−1.591(6)	1.570(7)−1.588(8)	1.573(12)−1.597(11)	1.560(7), 1.575(7)
N−C$_{extra}$	1.451(8)−1.484(5)	1.470(3)−1.479(2)	1.40(1)−1.47(1)	1.472(6)−1.488(6)	1.408(17)−1.549(15)	1.473(6), 1.476(6)
C−M−C	175.2(1), 180.0(3)	174.71(8)	159.27(13)	175.3(2)	175.6(3), 176.1(3)	
B−C−B	103.1(3)−104.1(3)	102.7, 102.8(2)	103.1(3), 103.6(3)	102.8(4), 103(5)	102.2(5), 103.0(6)	100.3(4)
B−C$_{intra}$−C$_{extra}$	114.2(11)−137.4(8)	122.6(2)−126.7(2)	124.4(3)−125.3(3)	122.8(4)−127.8(5)	123.3(6)−124.8(6)	117.0(4), 117.3(4)
N−B−C$_{intra}$	107.4(3)−108.4(4)	108.2(2)−109.0(2)	108.2(3)−109.1(3)	108.0(4)−109.0(4)	107.6(6)−109.3(7)	108.9(4), 109.2(4)
C$_{intra}$−B−C$_{extra}$	113.8(7)−127.7(4)	125.0(2)−128.7(2)	125.4(3)−128.6(4)	124.4(4)−129.6(5)	125.0(6)−127.2(6)	125.7(4), 127.5(4)
N−B−C$_{extra}$	123.3(4)−138.4(7)	122.7(2)−126.0(2)	122.3(4)−125.5(4)	121.3(5)−127(4)	124.0(6)−126.5(6)	123.3(4), 125.4(4)
B−N−N	108.8(3)−110.9(3)	109.4(2)−110.2(2)	108.6(3)−109.3(3)	109.1(4)−110.2(4)	108.8(7)−110.3(6)	110.4(4), 111.0(4)
B−N−C$_{extra}$	122.4(4)−145.7(5)	124.6(2)−128.1(2)	111.0(5)−141.4(5)	124.6(4)−128.2(4)	111.1(8)−147.6(10)	125.2(4), 130.2(4)
N−N−C$_{extra}$	102.3(4)−124.5(3)	117.1(2)−120.2(2)	103.2(5)−129.4(4)	116.3(4)−120.7(4)	100.1(8)−132.4(8)	119.3(4), 123.3(4)
M−C/CB$_2$N$_2$	81.1, 82.6, 80.3	86.9, 87.8	85.0, 87.7	87.6, 87.9	87.6, 88.9	64.1
C−C/CB$_2$N$_2$	12.2, 14.4, 16.2	19.7, 20.2	15.6, 19.1	17.6, 18.4	20.2, 21.7	48.1
$\Sigma_{pentagn\ angles}$	538.9, 539.1	539.5, 539.6	239.0, 538.6	539.7, 539.7	539.0, 539.1	539.8

[a] C$_{intra}$ and C$_{extra}$ indicate carbon atoms that are part of the ring (intraannular) and directly connected to the ring (extraannular), respectively. [b] The structure of **4a** is heavily disordered.

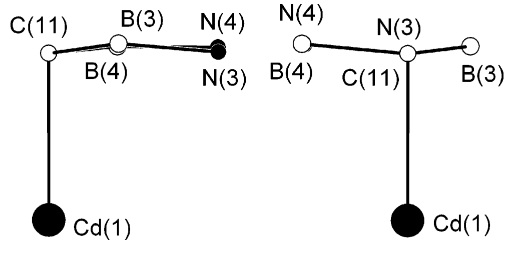


Figure 1. Side views illustrating the envelope conformation of one of the CB$_2$N$_2$ rings in **3a**·BrLi(THF)$_3$: (left) folding along the B(3)···B(4) axis; (right) folding along the C(11)···N(3) axis. For clarity, only the metal and the ring atoms are represented. Two pairs of ring atoms are eclipsed in each drawing.

In all complexes, the intraannular C−B bonds (1.507(6)−1.557(9) Å) tend to be shorter than the extraannular C−B bonds (1.570(7)−1.597(11) Å), in agreement with the expected multiple-bond character. The B−N bond lengths, ranging between 1.390(12) and 1.444(7) Å, are comparable to the B−N bond lengths observed in borazines (1.42−1.44 Å).[11] It is interesting to note that the intraannular B−C bonds are slightly longer in the group 12 complexes presented here than in the alkali-metal salts of the same ligands (1.486(6)−1.514(3) Å),[10] while the B−N bonds are shorter than those observed in the group 1 metallocenes (1.452(3)−1.481(3) Å). A similar behavior was observed for the corresponding C−C bonds in cyclopentadienyl complexes of the group 12 metals by comparison to alkali-metal cyclopentadienyls, which was explained by the strong involvement of one carbon atom in the binding to the metal and the consequent decrease in the aromaticity of the ligand in the former derivatives. The N−N bonds in complexes **2**−**4** (1.424(4)−1.486(12) Å) are close in length to the single N−N bond in hydrazine (1.45 Å).[12] It can therefore be

---

(11) (a) Boese, R.; Maulitz, A. H.; Stellberg, P. *Chem. Ber.* **1994**, *127*, 1887. (b) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424. (c) Jäschke, T.; Jansen, M. *Z. Anorg. Allg. Chem.* **2004**, *630*, 239.

(12) Kohata, K.; Fukuyama, T.; Kuchitsu, K. *J. Phys. Chem.* **1982**, *86*, 602.

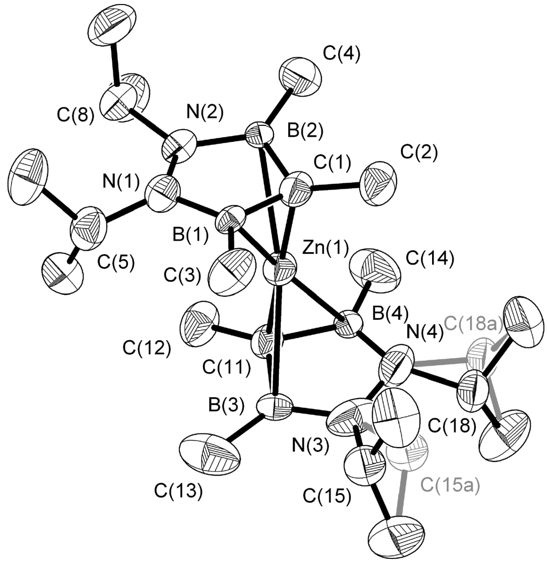


Figure 2. Structure of one of the two independent molecules in **2a**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

concluded that the π electron delocalization over the N−B−C−B−N skeleton of the ligand is similar to but slightly less significant than that in the alkali-metal complexes of the same ligands and, as is the case in the latter complexes, it does not include the N−N bond. An extensive comparison of the metric parameters of the ligands in alkali-metal complexes containing diazadiborolidines to those observed in related complexes featuring heterocyclic π ligands was recently reported.[10b]

The orientation of the ring substituents with respect to the ligand plane is similar in all complexes. The methyl substituent on the ring carbon is bent noticeably away from the metal, with the C−C bond forming angles of 12.2−21.7° with the CB_2N_2 plane. This is common in metallocenes of group 12 metals and was correlated to the partial sp^3 hybridization of the carbon connected to the metal and to a σ component of the η^1 coordination mode. In the methyl derivatives, one of the extraannular B−C bonds lies closer to the ligand plane ($B-C/CB_2N_2 = 1.0-5.3°$), while the other is bent away more pronouncedly from the metal ($B-C/CB_2N_2 = 7.9-13.8°$). In both **2b** and **3b** the phenyl substituents on boron are only slightly bent away from the metal, with angles between the B−C bonds and the CB_2N_2 plane of 0.1−4.9°. As observed in the alkali-metal salts of these ligands,[10] the isopropyl substituents on nitrogen alternate above and below the ligand plane, with one of the N−C bonds tilted toward the metal ($N-C/CB_2N_2 = 10.5-25.8°$) and the other away from the metal ($N-C/CB_2N_2 = 5.8-18.4°$). This orientation is in disagreement with the partial multiple-bond character of the B−N bonds and does not appear to be sterically induced, since it is not visibly affected by the replacement of methyl substituents on boron with phenyl groups.

The structure of **2a** contains two independent molecules that are very similar and will be discussed together (Figure 2).[10a] The zinc atom is relatively symmetrically coordinated by the two parallel ligands, which form angles of 0 and 8.9° with each other. All previously reported zincocenes are asymmetric, featuring a η^1:η^2 or η^1:η^5 coordination mode of the cyclopentadienyl ligand.[4] A symmetric η^5 coordination mode has been observed in dizincocenes.[8] The zinc center in **2a** lies almost above the ring carbon, with its projection onto the ligand plane falling only slightly inside the ligand pentagon (Figure 7). Its coordination can be described as either η^1:η^1 or η^3:η^3, and although the Zn···B distances (2.443(4)−2.546(5) Å) are longer than the shortest Zn−B bonds observed in sandwich compounds containing boranes as ligands ($[Zn(B_{10}H_{12})_2]^{2-}$ (2.191(7)−2.209(10) Å)[13a,b] and $[(nido\text{-}C_2B_9H_{11})ZnNMe_3]_2$ (2.160(3)−2.177(3) Å)[13c]), the latter description was chosen, given the small yet distinct difference with respect to the other structures reported herein.

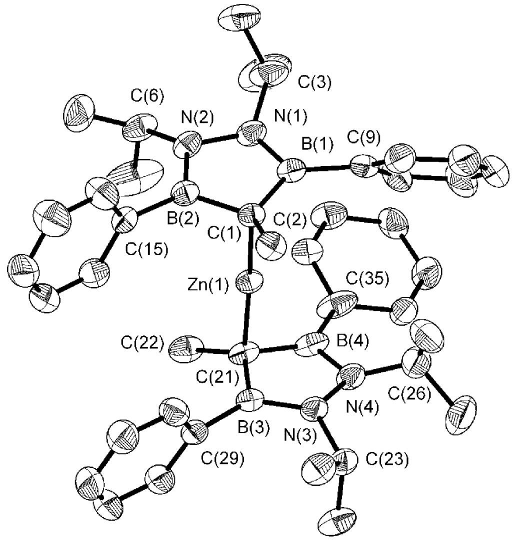


Figure 3. Molecular structure of **2b** with 50% probability level thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

The structure of **2b** (Figure 3) is very similar to that of its methyl analogue. The main difference is that the Zn−C bond is nearly perpendicular to the CB_2N_2 plane (86.9 and 87.8° in **2b** vs 81.1, 82.6, and 80.3° in **2a**). The coordination mode is therefore typical η^1 (Figure 7). For the rest of this work, an η^1 coordination mode will refer to a monoconnective binding involving the π cloud of the ligand and a planar geometry of the sp^2-hybridized ring carbon, as described by Jutzi and Burford for π cyclopentadienyl complexes.[1c] The classical notation σ refers to a monoconnective binding of the ligand, involving a tetrahedral, sp^3-hybridized ring carbon. Although these are idealized situations, most structures resemble one of these geometries more than the other and can be conveniently assigned to one of the two categories. The Zn−C bond lengths are very similar in **2a** and **2b** (1.999(2)−2.004(4) Å) and quite short in comparison to those found in cyclopentadienyl complexes (1.99−2.37 Å for η^5 coordination and 1.95−2.22 Å for η^1 coordination).[4] From all five crystal structures of zincocenes with η^1:η^5 coordination that have been determined, only $Zn[C_5Me_4(SiMe_3)]_2$ is not disordered and provides a reliable comparison for the ligand geometry. As opposed to the case for **2a**,**b**, this compound features a structure with a σ-bonded cyclopentadienyl and a distorted-tetrahedral ring carbon. The Zn−C and C−C bonds involving the ring carbon form angles of 69.0 and 43.0°, respectively, with the ring plane. With $C-C/CB_2N_2$ angles of 12.2−20.2°, the methyl substituent on the ring carbon is bent much less out of the ring plane in the two zincocenes incorporating diazadiborolyl ligands. The Zn···B distances in **2b** (2.564(2)−2.626(2) Å) are even larger than in **2a**.

The two cadmium complexes **3a**·BrLi(THF)$_3$ (Figure 4) and **3b** (Figure 5) feature very similar η^1 coordination modes of

---

(13) (a) Greenwood, N. N.; McGinnety, J. A.; Owen, J. D. *J. Chem. Soc. A* **1971**, 809. (b) Allmann, R.; Bätzel, V.; Pfeil, R.; Schmid, G. *Z. Naturforsch.* **1976**, *31B*, 1329. (c) Goeta, A. E.; Howard, J. A. K.; Hughes, A. K.; Johnson, A. L.; Wade, K. *Chem. Commun.* **1998**, 1713.

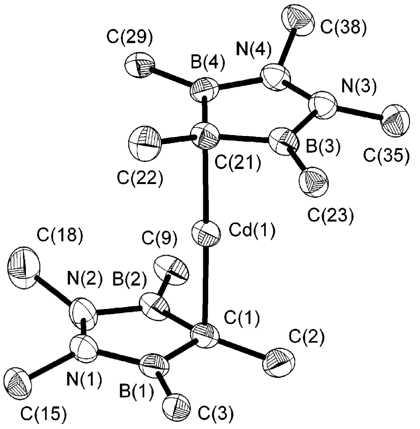


Figure 4. Molecular structure of **3b** with 50% probability level thermal ellipsoids. For clarity, only the α-carbon atoms in the organic substituents are represented and all hydrogen atoms have been omitted.

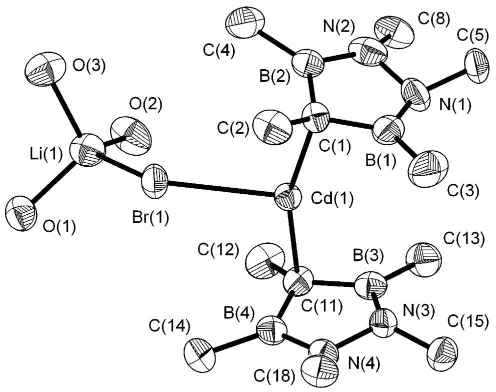


Figure 5. Structure of **3a**·BrLi(THF)$_3$ in the solid state, with thermal ellipsoids drawn at the 50% probability level. Only the α-carbon atoms are represented for the ring substituents, and all hydrogen atoms, as well as the methylene groups in THF, have been omitted. The disorder involving the bromine atom and the isopropyl groups (C5 and C8) is not depicted.

the ligands, with the Cd−C bonds forming angles of 85.0−87.9° with the ring planes (Figure 7). In both compounds, the angles formed by the C−C bonds involving the ring carbons with the ring plane fall in a narrow range, between 15.6 and 19.1°. Derivative **3b** is isocrystalline with **2b**, contains parallel ligands (dihedral angle 7.5°), and displays an almost linear geometry at cadmium (C−Cd−C = 175.3°). Only two base-free cadmocenes have been crystallographically characterized, featuring η^1:η^1 and η^1:η^2 coordinating cyclopentadienyl ligands, respectively.[6e] The latter structure is disordered, and therefore only the former, (tBu$_3$C$_5$H$_2$)$_2$Cd, provides a basis for a rigorous comparison of the metric parameters. This structure is quite similar to that of **3b**, with the Cd−C and C−C$_{\mathrm{Cd}}$ bonds forming angles of 87.2 and 28.6° with the plane of the ring skeleton. The lengths of the Cd−C bonds are identical in **3b** (2.201(5), 2.206(5) Å) and (tBu$_3$C$_5$H$_2$)$_2$Cd (2.201(2) Å). In the complex **3a**·BrLi(THF)$_3$, the coordination of the BrLi(THF)$_3$ unit through a long Br−Cd bond (2.731(8) and 2.7916(14) Å vs 2.55−2.59 Å in CdBr$_4^{2-}$)[14] imposes a narrower C−Cd−C angle of 159.27(13)° and prevents the ligands from adopting a parallel arrangement (dihedral angle 19.6°). The Br atom is disordered between two positions, and the lithium atom has the expected distorted-tetrahedral geometry. All three reported structures of cad-

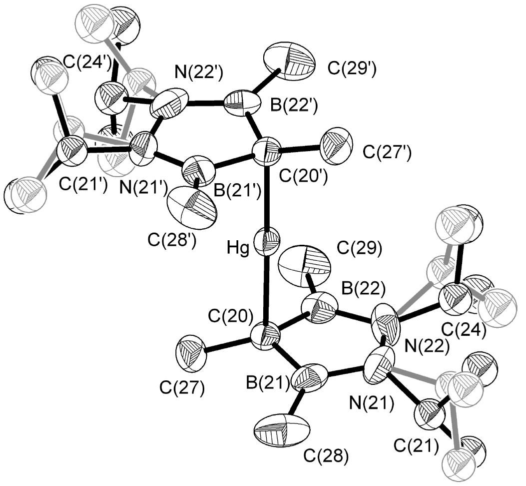


Figure 6. Molecular structure of **4a** with 50% probability level thermal ellipsoids. Hydrogen atoms have been omitted for clarity, and only two of the ligands disordered around the mercury center are represented.

mocenes containing Lewis bases coordinated to the metal feature cyclopentadienyl as a ligand and have two or three nitrogen atoms completing the coordination sphere of cadmium.[6a,b,d] The cyclopentadienyl ligand displays σ, η^1, and η^2 coordination in these compounds, and the Cd−C bonds are longer in the complexes featuring η^1 coordination (2.307(5)−2.410(6) Å) than in **3a**·BrLi(THF)$_3$ (2.248(3), 2.255(3) Å). This is likely due to the better donor ability of the nitrogen bases and their capacity to reduce the electrophilicity of cadmium and hence its affinity for the cyclopentadienyl ligands. The angles formed by the Cd−C bonds with the planes of the cyclopentadienyl rings measure ca. 77−81° for the η^1 binding mode and ca. 59° for the σ binding mode, being noticeably more acute than the corresponding angles in **3a**·BrLi(THF)$_3$. Also, the C−Cd−C angles are more acute in the cyclopentadienyl derivatives (111.4(2) and 129.1(2)°). The Cd···B distances in **3a**·BrLi(THF)$_3$ and **3b** range from 2.706(6) to 2.872(4) Å and are substantially longer than the shortest Cd−B bonds observed in the three compounds available for comparison ([(Et$_2$O)$_2$Cd(B$_{10}$H$_{12}$)]$_2$ (2.37(3)−2.46(3) Å),[15a] [Cd(B$_9$H$_{13}$)$_2$]$^{2-}$ (2.272(4)−2.302(4) Å),[15b] and [Cd(B$_6$H$_6$)$_2$]$^{2-}$ (2.388(10)−2.451(14) Å)[15c]).

The structure of the mercury metallocene **4a** is heavily disordered, with two equally abundant molecules occupying the same position in the crystal lattice. The Hg center in the two molecules having nearly perpendicular C−Hg−C axes occupies the same crystallographic position. The isopropyl substituents in each of these molecules are also disordered between two positions (Figure 6). Careful modeling allowed for a good refinement of the structure, and the crystallographic and metric parameters are presented in Tables 1 and 2, respectively. Like the previous structures presented in this paper, the mercury complex features η^1 coordinating ligands (C−Hg/CB$_2$N$_2$ angles of 87.6 and 88.9°) and a nearly linear geometry at mercury (C−Hg−C angles of 175.6(3) and 176.1(3)°). Further indicative of an η^1 binding mode, the angles formed by the Me−C bonds involving the ring carbons with the planes of the ring skeletons are relatively acute (20.2 and 21.7°). The C−Hg bonds measure 2.168(6) and 2.177(6) Å and are comparable to the bonds observed in the three mercurocenes that have been crystallo-

---

[14] Hasselgren, C.; Dean, P. A. W.; Scudder, M. L.; Craig, D. C.; Dance, I. G. *J. Chem. Soc., Dalton Trans.* **1997**, 2019.

[15] (a) Greenwood, N. N.; McGinnety, J. A.; Owen, J. D. *J. Chem. Soc., Dalton Trans.* **1972**, 989. (b) Schaper, T.; Preetz, W. *Inorg. Chem.* **1998**, *37*, 363. (c) Littger, R.; Englich, U.; Spencer, J. T. *Inorg. Chem.* **1997**, *36*, 6434.

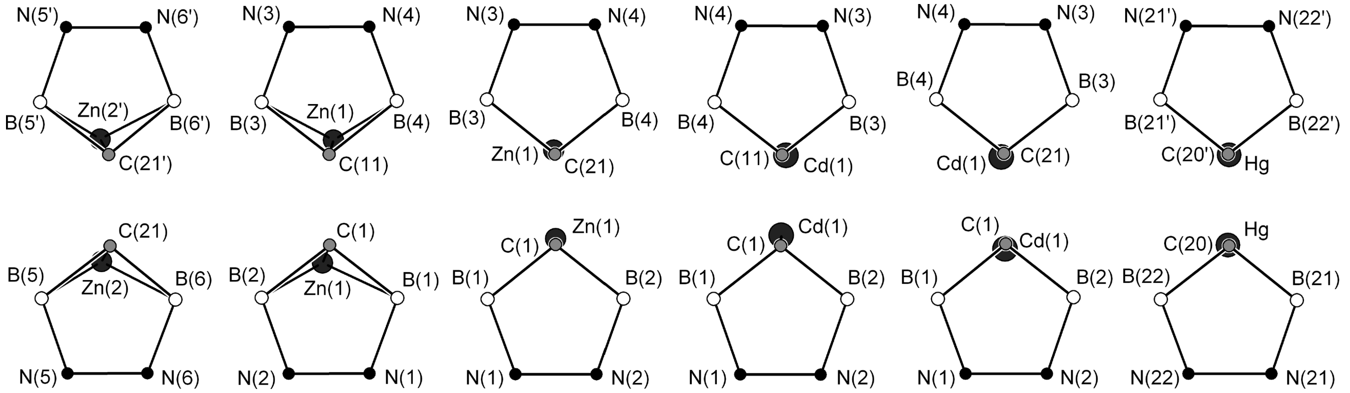


Figure 7. Perpendicular projection onto the CB_2N_2 planes, revealing the hapticity of the ligand. From left to right: **2a** (two independent molecules, η^3 coordination), **2b**, **3a**·BrLi(THF)$_3$, **3b**, and **4a** (η^1 coordination).

graphically characterized, all featuring monoconnective binding modes of the ligands (2.09(2)−2.163(3) Å).[7b,d,e] The bonding in these latter compounds can also be described as η^1; however, the geometries of these derivatives indicate a significant σ bonding component. The Hg−C and C−C$_{Hg}$ bonds in these complexes form angles of 68.1−77.3 and 31.9−37.7°, respectively, with the planes of the cyclopentadienyl rings. The Hg···B distances in **4a** (2.729(7)−2.780(6) Å) are much longer than the shortest Hg−B bonds observed in mercury half-sandwich compounds featuring 7,8-dicarba-*nido*-undecaboranes as ligands (2.178(8)−2.208(6) Å).[16]

In order to gain further information regarding the monoconnective coordination mode of the diazadiborolyl ligand, complexes **5a**,**b**, expected to display σ bonding, were synthesized by reacting the alkali-metal salts **1a**,**b** with $SiCl_4$. Recrystallization from hexane yielded the desired compounds as colorless crystalline solids. The ^{1}H and ^{13}C NMR spectra of these derivatives featured the expected signals corresponding to a C_s symmetry, and the identity of **5b** was confirmed with a high-resolution mass spectrum. The broad resonance corresponding to the ring carbon appeared at 35.4 and 35.2 ppm in the two derivatives, ca. 40 ppm upfield from the signals displayed by derivatives **2**−**4** and only ca. 10 ppm downfield from the signals displayed by the protonated ligands.[10b] This is a clear indication for the pronounced sp^3 character of the ring carbon in **5**, expected for the σ bonding, versus sp^2 in complexes **2**−**4** featuring η^1 coordination. Because of the electronic influence of the neighboring boron atoms, a direct comparison to cyclopentadienyl complexes in this regard is not feasible. As expected, the ^{11}B and ^{29}Si NMR spectra of **5a** (43.9 and 5.7 ppm, respectively) and **5b** (41.8 and 7.0 ppm, respectively) displayed singlet resonances. A crystallographic determination of **5b** (Table 1 and 2) validates the proposed structure containing a tetrahedral $SiCl_3$ moiety σ bonded to the diazadiborolyl ligand (Figure 8). The lengths of the Si−C and Si−Cl bonds (1.829(5) and 2.038(2)−2.040(2) Å, respectively) are comparable to those found in other alkyltrichlorosilanes such as 1,2-bis(trichlorosilyl)ethane (Si−C = 1.847(2) Å and Si−Cl = 2.0225(6)−2.0283(6) Å).[17] Typical for a distorted-tetrahedral geometry, the C−Si−Cl and Cl−Si−Cl angles measure 111.44(16)−113.28(15) and 104.02(8)−107.29(9)°, respectively. The geometry of the ligand skeleton is similar in **5b** and the group 12 complexes described in this paper. The envelope conformation

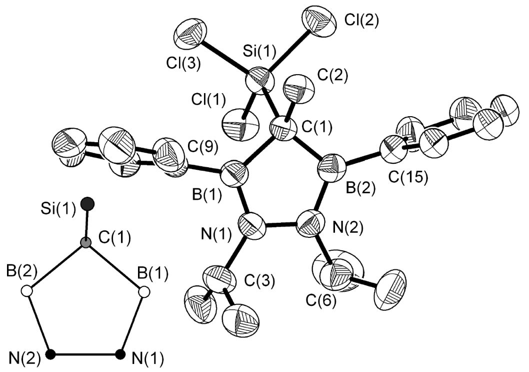


Figure 8. Structure of **5b**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and the pentane molecule have been omitted for clarity. On lower left is given a perpendicular projection onto the CB_2N_2 plane, revealing the hapticity of the ligand.

of the CB_2N_2 ring has a folding angle of only 4.1° along one of the transannular C···N axes, and the deviation of the substituents on boron and nitrogen out of the ring plane is less than 4.3°, which is significantly less pronounced than in the group 12 complexes. Distinctive for a σ binding mode, the ring carbon is distorted tetrahedral, with the Si(1)−C(1) and C(2)−C(1) bonds forming angles of 64.1 and 48.1° with the CB_2N_2 plane, respectively. By comparison, these angles range between 80.3 and 88.9° for the M−C bond and between 12.2 and 21.7° for the C−C bond in complexes **2**−**4**, where the metal−carbon bond is nearly perpendicular to the ring plane and the carbon−carbon bond is situated much closer to this plane. In agreement with the more pronounced sp^3 character of the ring carbon in **5b**, the bonds this atom forms to carbon and boron are slightly but systematically longer (0.01−0.05 and 0.03−0.09 Å, respectively) than in derivatives **2**−**4**. The B−N bonds are only marginally shorter in **5b** in comparison to those in the group 12 metallocenes described herein (on average 0.03 Å). A very similar structure was reported for Cp*$SiCl_3$, with a planar ring skeleton and a Si−C bond length of 1.867(3) Å.[18] In this derivative, the angles formed by the Si−C and C−C(Si) bonds with the ligand plane measure 64.9 and 45.8°, respectively: nearly identical with the values observed in **5b**. The structural analysis reveals very different monoconnective coordination modes of the diazadiborolyl ligand in **5b** (σ, nearly tetrahedral ring carbon) and the group 12 complexes described in this paper (π, nearly planar ring carbon).

---

(16) (a) Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.*, **1979**, 619. (b) Lewis, Z. G.; Welch, A. J. *Acta Crystallogr.* **1993**, *C*49, 715. (c) Teixidor, F.; Ayllòn, J. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Casabò, J. *J. Organomet. Chem.* **1994**, *483*, 153.

(17) Mitzel, N. W.; Riede, J.; Schmidbaur, H. *Acta Crystallogr.* **1997**, *C53*, 1335.

(18) Cowley, A. H.; Ebsworth, E. A. V.; Mehrotra, S. K.; Rankin, D. W. H.; Walkinshaw, M. D. *J. Chem. Soc., Chem. Commun.* **1982**, 1099.

Conclusions

Zinc, cadmium, and mercury metallocenes containing 1,2-diisopropyl-3,5-dimethyl-1,2-diaza-3,5-diborolyl and 1,2-diisopropyl-3,5-diphenyl-1,2-diaza-3,5-diborolyl ligands were synthesized and characterized. In all complexes, the ring carbon plays the essential role in the binding of the ligand to the metal and the geometry of the complexes is, in contrast to the zinc cyclopentadienyl analogs, fairly symmetric. Four base-free complexes were isolated and featured linear environments around the metal, with C−M−C angles situated between 174 and 180°. Compound **3a** crystallized with one unit of BrLi(THF)$_3$ coordinated to the cadmium center and featured a C−Cd−C angle of 159°. Except for the zinc complex **2a**, where the Zn−C bond is noticeably tilted toward the ligand and the coordination is better described as η^3:η^3, the coordination mode of the ligand is typical η^1:η^1 in all other group 12 complexes. The M−C bond is nearly perpendicular to the CB_2N_2 plane in compounds **2b**, **3a**·BrLi(THF)$_3$, **3b**, and **4a** (85.0−88.9°), while the C−C bond involving the ring carbon forms angles of 12.2−21.7° with the same plane. In all group 12 cyclopentadienyl derivatives available for comparison, the σ character of the metal-to-ligand bonding is more pronounced than in the complexes described herein. This suggests that the stabilization of a planar configuration for the negatively charged carbon involved in the binding to the metal, through π donation to the electron-deficient boron atoms in the 1,2-diaza-3,5-diborolyl group, is more effective than the stabilization through delocalization over the ring in the cyclopentadienyl group. For comparison, the structure of the trichlorosilyl derivative **5b** was determined and featured a typical σ binding mode of the 1,2-diaza-3,5-diborolyl ligand to the metal. The metal−carbon bond lengths in all compounds are comparable to those observed in the cyclopentadienyl analogues.

Multinuclear NMR spectroscopy shows that, unlike the related alkali-metal derivatives, in solution the ligand does not dissociate and the structure is preserved for the group 12 metallocenes presented in this paper. This is in agreement with the higher covalent character of the metal−ligand interaction in the latter compounds and is consistent with the behavior of the corresponding cyclopentadienyl complexes.

Experimental Section

General Considerations. All operations were performed under an argon atmosphere using standard Schlenk and glovebox techniques. Solvents were dried and deoxygenated prior to use. Tetraphenyltin, potassium bis(trimethylsilyl)amide, zinc(II) chloride, cadmium(II) bromide, and mercury(II) chloride were purchased from commercial suppliers and used without further purification. Triethylamine was distilled over CaH_2 prior to use. The lithium and potassium salts **1a**,**b**, respectively, were prepared according to reported procedures.[10] NMR spectra were recorded on Bruker Advance DRX-400 and AMX-300 spectrometers and calibrated with respect to C_6D_5H (^{1}H, 7.15 ppm), THF-d_7 (^{1}H, 3.58 ppm), C_6D_6 (^{13}C, 128.39 ppm), THF-d_8 (^{13}C, 67.57 ppm), BF_3·Et_2O (^{11}B, 0 ppm), $CdClO_4$ in D_2O (^{113}Cd, 0 ppm), and $HgCl_2$ in THF-d_8 (^{199}Hg, −1498 ppm). The electron impact (EI), electrospray ionization (ESI), and high-resolution mass spectrometry (HRMS) measurements were performed by the Analytical Instrumentation Laboratory, Department of Chemistry, University of Calgary.

Synthesis of Bis(1,2-diisopropyl-3,5-diphenyl-1,2-diaza-3,5-diborolyl)zinc (2b). A solution of **1b** (0.100 g, 0.280 mmol) and anhydrous $ZnCl_2$ (0.019 g, 0.140 mmol) in THF (30 mL) was stirred for 3 h at ambient temperature, forming a fine suspension. Volatiles were removed in vacuo, and the residue was extracted with hexane (20 mL). Subsequent solvent removal left behind the target compound as a colorless powder. Colorless blocklike crystals of **2b** (57 mg, 58%) were obtained by cooling a concentrated pentane solution to −35 °C. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 1.14 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.27 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.53 (s, 3H, CCH_3), 4.18 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 7.22−7.36 (m, 6H, *m*- + *p*-C$_6H_5$), 7.36−7.38 (m, 4H, *o*-C$_6H_5$). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 25 °C): δ 11.7 (s, CCH$_3$), 23.8 (s, CH(CH$_3$)$_2$), 24.6 (s, CH(CH$_3$)$_2$), 50.6 (s, CH(CH$_3$)$_2$), 69.3 (s, br, B$_2$$CCH_3$), 127.5 (s, *p*-$C_6H_5$), 128.3 (s, *m*-$C_6H_5$), 134.0 (s, *o*-$C_6H_5$), 142.0 (s, br, *i*-$C_6H_5$). ^{11}B{^{1}H} NMR (128 MHz, C_6D_6, 25 °C): δ = 39.0 (s, br, LW$_{1/2}$ = 876 Hz). ESI-MS (CH$_3$CN; *m*/*z* (%)): 698.2 (5) [ZnL$_2$]$^+$, 381.0 (100) [ZnL]$^+$, 319.1 (50) [L + H]$^+$.

Synthesis of Bis(1,2-diisopropyl-3,5-dimethyl-1,2-diaza-3,5-diborolyl)cadmium (3a). A solution of **1a** (0.100 g, 0.500 mmol) and anhydrous $CdBr_2$ (0.068 g, 0.250 mmol) in THF (30 mL) was sonicated for 30 min, forming a fine gray suspension. The solvent was subsequently removed in vacuo, and the oily residue was extracted with hexane (20 mL). Solvent removal left behind **3a** as a colorless crystalline solid (138 mg, 94%). Colorless needles of the target compound were obtained by cooling a concentrated pentane solution to −35 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.74 (s, 6H, $^4J_{CdH}$ = 8.7 Hz, BCH_3), 1.24 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.26 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.84 (s, 3H, $^3J_{CdH}$ = 59.6 Hz, CCH_3), 3.85 (sep, 2H, $^3J_{HH}$ = 6.9 Hz, CH(CH$_3$)$_2$). ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 0.47 (s, 6H, $^4J_{CdH}$ = 7.7 Hz, BCH_3), 1.18 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.27 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.50 (s, 3H, $^3J_{CdH}$ = 46.4 Hz, CCH_3), 3.77 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ −0.26 (s, br, BCH$_3$), 13.2 (s, $^2J_{CdC}$ = 39.7 Hz, CCH$_3$), 23.4 (s, CH(CH$_3$)$_2$), 23.7 (s, CH(CH$_3$)$_2$), 47.8 (s, CH(CH$_3$)$_2$), 77.6 (s, br, B$_2$$CCH_3$). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, D1 = 10 s, LB = 3 Hz, 25 °C): δ 1.44 (s, br, BCH$_3$), 14.3 (s, $^2J_{CdC}$ = 43.1 Hz, CCH$_3$), 23.2 (s, CH(CH$_3$)$_2$), 23.8 (s, CH(CH$_3$)$_2$), 48.3 (s, CH(CH$_3$)$_2$), 70.6 (s, br, B$_2$$CCH_3$). ^{11}B{^{1}H} NMR (128 MHz, C_6D_6, 25 °C): δ 37.9 (s, br). ^{11}B{^{1}H} NMR (128 MHz, THF-d_8, 25 °C): δ 40.9 (s, br, LW$_{1/2}$ = 486 Hz). ^{113}Cd{^{1}H} NMR (88 MHz, C_6D_6, 25 °C): δ 256.2 (s). ^{113}Cd{^{1}H} NMR (66 MHz, THF-d_8, 25 °C): δ 397.9 (s). MS (EI$^+$, 70 eV; *m*/*z* (%)): 498.7 (60) [CdL$_2$]$^+$, 305.3 (26) [CdL]$^+$, 192.3 (63) [L]$^+$. HRMS for $H_{46}C_{20}N_4{}^{11}B_4{}^{112}Cd$ (*m*/*z*): calcd, 498.3122; found, 498.3124.

Synthesis of Bis(1,2-diisopropyl-3,5-diphenyl-1,2-diaza-3,5-diborolyl)cadmium (3b). A mixture of **1b** (0.100 g, 0.280 mmol) and anhydrous $CdBr_2$ (0.038 g, 0.140 mmol) in THF (30 mL) was sonicated for 30 min, forming a gray suspension. The solvent was subsequently removed in vacuo, and the residue was extracted with hexane (20 mL). Solvent removal left behind **3b** as a colorless powder. Pale yellow prismatic crystals (84 mg, 80%) of the target compound were obtained by cooling a concentrated pentane solution to −35 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 1.13 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.17 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.87 (s, 3H, $^3J_{CdH}$ = 58.7 Hz, CCH_3), 4.06 (sep, 2H, $^3J_{HH}$ 6.8 Hz, CH(CH$_3$)$_2$), 7.22 (t, 2H, *p*-C$_6H_5$), 7.31 (t, 4H, *m*-C$_6H_5$), 7.62 (d, 4H, *o*-C$_6H_5$). ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 1.16 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.24 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.58 (s, 3H, $^3J_{CdH}$ = 58.7 Hz, CCH_3), 4.16 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 7.23−7.29 (m, 6H, *m*- + *p*-C$_6H_5$), 7.40−7.43 (m, 4H, *o*-C$_6H_5$). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 25 °C): δ 13.2 (s, $^2J_{CdC}$ = 42.2 Hz, CCH$_3$), 23.9 (s, CH(CH$_3$)$_2$), 24.3 (s, CH(CH$_3$)$_2$), 50.4 (s, CH(CH$_3$)$_2$), 77.4 (s, br, B$_2$$CCH_3$), 127.7 (s, *p*-$C_6H_5$), 128.4 (s, *m*-$C_6H_5$), 134.2 (s, *o*-$C_6H_5$), 142.2 (s, br, *i*-$C_6H_5$). ^{11}B{^{1}H} NMR (128 MHz, THF-d_8, 25 °C): δ 36.6 (s, br, LW$_{1/2}$ = 897 Hz). ^{113}Cd NMR (88 MHz, C_6D_6, 25 °C): δ 286.1 (sep, $^3J_{CdH}$ = 60.5 Hz). ESI-MS (CH$_3$CN; *m*/*z* (%)): 745.1 (6) [CdL$_2$−H]$^+$, 430.1 (25) [CdL]$^+$, 317.1 (100) [L]$^+$.

Synthesis of Bis(1,2-diisopropyl-3,5-dimethyl-1,2-diaza-3,5-diborolyl)mercury (4a). A solution of **1a** (0.100 g, 0.500 mmol) and anhydrous $HgCl_2$ (0.068 g, 0.250 mmol) in THF (30 mL) was stirred for 3 h at ambient temperature, forming a gray suspension. The solvent was removed in vacuo, and the residue was extracted with hexane (30 mL). Removal of the solvent in vacuo left behind colorless, crystalline **4a** (138 mg, 94%). X-ray-quality single crystals of **4a** were obtained by slow evaporation of a pentane solution at −35 °C. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 0.71 (s, 6H, $^4J_{HgH}$ = 20.2 Hz, BCH_3), 1.26 (d, 6H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.29 (d, 6H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.84 (s, 3H, $^3J_{HgH}$ = 142.5 Hz, CCH_3), 3.82 (sep, 2H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$). ^1H NMR (400 MHz, THF-d_8, 25 °C): δ 0.45 (s, 6H, $^4J_{HgH}$ = 19.8 Hz, BCH_3), 1.29 (d, 6H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.32 (d, 6H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.59 (s, 3H, $^3J_{HgH}$ = 143.4 Hz, CCH_3), 3.96 (sep, 2H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ −0.13 (s, br, BCH_3), 13.6 (s, $^2J_{HgC}$ = 64.5 Hz, CCH_3), 23.4 (s, $CH(CH_3)_2$), 23.8 (s, $CH(CH_3)_2$), 47.9 (s, $CH(CH_3)_2$), 77.8 (s, br, B_2CCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8, −20 °C): δ −0.35 (s, br, BCH_3), 13.5 (s, CCH_3), 23.4 (s, $CH(CH_3)_2$), 23.8 (s, $CH(CH_3)_2$), 48.2 (s, br, $CH(CH_3)_2$), 77.3 (s, br, B_2CCH_3). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6, 25 °C): δ 39.0 (s, br). $^{11}B\{^1H\}$ NMR (128 MHz, THF-d_8, 25 °C): δ 38.9 (s, br, $LW_{1/2}$ = 523 Hz). $^{199}Hg\{^1H\}$ NMR (71 MHz, C_6D_6, 25 °C): δ −2063.3 (s). MS (EI^+, 70 eV; m/z (%)): 586.5 (21) $[HgL_2]^+$, 393.3 (1) $[HgL]^+$, 193.3 (20) $[L]^+$.

Synthesis of (1,2-Diisopropyl-3,5-dimethyl-1,2-diaza-3,5-diborolyl)trichlorosilane (5a). Silicon tetrachloride (97 μL, 0.85 mmol) was added to a colorless solution of **1a** (0.17 g, 0.85 mmol) in THF (15 mL). The clear mixture was stirred at ambient temperature for 2 h, and the volatiles were subsequently removed under vacuum, leaving behind a thick residue. The product was extracted with hexane and isolated upon removal of the solvent in the form of a colorless crystalline solid (0.21 g, 75%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 0.64 (s, 6H, BCH_3), 1.08 (d, 6H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.13 (d, 6H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.29 (s, 3H, CCH_3, $^3J_{SiH}$ = 13.0 Hz), 3.68 (sep, 2H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$). ^1H NMR (400 MHz, THF-d_8, 25 °C): δ 0.55 (s, 6H, BCH_3), 1.26 (s, 3H, CCH_3), 1.34 (d, 6H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.37 (d, 6H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 4.07 (sep, 2H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8, 25 °C): δ 0.6 (s, br, BCH_3), 10.7 (s, CCH_3), 22.3 (s, $CH(CH_3)_2$), 22.9 (s, $CH(CH_3)_2$), 35.4 (s, br, B_2CCH_3), 47.6 (s, $CH(CH_3)_2$). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6, 25 °C): δ 43.9 (s, br, $LW_{1/2}$ = 321 Hz). $^{29}Si\{^1H\}$ NMR (79 MHz, THF-d_8, 25 °C): δ 5.7 (s). MS (EI^+, 70 eV; m/z (%)): 327 (13) $[M]^+$, 312 (40) $[M - Me]^+$, 269 (14) $[M - Me - iPr]^+$.

Synthesis of (1,2-Diisopropyl-3,5-diphenyl-1,2-diaza-3,5-diborolyl)trichlorosilane (5b). Silicon tetrachloride (32 μL, 0.28 mmol) was added to a colorless solution of **1b** (0.10 g, 0.28 mmol) in THF (15 mL). The pale yellow mixture was stirred at ambient temperature for 2 h, and the volatiles were subsequently removed under vacuum, leaving behind a thick residue. The product was extracted with hexane and isolated upon removal of the solvent in the form of a colorless crystalline solid (0.10 g, 79%). Colorless crystals of **5b**·$0.25C_5H_{12}$ were obtained by cooling a concentrated pentane solution of **5b** at −35 °C. ^1H NMR (400 MHz, THF-d_8, 25 °C): δ 1.20 (d, br, 6H, $^3J_{HH}$ = 6.3 Hz, $CH(CH_3)_2$), 1.31 (d, 6H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.43 (s, 3H, $^3J_{SiH}$ = 12.9 Hz, CCH_3), 4.19 (sep, 2H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 7.25−7.31 (m, 6H, m- + p-C_6H_5), 7.35 (d, 4H, o-C_6H_5). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8, 25 °C): δ 10.2 (s, CCH_3), 23.7 (s, $CH(CH_3)_2$), 24.3 (s, $CH(CH_3)_2$), 36.2 (s, br, B_2CCH_3), 49.9 (s, $CH(CH_3)_2$), 128.0 (s, m-C_6H_5), 128.3 (s, p-C_6H_5), 132.7 (s, o-C_6H_5), 140.0 (s, br, i-C_6H_5). $^{11}B\{^1H\}$ NMR (128 MHz, THF-d_8, 25 °C): δ 41.8 (s, br, $LW_{1/2}$ = 428 Hz). $^{29}Si\{^1H\}$ NMR (79 MHz, THF-d_8, 25 °C): δ 7.0 (s). MS (EI^+, 70 eV; m/z (%)): 450 (100) $[M]^+$, 435 (96) $[M- Me]^+$, 407 (10) $[M- iPr]^+$, 393 (20) $[M - Me - iPr + H]^+$. HRMS for $H_{27}C_{20}N_2{}^{11}B_2{}^{35}Cl_3Si$ (m/z): calcd, 450.1195; found, 450.1199. HRMS for $H_{27}C_{20}N_2{}^{11}B_2{}^{35}Cl_2{}^{37}ClSi$ (m/z): calcd, 452.1166; found, 452.1157.

X-ray Crystallography. Single crystals of **2b, 3b**, **3a**·BrLi$(THF)_3$, and **5b**·$0.25C_5H_{12}$ were coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The crystal data and data collection and refinement parameters for the complexes are given in Table 1. The data were collected[19] at a temperature of 173(2) K using ω and φ scans and corrected for Lorentz and polarization effects and for absorption using multiscan methods.[20] Since the crystals did not show any sign of decay during data collection, a decay correction was deemed unnecessary. Data for the crystal of **4a** were measured at 193(2) K on a Bruker SMART 1000 CCD/PLATFORM diffractometer with graphite-monochromated Mo Kα radiation using ω scans.[21]

The structures were solved by direct methods[22] and expanded using Fourier techniques.[23] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. The final cycle of full-matrix least-squares refinement using SHELXL97[24] converged with unweighted and weighted agreement factors, R and R_w (all data), respectively, and goodness of fit, F^2. The weighting scheme was based on counting statistics, and the final difference map was essentially featureless. The figures were plotted with the aid of Diamond.[25]

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada, the Canada Foundation for Innovation, and the Alberta Science and Research Investments Program.

Supporting Information Available: CIF files giving complete crystallographic data of the complexes **2b**, **3a**·BrLi$(THF)_3$, **3b**, **4a**, and **5b** and figures giving NMR spectra of all new compounds as evidence of purity, in the absence of satisfactory elemental analyses. This material is available free of charge via the Internet at http://pubs.acs.org. CIF files are also available online from the Cambridge Crystallographic Data Centre (CCDC Nos. 635572 (**2b**), 635573 (**3a**·BrLi$(THF)_3$), 635574 (**3b**), 635575 (**4a**), and 635576 (**5b**)).

OM070230N

---

[19] Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

[20] Hooft, R. COLLECT; Nonius BV, Delft, The Netherlands, 1998.

[21] Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker.

[22] Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

[23] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

[24] Sheldrick, G. M. SHELXL97; University of Göttingen, Göttingen, Germany, 1997.

[25] DIAMOND-Visual Crystal Structure Information System; CRYSTAL IMPACT, Postfach 1251, D-53002 Bonn, Germany.