Syntheses and ^{13}C NMR Investigations of an Extensive Series of [HB(3,5-$Me_2pz)_3$]Cd(alkyl) Complexes

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The complexes [HB(3,5-$Me_2pz)_3$]CdR (pz = pyrazolyl ring; R = methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *tert*-butyl, phenyl) are prepared by the reaction of dialkylcadmium complexes with 1 equiv of Tl[HB(3,5-$Me_2pz)_3$]. These complexes are air stable in the solid phase and do not thermally decompose in solution below 80 °C. They undergo ligand-exchange reactions with dialkylcadmium compounds and poly(pyrazolyl)borate complexes of cadmium. The effect of the [HB(3,5-$Me_2pz)_3$]Cd group on the chemical shifts in the ^{13}C NMR spectra of alkyl carbon atoms has been determined. The chemical shifts of the metal-bonded alkyl carbon atoms, especially for the methyl derivative (−17.98 ppm), are shifted to an unusually high field.

Introduction

We have recently demonstrated that the poly(pyrazolyl)borate family of ligands are extremely well-suited for the formation of unusually stable complexes of the metals in groups 13 and 14.[1] In particular, we have been able to prepare a series of air-stable alkylgallium and alkylindium complexes such as $[H_2B(pz)_2]M(CH_3)_2$, $[H_2B(pz)_2]_2MCH_3$, and $[B(pz)_4]_2MCH_3$ (pz = pyrazolyl ring).[1a-c,f] Given our long-standing interests in the syntheses and investigations of alkylmetal complexes,[2] we are expanding these efforts to include other alkyl groups with these metals and, in addition, alkylmetal complexes of other post-transition metals.

Cadmium is a metal of particular importance to us. We are interested in examining the types of complexes that can be prepared with this metal using the poly(pyrazolyl)borate ligands, an area of chemistry that is virtually unexplored.[3] An important driving force for this chemistry is the fact that cadmium has two important isotopes that are NMR active with spins = 1/2. A number of research groups have been using ^{113}Cd NMR as a "spin spy" in the study of zinc-containing proteins.[4] The strategy here is to replace the zinc, a metal with few good spectroscopic handles, with cadmium and use NMR to explore the properties of the proteins.

We have initiated an investigation into the synthesis and characterization of complexes of the type LCdR where L is a polydentate, anionic ligand. Reported here are the syntheses and characterizations of a series of stable, complexes of the type [HB(3,5-$Me_2pz)_3$]Cd(alkyl) (alkyl = methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *tert*-butyl) and [HB(3,5-$Me_2pz)_3$]Cd(phenyl). The ^{13}C NMR chemical shift values of these complexes have been analyzed to give the group additivity of the [HB(3,5-$Me_2pz)_3$]Cd substituent. Solution and solid-state ^{113}Cd NMR studies on these complexes will be reported separately.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere either by standard Schlenk techniques or in a Vacuum Atmospheres HE-49 drybox. All solvents were dried, degassed, and distilled prior to use. The ^1H and ^{13}C solution NMR spectra were recorded on a Bruker AM300 or AM500 spectrometer using a 5-mm broad-band probe. Proton and ^{13}C chemical shifts are reported in ppm vs Me_4Si. The gated decoupling mode was used to determine the ^{13}C NMR spectra for the methyl and ethyl compounds; other ^{13}C spectra were acquired with broad-band proton decoupling. Refocused INEPT sequences were carried out to verify the assignments of the alkyl ligands resonances in the ^{13}C NMR spectra.[5] The cadmium coupling constants reported are for the ^{113}Cd isotope. The ^{111}Cd coupling constants are 4.4% smaller. Melting points were measured at atmospheric pressure using differential scanning calorimetry on a Perkin-Elmer DSC7 instrument. Mass spectra were run on a Finnigan 4521 GC-mass spectrometer or a VG 70SQ spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present.

K[HB(3,5-$Me_2pz)_3$] was prepared according to the published method.[6] Tl[HB(3,5-$Me_2pz)_3$] was prepared from K[HB(3,5-$Me_2pz)_3$] in a method analogous to that reported for Tl[HB(3-$Bu^tpz)_3$].[7] Anhydrous $CdCl_2$; methyl- (in diethyl ether), *n*-butyl- (in hexanes), *sec*-butyl- (in cyclohexane), and *tert*-butyllithium (in pentane); and ethyl-, *n*-propyl-, isopropyl-, and isobutylmagnesium chloride (in diethyl ether) were purchased from Aldrich Chemical Co. Phenyllithium (in cyclohexane–diethyl ether) was purchased from Alfa. These reagents were used as received. Elemental analyses were performed by Robertson Laboratory, Inc. Molecular weights were determined by freezing point depression measurements in an apparatus similar in basic

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design to that described by Schriver.[8] A working calibration curve of ΔT verses molality was obtained by using known concentrations of doubly sublimed ferrocene. Data acquisition and processing were automated by interfacing the apparatus to a Gateway 2000 486/33C computer. Typically, the mass of a sample was determined on a benchtop analytical balance, and the sample was then quickly transported into the drybox. The solute and solvent were then introduced to the cryoscopy cell under the nitrogen atmosphere.

Note: Cadmium and thallium compounds and their wastes are extremely toxic and must be handled carefully.

[Tris(3,5-dimethyl-1-pyrazolyl)borato](methyl)cadmium(II), {[HB(3,5-Me$_2$pz)$_3$]CdCH$_3$}. $CdCl_2$ (0.25 g, 1.4 mmol) was suspended in $(CH_3CH_2)_2O$ (20 mL) and the suspension cooled to −78 °C. CH_3Li (2.0 mL, 1.4 M, 2.8 mmol) was added via syringe and the solution allowed to warm to room temperature (1 h). A solution of Tl[HB(3,5-Me$_2$pz)$_3$] (0.60 g, 1.2 mmol) in THF (20 mL) was added via cannulae and the resulting black solution stirred for 2 h. The solvent was removed under vacuum and the resulting black solid extracted with benzene (25 mL) and filtered. The benzene was removed under vacuum to yield a white solid. This solid was extracted with toluene (20 mL) and filtered, and the toluene was removed under vacuum, leaving a white solid (0.38 g, 0.90 mmol, 66%); sublimation point (756 Torr) = 266 °C. ^{1}H NMR ($CDCl_3$): δ 5.70 (s; 3; 4-H pz*); 2.35, 2.22 (s, s; 9, 9; 3,5-CH_3 pz*); −0.28 (s; 3; J_{CdH} = 38.7 Hz; CH_3). ^{13}C NMR ($CDCl_3$): δ 148.97, 145.23 (3,5-C pz*); 104.98 (d; J_{CH} = 172.2 Hz; 4-C pz*); 13.92, 13.17 (q, q; J_{CH} = 127.0 Hz; 3,5-CH_3 pz*); −17.98 (q; J_{CH} = 126.1 Hz, J_{CdC} = 491.2 Hz; CH_3). Mass spectrum: *m/z* 425 (M^+ − H), 411 (M^+ − CH_3). Anal. Calcd for $C_{16}H_{25}BCdN_6$: C, 45.25; H, 5.95; N, 19.79. Found: C, 45.09; H, 5.70; N, 19.75. Cryoscopic molecular weight (benzene), calcd formula weight 425 (observed molality, observed molecular weight): 0.0485, 431; 0.0414, 441.

[Tris(3,5-dimethyl-1-pyrazolyl)borato](ethyl)cadmium(II), {[HB(3,5-Me$_2$pz)$_3$]CdCH$_2$CH$_3$}. $CdCl_2$ (0.25 g, 1.4 mmol) was suspended in $(CH_3CH_2)_2O$ (20 mL) and cooled to −78 °C. Ethylmagnesium chloride (1.4 mL, 2.0 M, 2.8 mmol) was added via syringe, and the solution was allowed to warm to room temperature (1 h). The solution was concentrated to a thick slurry, extracted with benzene (20 mL), and filtered. Solid Tl[HB(3,5-Me$_2$pz)$_3$] (0.60 g, 1.2 mmol) was added to the solution. The resulting black solution was stirred for 2 h and filtered. The solvent was removed under vacuum to leave a white solid. This solid was extracted with toluene (20 mL) and filtered, and the toluene was removed under vacuum to yield a white solid (0.18 g, 0.41 mmol, 30%); mp = 247 °C. ^{1}H NMR ($CDCl_3$): δ 5.70 (s; 3; 4-H pz*); 2.35, 2.22 (s, s; 9, 9; 3,5-CH_3 pz*); 1.52 (t; 3; J_{HH} = 8.0 Hz; J_{CdH} = 43.5 Hz; CH_2CH_3); 0.78 (q; 2; J_{HH} = 8.1 Hz; J_{CdH} = 44.2 Hz; CH_2). ^{13}C NMR ($CDCl_3$): δ 148.80, 145.25 (3,5-C pz*); 104.98 (d; J_{CH} = 172.3 Hz; 4-C pz*); 15.65 (q; J_{CH} = 123.7 Hz, J_{CdC} = 19.4 Hz; CH_2CH_3); 13.98, 13.17 (q, q; J_{CH} = 127.1 Hz, 3,5-CH_3 pz*); −0.59 (t; J_{CH} = 125.0 Hz, J_{CdC} = 473.6 Hz; CH_2). Mass spectrum: *m/z* 439 (M^+ − H), 411 (M^+ − C_2H_5). Anal. Calcd for $C_{17}H_{27}BCdN_6$: C, 46.54; H, 6.22; N, 19.16. Found: C, 46.82; H, 6.31; N, 19.59. Cryoscopic molecular weight (benzene), calcd formula weight 439 (observed molality, observed molecular weight): 0.0269, 461; 0.0281, 441.

[Tris(3,5-dimethyl-1-pyrazolyl)borato](*n*-propyl)cadmium(II), {[HB(3,5-Me$_2$pz)$_3$]CdCH$_2$CH$_2$CH$_3$}. This complex was prepared as above for the ethyl analog in 35% yield; mp = 239 °C. ^{1}H NMR ($CDCl_3$): δ 5.71 (s; 3; 4-H pz*); 2.36, 2.22 (s, s; 9, 9; 3,5-CH_3 pz*); 1.89 (m; 2; J_{HH} = 7.3 Hz; J_{CdH} = 41.0 Hz; CH_2CH_3); 1.10 (t; 3; J_{HH} = 7.2 Hz; CH_2CH_3); 0.96 (t; 2; J_{HH} = 7.5 Hz; J_{CdH} = 43.8 Hz; $CdCH_2$). ^{13}C NMR ($CDCl_3$): δ 148.86, 145.22 (3,5-C pz*); 105.02 (4-C pz*); 24.09 (J_{CdC} = 17.0 Hz; CH_2CH_3); 22.26 (J_{CdC} = 32.2 Hz; CH_2CH_3); 14.02, 13.19 (3,5-CH_3 pz*); 12.26 (J_{CdC} = 487.1 Hz; $CdCH_2$). Mass spectrum: *m/z* 453 (M^+ − H), 411 (M^+ − C_3H_7). Anal. Calcd for $C_{18}H_{29}BCdN_6$: C, 47.75; H, 6.47; N, 18.57. Found: C, 48.02; H, 6.25; N, 18.77.

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[Tris(3,5-dimethyl-1-pyrazolyl)borato](isopropyl)cadmium(II), {[HB(3,5-Me$_2$pz)$_3$]CdCH(CH$_3$)$_2$. This complex was prepared as above for the ethyl analog in 16% yield; mp = 234 °C. ^{1}H NMR ($CDCl_3$): δ 5.70 (s; 3; 4-H pz*); 2.34, 2.23 (s, s; 9, 9; 3,5-CH_3 pz*); 1.59 (d; 6; J_{HH} = 6.7 Hz; J_{CdH} = 41.6 Hz; $CH(CH_3)_2$); 0.77 (m; 1; CH). ^{13}C NMR ($CDCl_3$): δ 148.71, 145.28 (3,5-C pz*); 105.04 (4-C pz*); 26.88 ($CH(CH_3)_2$); 15.67 (CH); 14.09, 13.19 (3,5-CH_3 pz*). Mass spectrum: *m/z* 452 (M^+ − 2H), 411 (M^+ − C_3H_7).

[Tris(3,5-dimethyl-1-pyrazolyl)borato](*n*-butyl)cadmium(II), {[HB(3,5-Me$_2$pz)$_3$]Cd(CH$_2$)$_3$CH$_3$}. This complex was prepared as above for the methyl analog in 62% yield; mp = 241 °C. ^{1}H NMR ($CDCl_3$): δ 5.71 (s; 3; 4-H pz*); 2.35, 2.23 (s, s; 9, 9; 3,5-CH_3 pz*); 1.83 (m; 2; J_{HH} = 7.5 Hz; J_{CdH} = 35.5 Hz; $CdCH_2CH_2$); 1.42 (m; 2; J_{HH} = 7.4 Hz; $CdCH_2CH_2CH_2$); 0.941 (t; 3; J_{HH} = 7.3 Hz; CH_2CH_3); 0.936 (t; 2; J_{HH} = 7.7 Hz; J_{CdH} = 42.2 Hz; $CdCH_2$). ^{13}C NMR ($CDCl_3$): δ 148.85, 145.22 (3,5-C pz*); 105.02 (4-C pz*); 33.23 (J_{CdC} = 16.9 Hz; $CdCH_2CH_2$); 30.91 (J_{CdC} = 31.7 Hz; $CdCH_2CH_2CH_2$); 14.50 (CH_2CH_3); 14.01, 13.19 (3,5-CH_3 pz*); 9.16 (J_{CdC} = 508.9 Hz; $CdCH_2$). Mass spectrum: *m/z* 467 (M^+ − H), 411 (M^+ − C_4H_9). Anal. Calcd for $C_{19}H_{31}BCdN_6$: C, 48.89; H, 6.70; N, 18.01. Found: C, 49.18; H, 6.73; N, 18.01.

[Tris(3,5-dimethyl-1-pyrazolyl)borato](*sec*-butyl)cadmium(II), {[HB(3,5-Me$_2$pz)$_3$CdCH(CH$_3$)CH$_2$CH$_3$}. This complex was prepared as above for the methyl analog in 67% yield; dec pt 262 °C. ^{1}H NMR ($CDCl_3$): δ 5.71 (s; 3; 4-H pz*); 2.35, 2.23 (s, s; 9, 9; 3, 5-CH_3 pz*); 1.83 (m; 2; J_{HH} = 6.1, 7.1 Hz; J_{CdH} = 44.8 Hz; CH_2); 1.49 (d; 3; J_{HH} = 6.6 Hz; $CH(CH_3)$); 1.26 (m; 1; CH); 1.12 (t; 3; J_{HH} = 7.2 Hz; CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 148.80, 145.26 (3,5-C pz*); 105.13 (4-C pz*); 33.61 (CH_2); 27.33 (CdCH); 23.72 (CH_2CH_3); 18.36 (J_{CdC} = 14.9 Hz; $CH(CH_3)$); 14.10, 13.23 (3,5-CH_3 pz*). Mass spectrum *m/z* 467 (M^+ − H), 411 (M^+ − C_4H_9). The accurate mass spectrum (*m/z*) for M^+ − H: calcd for $C_{19}H_{30}N_6{}^{11}B^{114}Cd$ 467.1659, found 467.1660.

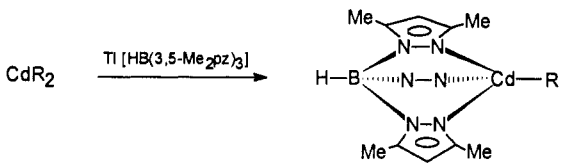
[Tris(3,5-dimethyl-1-pyrazolyl)borato](isobutyl)cadmium(II), {[HB(3,5-Me$_2$pz)$_3$]CdCH$_2$CH(CH$_3$)$_2$}. This complex was prepared as above for the ethyl analog in 51% yield; mp = 209 °C. ^{1}H NMR ($CDCl_3$): δ 5.71 (s; 3; 4-H pz*); 2.36, 2.24 (s, s; 9, 9; 3,5-CH_3 pz*); 1.20 (m; 1; CH); 1.08 (d; 6; J_{HH} = 6.5 Hz; $CH(CH_3)_2$); 1.01 (d; 2; J_{HH} = 6.9 Hz; J_{CdH} = 43.7 Hz; CH_2). ^{13}C NMR ($CDCl_3$): δ 148.95, 145.19 (3,5-C pz*); 105.10 (4-C pz*); 29.89 (J_{CdC} = 14.5 Hz; CH); 29.89 (J_{CdC} = 30.4 Hz; $CH(CH_3)_2$); 23.82 (CH_2); 14.13, 13.21 (3,5-CH_3 pz*). Mass spectrum: *m/z* 467 (M^+ − H), 411 (M^+ − C_4H_9). The accurate mass spectrum (*m/z*) for M^+ − H: calcd for $C_{19}H_{30}N_6{}^{11}B^{114}Cd$ 467.1659, found 467.1666.

[Tris(3,5-dimethyl-1-pyrazolyl)borato](*tert*-butyl)cadmium(II), {[HB(3,5-Me$_2$pz)$_3$]CdC(CH$_3$)$_3$}. This complex was prepared as above for the methyl analog in 47% yield; mp = 210 °C. ^{1}H NMR ($CDCl_3$): δ 5.72 (s; 3; 4-H pz*); 2.35, 2.25 (s, s; 9, 9; 3,5-CH_3 pz*); 1.41 (s; 9; J_{CdH} = 35.5 Hz; $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 148.71, 145.34 (3,5-C pz*); 105.18 (4-C pz*); 35.68 (J_{CdC} = 15.1 Hz; $C(CH_3)_3$); 27.97 (J_{CdC} = 438.6 Hz; $C(CH_3)_3$); 14.26, 13.22 (3,5-CH_3 pz*). Mass spectrum: *m/z* 411 (M^+ − C_4H_9). Anal. Calcd for $C_{19}H_{31}BCdN_6$: C, 48.89; H, 6.70; N, 18.01. Found: C, 48.97; H, 6.34; N, 17.78.

[Tris(3,5-dimethyl-1-pyrazolyl)borato](phenyl)cadmium(II), {[HB(3,5-Me$_2$pz)$_3$]CdC$_6$H$_5$} (9). This complex was prepared as above for the methyl analog in 46% yield; dec pt 205 °C. ^{1}H NMR ($CDCl_3$): δ 7.76 (m; 2; J_{HH} = 7.8 Hz; J_{CdH} = 27.4 Hz; ortho-H Ph); 7.32 (m; 2; J_{HH} = 7.4 Hz; meta-H Ph); 7.23 (t; 1; J_{HH} = 7.6 Hz; para-H Ph); 5.75 (s; 3; 4-H pz*); 2.38, 2.25 (s, s; 9, 9; 3,5-CH_3 pz*). ^{13}C NMR ($CDCl_3$): δ 154.24 (ipso); 149.23 (J_{CdC} = 13.8 Hz; ortho); 149.12, 145.63 (3,5-C pz*); 141.28 (meta); 127.93 (para); 105.19 (4-C pz*); 14.27, 13.25 (3,5-CH_3 pz*). Mass spectrum: *m/z* 487 (M^+), 411 (M^+ − C_6H_5). Anal. Calcd for $C_{21}H_{27}BCdN_6$: C, 51.82; H, 5.60; N, 17.27. Found: C, 51.87; H, 5.53; N, 17.27.

Results and Discussion

The reaction of dialkylcadmium complexes with 1 equiv of Tl[HB(3,5-$Me_2pz)_3$] yields the desired [HB(3,5-



R = methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, isobutyl, *tert*-butyl, phenyl

$Me_2pz)_3$]CdR complexes in good yield. The success of the reaction is indicated by formation of black thallium metal. In these preparations, the CdR_2 starting materials are generated *in situ* from the reaction of $CdCl_2$ and either alkyllithium or Grignard reagents, followed by addition of Tl[HB(3,5-$Me_2pz)_3$]. In the case of the Grignard reactions, the ether solutions of the dialkylcadmium preparation are first concentrated and then diluted with benzene and filtered prior to addition of the ligand. This procedure removes most of the magnesium salts and is needed to prevent formation of [HB(3,5-$Me_2pz)_3]_2Mg$. The ligand is added in a less than stoichiometric amount to limit the formation of [HB(3,5-$Me_2pz)_3]_2Cd$, an impurity that also forms in these reactions. This impurity (ca. 25%) is removed by a toluene extraction step in the workup.

These alkylcadmium complexes are soluble in aromatic and halocarbon solvents, but not in hydrocarbon solvents. Molecular weight studies show that the methyl and ethyl derivatives are monomeric in solution. They are air stable in the solid phase, but react slowly (days) in solution with oxygen. Above 80 °C, they undergo ligand redistribution in solution to produce [HB(3,5-$Me_2pz)_3]_2Cd$ and CdR_2. These reactions are analogous to the Schlenk equilibrium[9] and similar reactions have been reported for [HB(3,5-$Me_2pz)_3$]Mg(alkyl) complexes.[10]

The alkyl ligands in these alkylcadmium derivatives readily exchange with the alkyl groups in CdR_2 compounds. Mixing [HB(3,5-$Me_2pz)_3$]$CdCH_2CH_3$ with 0.5 equiv of $Cd(CH_3)_2$ in solution leads to the isolation of a 1/1 mixture of [HB(3,5-$Me_2pz)_3$]$CdCH_2CH_3$ and [HB(3,5-$Me_2pz)_3$]$CdCH_3$. Exchange in solution also occurs when [HB(3,5-$Me_2pz)_3$]$CdCH_2CH_3$ and [B(3-Mepz)$_4$]$CdCH_3$[11] are mixed to form a mixture of these two complexes and [HB(3,5-$Me_2pz)_3$]$CdCH_3$ and [B(3-Mepz)$_4$]$CdCH_2CH_3$. These reactions are not necessarily "alkyl" exchange reactions because mixing [HB(3,5-$Me_2pz)_3$]$CdCH_3$ and [B(3-Mepz)$_4]_2Cd$[11] in solution leads to the formation of [B(3-Mepz)$_4$]$CdCH_3$, indicating that the poly(pyrazolyl)-borate ligands can also undergo exchange reactions.

These [HB(3,5-$Me_2pz)_3$]CdR complexes represent the first extensive series of (ligand)Cd(alkyl) complexes, where ligand = monoanionic, chelate ligand, to be prepared to date. They add to the growing list of organometallic complexes of the post-transition metals that also contain poly(pyrazolyl)borate ligands.[1a-c,12]

Table I. ^{13}C Shielding Effects for Saturated Carbon Atoms, [HB(3,5-$Me_2pz)_3$]Cd, and (η^5-C_5H_5)Fe(CO)(PPh_3)

	α	β	γ
saturated carbon atoms	9.1	9.4	−2.5
[HB(3,5-$Me_2pz)_3$]Cd	−5.9	9.8	7.4
(η^5-C_5H_5)Fe(CO)(PPh_3)	−9.0	15.4	3.4

Carbon-13 NMR Studies. The ^{13}C NMR parameters for these new alkylcadmium complexes are given in the Experimental Section. As we have noted previously with alkyliron complexes,[13] the α-carbon atom of the alkyl chain is significantly shielded, especially for the methyl complex. In fact, the resonance position for the methyl group in [HB(3,5-$Me_2pz)_3$]$CdCH_3$, −17.98 ppm, might not be included in the window of some standard conditions established for obtaining ^{13}C NMR spectra. These chemical shift values for methylmetal compounds are almost as characteristic for this functional group as the highly shielded ^1H NMR resonances are for metal hydrides.[14]

Parkin has reported similar shielding effects for the alkyl derivatives of poly(pyrazolyl)borate complexes of magnesium, aluminum, and zinc. The methylmagnesium resonance for [HB(3,5-$Me_2pz)_3$]$MgCH_3$ is at −17.1 ppm, and for other methyl derivatives of these metals coordinated to the bulky [HB(3-$Bu^tpz)_3$] ligand the resonances range from −2.8 to −5.2 ppm.[7,12]

Empirical correlations of ^{13}C NMR chemical shifts have been effective in predicting the chemical shifts of many organic compounds. In this procedure, the chemical shift of a given carbon atom is calculated from a table of constants that reflect the effect of replacing a hydrogen atom, α, β, γ, etc., with a given substituent. We have used the method of Lindeman and Adams[15] to calculate the effect of replacing a hydrogen atom in a saturated alkane with the [HB(3,5-$Me_2pz)_3$]Cd group. These values are listed in Table I, along with the values for saturated carbon atoms and those calculated earlier for $CpFe(CO)(PPh_3)$.[16] Most notable is the large α-shielding effect for both the metal systems and the large γ-deshielding effect for [HB(3,5-$Me_2pz)_3$]Cd. Good agreement between calculated and observed values is noted except at carbon atoms bonded to two or more other carbon atoms. Deviations at branched carbon atoms are not surprising, given the considerable steric effects expected from the bulky [HB(3,5-$Me_2pz)_3$]Cd group.

These predicted values were used to help sort out the assignment of the ^{13}C spectrum of [HB(3,5-$Me_2pz)_3$]-$CdCH_2CH(CH_3)_2$. The spectrum of this complex ($CDCl_3$) in the alkyl region shows a resonance at 23.3 ppm that is clearly assigned to the methylene carbon atom, two

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resonances at 13.2 and 14.2 ppm that are assigned to the methyl groups on the [HB(3,5-Me$_2$pz)$_3$] ligand, and only one additional resonance at 29.9 ppm. The calculations predicted that the methine (33.3 ppm) and methyl (32.0 ppm) resonances would be located in the same region of the spectrum as this remaining resonance. A C–H correlated 2-D NMR spectrum demonstrated that these two resonances have the same chemical shifts (are isochronous), even at 126 MHz. This conclusion was verified by the observation of two sets of ^{113}Cd satellite resonances about the 29.9 ppm resonance with J = 14.5 Hz (two-bond coupling) and 30.4 Hz (three-bond coupling). Also, these two resonances are not isochronous in spectra run in benzene.

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