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Indium(III) dihydrobis(pyrazolyl)borate complexes. Crystal and molecular structures of {[H2B(pz)2]In(CH3)Cl}2 and [H2B(pz)2]In(CH3)2

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Indium(III) Dihydrobis(pyrazolyl)borate Complexes. Crystal and Molecular Structures of $\{[H_2B(pz)_2]In(CH_3)Cl\}_2$ and $[H_2B(pz)_2]In(CH_3)_2$

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The reaction of $InCl_3$ with 1, 2 and 3 equiv of $K[H_2B(pz)_2]$ (pz = pyrazolyl ring) yields $[H_2B(pz)_2]InCl_2$ (**1**), $[H_2B(pz)_2]_2InCl$ (**2**), and $[H_2B(pz)_2]_3In$ (**3**), respectively. The methyl complexes $[H_2B(pz)_2]_2InCH_3$ (**4**) and $[H_2B(pz)_2]In(CH_3)Cl$ (**5**) are prepared from the reaction of CH_3InCl_2 with 2 and 1 equiv of $K[H_2B(pz)_2]$, respectively. Complex **5** is also formed by an exchange reaction between $(CH_3)_2InCl$ and **2**. The dimethyl complex $[H_2B(pz)_2]In(CH_3)_2$ (**6**) is prepared by the reaction of $(CH_3)_2InCl$ and 1 equiv of $K[H_2B(pz)_2]$. The reaction of $InCl_3$ with 1 equiv of $Na(O_2CCH_3)$ and 2 equiv of $K[H_2B(pz)_2]$ yields $[H_2B(pz)_2]_2In(O_2CCH_3)$ (**7**). Complex **7** can also be prepared by the reaction of complexes **3** and **4** with CH_3CO_2H and by the reaction of **2** with $Na(O_2CCH_3)$. $\{[H_2B(pz)_2]In(CH_3)(O_2CCH_3)\}_2$ (**8**) is formed by the reaction of $K[H_2B(pz)_2]$ and $Na(O_2CCH_3)$ with CH_3InCl_2. Complex **8** can also be obtained from the reaction of **6** with CH_3CO_2H. Compounds **2**–**8** are stable to air for extended periods of time. Molecular weight studies in benzene indicate that complexes **4**–**6** are monomeric. Molecular weight determinations for **7** in benzene yield a value between a monomer and a dimer. Complex **8** is a dimer in benzene solution. An X-ray crystallographic study shows that **5** is dimeric in the solid state with a highly asymmetric $In(\mu\text{-}Cl)_2In$ bridging unit and a distorted-trigonal-bipyramidal geometry about the indium: triclinic, $P\bar{1}$, $a = 7.6001\ (14)$ Å, $b = 8.6133\ (14)$ Å, $c = 19.960\ (4)$ Å, $\alpha = 79.086\ (15)°$, $\beta = 85.966\ (16)°$, $\gamma = 67.340\ (13)°$, $V = 1184.0\ (3)$ Å^3, $Z = 4$, $R(F) = 2.80\%$. The solid-state structure of **6** is monomeric with a distorted-tetrahedral geometry about indium: orthorhombic, $Pn2_1a$, $a = 13.482\ (6)$ Å, $b = 9.008\ (5)$ Å, $c = 9.761\ (4)$ Å, $V = 1179.7\ (8)$ Å^3, $Z = 4$, $R(F) = 2.45\%$.

Introduction

Our previous investigations[1] of poly(pyrazolyl)borate ligands to form stable complexes with group 3 metals and the lanthanides initiated our interest in the group 13 metals. The main similarity, of course, between the groups is that the chemistries of both are dominated by the +3 oxidation state. Also, both have many orbitals available (although somewhat high in energy for the main-group metals) to accept electrons, making steric saturation an important factor determining the chemistry of the metal. Our interests lie particularly in the use of anionic, chelating ligands to form stable organometallic complexes of main-group metals.

In our initial publications, we have reported the synthesis and characterization of a family of gallium dihydrobis(pyrazolyl)borate compounds of the general formula $[H_2B(pz)_2]_mGaCl_n(CH_3)_p$ $(m + n + p = 3)$.[2] As was anticipated, the dihydrobis(pyrazolyl)borate ligand has yielded exceptionally stable group 13 metal complexes. We have also prepared dihydrobis(pyrazolyl)borate compounds of gallium containing chelating acetate ligands.[2b] Previous to our work, Cowley reported the hydrotris(pyrazolyl)borate complex $\{[HB(3,5\text{-}Me_2pz)_3]_2Ga\}GaCl_4$.[3] Very recently, the synthesis of $R_2B(pz)_2Ga(CH_3)_2$ (R = H, CH_3) has been reported.[4] In addition, two complexes of indium, $[HB(3,5\text{-}Me_2pz)_3]InCl_2(NCCH_3)$[3] and $[H_2B(pz)_2]_3In$,[5] have been reported. There is also a recent report of poly(pyrazolyl)borate complexes of aluminum.[6] Reported here is the preparation and characterization of dihydrobis(pyrazolyl)borate complexes of indium analogous to those we prepared with gallium, including the solid-state structures of $\{[H_2B(pz)_2]In(CH_3)Cl\}_2$ and $[H_2B(pz)_2]In(CH_3)_2$.

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. Infrared spectra were recorded on a Nicolet DX V4.56 spectrometer. The ^1H solution NMR spectra were recorded on a Bruker AM300 spectrometer using a 5-mm broad-band probe. Proton chemical shifts are reported in ppm vs Me_4Si. In each $[H_2B(pz)_2]$ complex, the BH_2 resonance is a broad (covers ca. 1.3 ppm) quartet with the center located as indicated for each compound. 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. Elemental analyses were performed by Robertson Laboratory, Inc. $K[H_2B(pz)_2]$[7] was prepared by the published method. Anhydrous $InCl_3$ was purchased from Cerac Inc. and $InCl_3{\cdot}4H_2O$ from Alfa. Molecular weights were determined by freezing point depression measurements in an apparatus similar in basic design to that described by Shriver.[8] The cell contains a Fenwal GB41P2 10-kΩ thermistor, balanced against a Leeds & Northrup bridge circuit. A working calibration curve of ΔT versus molality was obtained by

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using known concentrations of doubly sublimed ferrocene. Data acquisition and processing were automated by interfacing the apparatus to a WYSE 286 computer. Typically, the mass of a sample was determined on a benchtop analytical balance and the sample then quickly transported into the drybox. The solute and the solvent were then introduced to the cryoscopy cell under the nitrogen atmosphere.

[Dihydrobis(1-pyrazolyl)borato]dichloroindium(III), {$[H_2B(pz)_2]InCl_2$} (1). $K[H_2B(pz)_2]$ (0.45 g, 2.4 mmol) in THF (60 mL) was added dropwise to a solution of $InCl_3$ (0.60 g, 2.7 mmol) in THF (20 mL). The mixture was stirred at room temperature for 8 h. The solvent was then evaporated under vacuum. The white residue was extracted with CH_2Cl_2 (45 mL) and the extract filtered. CH_2Cl_2 was removed under vacuum to yield a white solid (0.64 g). NMR spectra of this solid indicate the presence of ca. 15% pyrazolyl-containing impurities (about half of which is 2). Attempts at purification lead to decomposition of 1. ^1H NMR ($CDCl_3$, δ): 7.65, 7.41 (2, 2; d, broad; J = 1.8 Hz; 3-H, 5-H (pz)); 6.23 (2; t; J = 2.2 Hz; 4-H (pz)); 3.7 (broad, BH_2). The mass spectrum shows clusters for $M^+ - HCl + pz$ and $M^+ - H$ at *m/e* 363 and 331. The accurate mass spectrum for $M^+ - H$ is as follows (*m/e*): calcd for $C_6H_7N_4{}^{11}B^{35}Cl_2{}^{115}In$, 330.9181; found, 330.9180.

Bis[dihydrobis(1-pyrazolyl)borato]chloroindium(III), {$[H_2B(pz)_2]_2InCl$} (2). $InCl_3\cdot 4H_2O$ (1.00 g, 0.34 mmol) and $K[H_2B(pz)_2]$ (1.27 g, 0.68 mmol) were placed in a round-bottomed flask. CH_2Cl_2 (60 mL) was added via syringe; the mixture was stirred at room temperature for 5 h and then filtered. CH_2Cl_2 was removed under vacuum to yield a white solid (1.35 g, 0.30 mmol, 89%), mp 140–141 °C. ^1H NMR ($CDCl_3$, δ): 7.68, 6.99 (4, 4; d, d; J = 1.7, 1.8 Hz; 3-H, 5-H (pz)); 6.14 (4; t; J = 2.2 Hz; 4-H (pz)); 3.5 (broad, BH_2). IR (toluene, cm^{-1}): 2423, 2390 (BH_2). The mass spectrum shows $M^+ - 4H$, $M^+ - H_3Bpz$, and $M^+ - H_3Bpz - Cl$ clusters at *m/e* 440, 363, and 328. Anal. Calcd for $C_{12}H_{16}N_8B_2ClIn$: C, 32.45; H, 3.64. Found: C, 32.53; H, 4.20.

Tris[dihydrobis(1-pyrazolyl)borato]indium(III), {$[H_2B(pz)_2]_3In$} (3). $InCl_3\cdot 4H_2O$ (1.00 g, 3.4 mmol) and $K[H_2B(pz)_2]$ (1.90 g, 10 mmol) were placed in a round-bottomed flask. THF (30 mL) was added via syringe, and the mixture was stirred at room temperature for 5 h. The solvent was then evaporated under vacuum. The residue was extracted with benzene (30 mL) and filtered. The benzene was removed under vacuum to yield a white solid (1.50 g, 2.7 mmol, 79%), mp 165–168 °C. ^1H NMR ($CDCl_3$, δ): 7.68, 6.98 (6, 6; d, d; J = 2.1 Hz; 3-H, 5-H (pz)); 6.13 (6; t; J = 2.2 Hz; 4-H (pz)); 3.5 (broad, BH_2). These values match those reported earlier.[6] IR (benzene, cm^{-1}): 2423, 2395 (BH_2). The mass spectrum shows $M^+ - H$ and $M^+ - H_2B(pz)_2$ clusters at *m/e* 555 and 408. Anal. Calcd for $C_{18}H_{24}N_{12}B_3In$: C, 38.91; H, 4.36. Found: C, 38.69; H, 4.29.

Bis[dihydrobis(1-pyrazolyl)borato]methylindium(III), {$[H_2B(pz)_2]_2InCH_3$} (4). $InCl_3$ (0.80 g, 3.6 mmol) and $(CH_3)_4Sn$ (0.50 mL, 3.6 mmol) were placed in a round-bottomed flask equipped with a condenser. The mixture was heated at reflux for 45 min. All volatiles were removed under vacuum, and the resultant white solid of CH_3InCl_2[9] was washed with hexane (2 × 20 mL). THF (10 mL) was added and the solution filtered. $K[H_2B(pz)_2]$ (1.34 g, 7.2 mmol) in THF (30 mL) was added, and the mixture was stirred at room temperature for 4 h. The solvent was then evaporated under vacuum. The white residue was extracted with benzene (30 mL) and the extract filtered. Benzene was removed under vacuum to yield a white solid (1.00 g, 2.4 mmol, 67%), mp 118–122 °C. ^1H NMR ($CDCl_3$, δ, ambient temperature): 7.63, 7.18 (4, 4; d, d; J = 2.1, 1.8 Hz; 3-H, 5-H (pz)); 6.19 (4; t; J = 2.1 Hz; 4-H (pz)); 3.6 (broad, BH_2); 0.34 (3; s; CH_3). ^1H NMR (C_7D_8, δ −80 °C): 7.38, 7.34, 6.83, 6.69 (2, 2, 2, 2; d, d, d, d; J = 2.1 Hz; 3-H, 5-H (pz)); 5.71, 5.61 (2, 2; t, t; J = 2.1 Hz; 4-H (pz)); 0.38 (3; s; CH_3). IR (benzene, cm^{-1}): 2457 (sh), 2435, 2398 (BH_2). The mass spectrum shows $M^+ - H$, $M^+ - CH_5$, and $M^+ - H_3Bpz$ clusters at *m/e* 423, 407, and 343. Anal. Calcd for $C_{13}H_{19}N_4B_2In$: C, 36.84; H, 4.53. Found: C, 36.97; H, 4.46. Cryoscopic molecular weight (benzene solution, formula weight 424; observed molality, observed molecular weight): 0.0356, 443; 0.0567, 417.

Chloro[dihydrobis(1-pyrazolyl)borato]methylindium(III), {$[H_2B(pz)_2]In(CH_3)Cl$} (5). 5 was prepared as in the preparation for 4 from $InCl_3$ (1.00 g, 4.5 mmol), $(CH_3)_4Sn$ (0.63 mL, 4.5 mmol), and $K[H_2B(pz)_2]$ (0.81 g, 4.4 mmol) to yield a white solid (1.20 g, 3.8 mmol, 84%), mp 98–100 °C. ^1H NMR ($CDCl_3$, δ): 7.73, 7.66 (2, 2; d, d; J = 2.1, 2.0 Hz; 3-H, 5-H (pz)); 6.31 (2; t; J = 2.2 Hz; 4-H (pz)); 3.6 (broad, (BH_2)); 0.59 (3; s; CH_3). IR (benzene, cm^{-1}): 2474, 2433 (BH_2). The mass spectrum shows $M^+ - H$ and $M^+ - Cl$ clusters at *m/e* 311 and 277. Anal. Calcd for $C_7H_{11}N_4BClIn$: C, 26.92; H, 3.55. Found: C, 27.02; H, 3.25. Cryoscopic molecular weight (benzene solution, formula weight 312; observed molality, observed molecular weight): 0.0408, 314; 0.0586, 329.

Dimethyl[dihydrobis(1-pyrazolyl)borato]indium(III), {$[H_2B(pz)_2]In(CH_3)_2$} (6). $InCl_3$ (1.00 g, 4.5 mmol) was suspended in diethyl ether (10 mL) and the suspension cooled to −78 °C. CH_3Li (9.0 mL, 9.0 mmol) was added via syringe. The suspension was stirred at room temperature for 2 days. To this solution of $(CH_3)_2InCl$[10] was added $K[H_2B(pz)_2]$ (0.85 g, 4.6 mmol), and the mixture was stirred overnight. Diethyl ether was then evaporated under vacuum. The white residue was extracted with hexane (40 mL) and the extract filtered. Hexane was removed under vacuum to yield a white solid (0.94 g, 3.2 mmol, 71%), mp 53–56 °C. ^1H NMR ($CDCl_3$, δ): 7.64, 7.50 (2, 2; d, d; J = 1.9 Hz; 3-H, 5-H (pz)); 6.23 (2; t; J = 2.1 Hz; 4-H (pz)); 3.6 (broad, BH_2); 0.09 (6; s; CH_3). IR (benzene, cm^{-1}): 2441 (sh), 2432, 2408 (BH_2). The mass spectrum shows clusters for $M^+ - H$, $M^+ - CH_3$, and $M^+ - C_2H_7$ at *m/e* 291, 277, and 261. Anal. Calcd for $C_8H_{14}N_4BIn$: C, 32.92; H, 4.84. Found: C, 33.29; H, 4.51. Cryoscopic molecular weight (benzene solution, formula weight 292; observed molality, observed molecular weight): 0.0447, 306; 0.0708, 290.

(Acetato)bis[dihydrobis(1-pyrazolyl)borato]indium(III), {$[H_2B(pz)_2]_2In(O_2CCH_3)$} (7). $InCl_3$ (0.500 g, 2.26 mmol), $K[H_2B(pz)_2]$ (0.840 g, 4.52 mmol), and $Na(O_2CCH_3)$ (0.185 g, 2.26 mmol) were placed in a round-bottomed flask. THF (50 mL) was added via syringe, and the mixture was stirred at room temperature for 5 h. The solvent was then evaporated under vacuum. The white residue was extracted with benzene (70 mL) and the extract filtered. Benzene was removed under vacuum to yield a white solid (1.01 g, 2.16 mmol, 96%); mp 166–170 °C. ^1H NMR ($CDCl_3$, δ): 7.65, 7.57 (4, 4; d, d; J = 2.1, 2.2 Hz; 3-H, 5-H (pz)); 6.26 (4; t; J = 2.2 Hz; 4-H (pz)); 3.6 (broad, BH_2); 2.22 (3; s; CH_3). IR (benzene, cm^{-1}): 2434 (sh), 2412 (BH_2); 1545 (CO_2). The mass spectrum shows $M^+ - H$, $M^+ - HO_2CCH_3$, and $M^+ - O_2CCH_3 - H_2B(pz)_2$ clusters at *m/e* 467, 407, and 261. Anal. Calcd for $C_{14}H_{19}N_8B_2O_2In$: C, 35.94; H, 4.10. Found: C, 35.82; H, 3.90. Cryoscopic molecular weight (benzene solution, formula weight 468; observed molality, observed molecular weight): 0.0314, 762; 0.0471, 752; 0.0647, 739.

Bis{(acetato)[dihydrobis(1-pyrazolyl)borato]methylindium(III)}, {$[H_2B(pz)_2]In(CH_3)(O_2CCH_3)$}$_2$ (8). $K[H_2B(pz)_2]$ (0.80 g, 4.3 mmol) and $Na(O_2CCH_3)$ (0.35 g, 4.3 mmol) in THF (40 mL) were added to CH_3InCl_2, prepared as in 4 from $InCl_3$ (1.00 g, 4.5 mmol) and $(CH_3)_4Sn$ (0.63 mL, 4.5 mmol). The mixture was stirred at room temperature for 8 h. The solvent was then evaporated under vacuum. The white residue was extracted with CH_2Cl_2 (40 mL) and the extract filtered. After the addition of hexane the solution was allowed to stand overnight to yield colorless crystals (1.27 g, 3.8 mmol, 84%), mp 88–90 °C. ^1H NMR ($CDCl_3$, δ): 7.73, 7.63 (2, 2; d, d; J = 2.1 Hz; 3-H, 5-H (pz)); 6.26 (2; t; J = 2.2 Hz; 4-H (pz)); 3.6 (broad, BH_2); 2.14 (3; s; O_2CCH_3); 0.38 (3; s; CH_3). IR (benzene, cm^{-1}): 2458 (sh), 2437, 2399 (sh) (BH_2); 1597, 1553, 1437 (CO_2). The mass spectrum shows clusters for $[M/2]^+ - H$, $[M/2]^+ - CH_3$, and $[M/2]^+ - O_2CCH_3$ at *m/e* 335, 321, and 277. Anal. Calcd for $C_9H_{14}N_4O_2BIn$: C, 32.18; H, 4.21. Found: C, 32.40; H, 3.65. Cryoscopic molecular weight (benzene solution, formula weight 672; observed molality, observed molecular weight): 0.0277, 712; 0.284, 691.

Crystallographic Analysis of 5 and 6. X-ray Data Collections for 5 and 6. Crystal, data collection, and refinement parameters for 5 and 6 are collected in Table I. Colorless crystals (5 grown from CH_2Cl_2–hexane at −20 °C and 6 grown from hexane at −70 °C) were mounted on glass fibers with epoxy cement. The unit-cell parameters were obtained from the least-squares fit of

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Table I. Crystallographic Data for 5 and 6

	5	6
	(a) Crystal Parameters	
formula	$[H_2B(pz)_2]In(CH_3)Cl$	$[H_2B(pz)_2]In(CH_3)_2$
space group	$P\bar{1}$	$Pn2_1a$
cryst syst	triclinic	orthorhombic
a, Å	7.6001 (14)	13.482 (6)
b, Å	8.6133 (14)	9.008 (5)
c, Å	19.960 (4)	9.761 (4)
α, deg	79.086 (15)	
β, deg	85.966 (16)	
γ, deg	67.340 (13)	
V, Å^3	1184.0 (3)	1179.7 (8)
Z	4	4
cryst dimens, mm	0.42 × 0.46 × 0.32	0.51 × 0.21 × 0.18
cryst color	colorless	colorless
D(calc), g/cm^3	1.751	1.635
μ(Mo Kα), cm^{-1}	24.18	19.44
temp, °C	23 (±1)	23 (±1)
T(max)/T(min)	1.130	1.106
	(b) Data Collection	
diffractometer	Nicolet R3m	
monochromator	graphite	
scan technique	Wyckoff	
radiation	Mo Kα (λ = 0.71073 Å)	
2θ scan range, deg	4–55	4–58
data collected	±10, ±12, +36	±19, +13, +14
scan speed, deg/min	var, 6–20	var, 4–20
no. of rflns collected	5669	3520
no. of indpt rflns	5425	1668
R(merg), %	1.05	1.55
no. of indpt rflns obs, $F_o \geq 5\sigma(F_o)$	4625	1175
std rflns	3 std/197 rflns	3 std/197 rflns
var in stds., %	<1%	<1%
	(c) Refinement	
$R(F)$, %	2.80	2.45
$R(wF)$, %	3.41	3.19
Δ/σ(max)	0.035	0.124
$\Delta(\rho)$, e/Å^3	0.631	0.633
N_o/N_v	18.2	16.6
GOF	1.158	1.037

25 reflections (20° ≤ 2θ ≤ 25°). Both data collections were at ambient temperatures (23 ± 1 °C). Preliminary photographic characterization showed $\bar{1}$ and *mmm* Laue symmetry for 5 and 6, respectively. For 5, the centrosymmetric alternative $P\bar{1}$ was suggested by E statistics and confirmed by the chemically sensible results of refinement. Systematic absences in the diffraction data of 6 established the space group as either *Pnma* or $Pn2_1a$. The noncentrosymmetric alternative $Pn2_1a$ was suggested by E statistics and confirmed through the chemically sensible results of refinement. Three standard reflections monitored every 197 reflections showed insignificant variations (<1% for 5 and 6). Empirical corrections for absorptions were applied to both sets (216 ψ-scan reflections, pseudoellipsoid model). The asymmetric unit for 5 consists of two chemically similar half-dimers.

Structure Solution and Refinement for 5 and 6. The indium atoms in 5 and 6 were located from Patterson syntheses. While the completion of the structure for 5 was straightforward, that for 6 was complicated by pseudo-mirror-plane duplication of difference-map peaks. It proved easier to create a completely mirror-plane-disordered structure in *Pnma*, then to remove the atoms extraneous to a single form of the molecule, and finally to refine this model in $Pn2_1a$ with a large damping factor. The correctness of the chosen enantiomorph was verified by convergence of both hands: $R(F)$ = 2.45% (as reported); $R(F)$ = 2.62% (opposite hand). All hydrogen atoms were included as idealized isotropic contributions (d(CH) = 0.960 Å, U = 1.2U of attached atom). All non-hydrogen atoms were refined with anisotropic thermal parameters. All computer programs and the sources of the scattering factors are contained in the SHELXTL program library (version 5.1, G. Sheldrick, Nicolet Corp., Madison, WI). Tables II and III contain the atomic coordinates and isotropic thermal parameters for 5 and 6, respectively, and Table IV contains selected bond distances and angles for both.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 5

	x	y	z	U^a
In	550.6 (3)	474.0 (6)	994.3 (1)	41.1 (1)
In′	297.5 (3)	−1200.0 (3)	4131.2 (1)	44.1 (1)
Cl	2369 (1)	−53 (1)	−31 (1)	54 (1)
Cl′	1891 (1)	391 (1)	4552 (1)	59 (1)
N(1)	2423 (4)	1472 (3)	1428 (1)	43 (1)
N(2)	1570 (4)	2742 (4)	1793 (1)	47 (1)
N(3)	−1591 (4)	4151 (4)	1193 (2)	50 (1)
N(4)	−1399 (4)	3093 (3)	738 (1)	45 (1)
C(1)	4267 (5)	1213 (5)	1389 (2)	58 (2)
C(2)	4618 (6)	2306 (6)	1724 (2)	66 (2)
C(3)	2884 (5)	3265 (6)	1967 (2)	59 (2)
C(4)	−2578 (6)	5735 (5)	908 (3)	71 (2)
C(5)	−3062 (7)	5768 (5)	248 (3)	79 (2)
C(6)	−2313 (5)	4094 (5)	175 (2)	59 (2)
C(7)	123 (7)	−1565 (6)	1660 (2)	69 (2)
B	−599 (5)	3400 (6)	1900 (2)	54 (2)
N(4′)	1562 (4)	−3719 (3)	4730 (1)	42 (1)
N(3′)	2494 (4)	−5067 (3)	4402 (1)	42 (1)
N(2′)	3294 (4)	−3668 (4)	3266 (1)	48 (1)
N(1′)	2602 (4)	−2014 (3)	3352 (1)	47 (1)
C(6′)	2011 (5)	−4288 (4)	5389 (2)	49 (1)
C(5′)	3196 (5)	−5981 (5)	5493 (2)	54 (1)
C(4′)	3458 (5)	−6416 (4)	4855 (2)	50 (1)
C(3′)	4837 (5)	−3938 (5)	2865 (2)	58 (2)
C(2′)	5152 (6)	−2472 (6)	2688 (2)	67 (2)
C(1′)	3748 (5)	−1284 (5)	3002 (2)	57 (2)
C(7′)	−2364 (6)	117 (6)	3632 (2)	72 (2)
B′	2273 (7)	−4874 (6)	3620 (2)	54 (2)

[a] Equivalent isotropic U, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 6

	x	y	z	U^a
In	7678.9 (2)	2500	2528.3 (3)	47.0 (1)*
N(1)	6784 (2)	4159 (5)	3731 (3)	48 (1)*
N(2)	6482 (3)	5458 (4)	3198 (4)	54 (1)*
N(3)	6855 (3)	3357 (5)	695 (4)	52 (1)*
N(4)	6462 (3)	4772 (4)	703 (3)	47 (1)*
B	6812 (4)	5940 (5)	1741 (6)	65 (1)*
Hba	6522	6887	1538	73
Hbb	7522	6015	1693	73
C(1)	5921 (3)	6182 (5)	4108 (4)	64 (1)*
C(2)	5845 (4)	5320 (6)	5262 (5)	73 (1)*
C(3)	6385 (4)	4055 (6)	4981 (4)	62 (1)*
C(4)	5796 (4)	4861 (7)	−308 (5)	66 (1)*
C(5)	5754 (4)	3551 (7)	−979 (4)	74 (1)*
C(6)	6431 (3)	2611 (7)	−322 (4)	66 (1)*
C(7)	9144 (4)	3407 (7)	2576 (4)	68 (1)*
C(8)	6882 (4)	492 (6)	2892 (5)	64 (1)*

[a] Asterisks denote equivalent isotropic U, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Results and Discussion

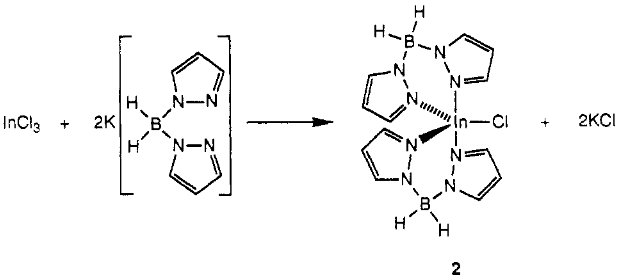
The reaction of $InCl_3$ with slightly less than 1 equiv of $K[H_2B(pz)_2]$ yields $[H_2B(pz)_2]InCl_2$ (**1**, eq 1). Complex

$$InCl_3 + K[H_2B(pz)_2] \rightarrow \underset{\mathbf{1}}{[H_2B(pz)_2]InCl_2} + KCl \quad (1)$$

1 is isolated from this reaction contaminated with other pyrazolyl-containing compounds (ca. 15%, mainly **2**, vide infra). Samples of the compound decomposed overnight, even when stored in a drybox or under vacuum. Attempts at the purification of **1** by recrystallization lead to sample decomposition. When exposed to air, **1** decomposes instantaneously both as a solid and in solution. **1** is the only dihydrobis(pyrazolyl)borate complex reported here that decomposed under these conditions. It is soluble in THF and halocarbon solvents, only slightly soluble in aromatic solvents, and insoluble in saturated hydrocarbon solvents. This limited solubility in comparison to that of the other complexes prepared here indicate that **1** is most likely oligomeric, in a fashion similar to that for several organometallic indium chloride compounds.[11-14]

The formation of **1** by the reaction of $InCl_3$ with 1 equiv of $K[H_2B(pz)_2]$ differs from the type of product obtained in a similar reaction with gallium. The reaction of $GaCl_3$ with 1 equiv of $K[H_2B(pz)_2]$ yields the salt $\{[H_2B(pz)_2]_2Ga\}GaCl_4$.[2b] Cowley has previously reported a similar result for the reaction of these two metal halides with a substituted hydrotris(pyrazolyl)borate ligand.[3]

The reaction of $InCl_3$ with 2 equiv of $K[H_2B(pz)_2]$ yields $[H_2B(pz)_2]_2InCl$ (**2**, eq 2). We propose that the structure of **2** is a trigonal bipyramid, analogous to the gallium analogue, which has been characterized crystallographically.[2a] Each dihydrobis(pyrazolyl)borate ligand occupies an equatorial and axial site with the chloride in the remaining equatorial site. It is a high-melting solid that is soluble in aromatic solvents and halocarbon solvents, but not in saturated hydrocarbon solvents. The complex is air-stable as a solid and in solution.



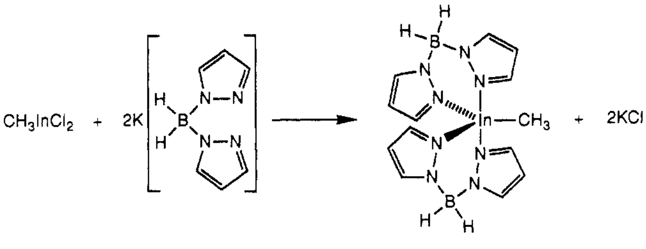
2

(2)

Finally, the reaction of $InCl_3$ with 3 equiv of $K[H_2B(pz)_2]$ results in the formation of $[H_2B(pz)_2]_3In$ (**3**, eq 3). This complex has been prepared previously by the reaction in water of the ligand salt and $In(NO_3)_3$ and has been characterized as pseudooctahedral in the solid state by X-ray crystallography.[5] Complex **3** is also a high-melting solid that is soluble in aromatic solvents as well as halocarbon solvents, but not in saturated hydrocarbon solvents.

$$InCl_3 + 3K[H_2B(pz)_2] \rightarrow \underset{\mathbf{3}}{[H_2B(pz)_2]_3In} + 3KCl \quad (3)$$

The organometallic complex $[H_2B(pz)_2]_2InCH_3$ (**4**) is synthesized from CH_3InCl_2 and 2 equiv of the ligand salt (eq 4). We developed an in situ preparation of CH_3InCl_2[9] from $InCl_3$ and $Sn(CH_3)_4$ in order to facilitate this preparation and the one reported below for $[H_2B(pz)_2]In(CH_3)Cl$. As with **2**, we propose that the structure of **4** is a trigonal bipyramid. This structure is supported by variable-temperature ^1H NMR results. At ambient temperature, the molecule is fluxional with only one resonance being observed for each of the three types of hydrogen atoms in the pyrazolyl rings. At −80 °C, each resonance type has split into two equal-intensity resonances, as expected for axial and equatorial pyrazolyl rings. There is no change observed in the methyl resonance. The barrier to the rearrangement process as calculated from the coalescence temperature of −55 °C from the resonance at δ 7.18 is 10.4 kcal/mol.



4

(4)

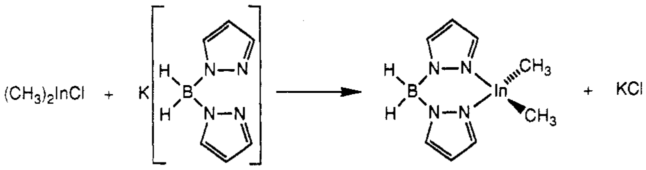
Complex **4** is a relatively high-melting solid that is freely soluble in aromatic solvents and halocarbon solvents, but not in saturated hydrocarbon solvents. The complex is stable in air both as a solid and in solution. Molecular weight studies in benzene show that this compound is monomeric in solution. It can also be prepared from the reaction of **2** with CH_3Li, but the reaction is not clean, yielding some of the dimethyl complex **6** (vide infra) and other byproducts. A similar result was observed in the reaction of $[H_2B(pz)_2]_2GaCl$ with CH_3Li.[2b]

The reaction of CH_3InCl_2 with 1 equiv of $K[H_2B(pz)_2]$ yields $[H_2B(pz)_2]In(CH_3)Cl$ (**5**, eq 5). This complex can also be formed by the exchange reaction of **2** with $(CH_3)_2InCl$ (eq 6). In this reaction, transmetalation of both a dihydrobis(pyrazolyl)borate ligand and a methyl ligand takes place. Complex **5** is freely soluble in aromatic solvents and halocarbon solvents and slightly soluble in saturated hydrocarbon solvents. The complex is stable in air as a solid and in solution. Molecular weight studies in benzene indicate that **5** is monomeric in solution. In contrast, a crystallographic analysis of the structure of **5** demonstrates that the complex is a weakly associated dimer in the solid state (Figure 1, vide infra).

$$CH_3InCl_2 + K[H_2B(pz)_2] \rightarrow \underset{\mathbf{5}}{[H_2B(pz)_2]In(CH_3)Cl} + KCl \quad (5)$$

$$[H_2B(pz)_2]_2InCl + (CH_3)_2InCl \rightarrow 2[H_2B(pz)_2]In(CH_3)Cl \quad (6)$$

The dimethyl compound $[H_2B(pz)_2]In(CH_3)_2$ (**6**) is prepared from $(CH_3)_2InCl$ as shown in eq 7. As with $(CH_3)InCl_2$, an in situ preparation of $(CH_3)_2InCl$[10] was developed for this reaction. An attempted preparation of the compound from $In(CH_3)_3$ and $K[H_2B(pz)_2]$ proved unsuccessful. Compound **6** is a relatively low-melting solid that is freely soluble in aromatic solvents and halocarbon solvents, as well as saturated hydrocarbon solvents. **6** is stable in air both as a solid and in solution. Molecular weight studies in benzene demonstrate that the complex is monomeric in solution. The crystallographic analysis of **6** shows it is also monomeric in the solid state (Figure 2, vide infra).



6

(7)

Reaction of $InCl_3$ with 2 equiv of $K[H_2B(pz)_2]$ and 1 equiv of $Na(O_2CCH_3)$ results in the formation of $[H_2B(pz)_2]_2In(O_2CCH_3)$ (**7**, eq 8). Complex **7** is a high-melting

$$InCl_3 + 2K[H_2B(pz)_2] + Na(O_2CCH_3) \rightarrow \underset{\mathbf{7}}{[H_2B(pz)_2]_2In(O_2CCH_3)} + 2KCl + NaCl \quad (8)$$

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Table IV. Selected Bond Distances and Angles for 5 and 6[a]

	5		6	
	molecule A	molecule B		
		(a) Bond Distances (Å)		
In-Cl	2.410 (1)	2.439 (1)	In-C(8)	2.133 (5)
In···Cl(a)	3.203 (1)	3.066 (1)		
In-C(7)	2.091 (5)	2.102 (4)	In-C(7)	2.138 (6)
In-N(4)	2.145 (2)	2.131 (2)	In-N(3)	2.243 (4)
In-N(1)	2.222 (3)	2.257 (3)	In-N(1)	2.251 (4)
N(1)-N(2)	1.365 (4)	1.359 (4)	N(3)-N(4)	1.380 (5)
N(3)-N(4)	1.378 (5)	1.377 (4)	N(1)-N(2)	1.344 (6)
N(2)-B	1.538 (5)	1.556 (6)	N(4)-B	1.535 (6)
N(3)-B	1.540 (5)	1.548 (5)	N(2)-B	1.551 (7)
		(b) Bond Angles (deg)		
Cl-In-C(7)	119.2 (1)	120.0 (1)	C(8)-In-C(7)	141.8 (2)
Cl-In-N(1)	95.9 (1)	91.5 (1)	C(8)-In-N(3)	100.1 (2)
Cl-In-N(4)	104.7 (1)	103.2 (1)	C(8)-In-N(1)	101.9 (2)
C(7)-In-N(1)	113.6 (2)	109.7 (1)	C(7)-In-N(3)	110.1 (2)
C(7)-In-N(4)	128.0 (1)	132.0 (2)	C(7)-In-N(1)	103.3 (2)
In-N(4)-N(3)	118.2 (2)	118.9 (2)	In-N(1)-N(2)	122.5 (2)
In-N(1)-N(2)	117.3 (2)	119.0 (2)	In-N(3)-N(4)	120.2 (2)
B-N(3)-N(4)	120.0 (3)	121.5 (2)	B-N(2)-N(1)	120.8 (4)
N(3)-B-N(2)	108.4 (3)	106.7 (4)	N(2)-B-N(4)	109.0 (4)
B-N(2)-N(1)	119.9 (3)	119.1 (3)	B-N(4)-N(3)	121.2 (3)
In-N(1)-C(1)	135.3 (3)	133.3 (3)	In-N(3)-C(6)	129.4 (4)
In-N(4)-C(6)	134.5 (3)	132.4 (2)	In-N(1)-C(3)	130.2 (3)
N(1)-In-N(4)	86.3 (1)	87.8 (1)	N(3)-In-N(1)	85.5 (1)
Cl-In-Cla	77.3 (1)	77.8 (1)		
In-Cl-Ina	102.7 (1)	102.2 (1)		
Cla-In-C(7)	83.3 (1)	85.7 (1)		
Cla-In-N(1)	162.9 (1)	164.3 (1)		
Cla-In-N(4)	80.3 (1)	93.8 (1)		

[a] Equivalent parameters in 5 and 6 are compared horizontally.

solid, soluble in aromatic solvents and halocarbon solvents, but not in saturated hydrocarbon solvents.

Compound 7 can also be prepared by the room-temperature reaction of CH_3CO_2H with either 3 or 4, resulting in the displacement of one dihydrobis(pyrazolyl)borate ligand and the elimination of the methyl ligand, respectively, and by the metathesis of the chloride in 2 with $Na(O_2CCH_3)$ (eqs 9–11). An analogous exchange reaction

$$[H_2B(pz)_2]_3In + CH_3CO_2H \rightarrow [H_2B(pz)_2]_2In(O_2CCH_3) + H[H_2B(pz)_2] \quad (9)$$

$$[H_2B(pz)_2]_2InCH_3 + CH_3CO_2H \rightarrow [H_2B(pz)_2]_2In(O_2CCH_3) + CH_4 \quad (10)$$

$$[H_2B(pz)_2]_2InCl + Na(O_2CCH) \rightarrow [H_2B(pz)_2]_2In(O_2CCH_3) + NaCl \quad (11)$$

(no attempt was made to isolate $H[H_2B(pz)_2]$, a known compound[7]) as in eq 9 also takes place for $[H_2B(pz)_2]_3Ga$. In contrast, acetic acid did not react with $[H_2B(pz)_2]_2GaCH_3$ under the conditions of reaction 10.[4b]

The determined molecular weight for 7 of 751 in benzene solution is between that expected for a monomer (molecular weight of 468) and a dimer (molecular weight of 936). A similar result was observed for the gallium analogue, even though in the solid state the gallium complex is a monomer.[2b]

The completely mixed-ligand compound $\{[H_2B(pz)_2]In(CH_3)(O_2CCH_3)\}_2$ (8) is formed by the reaction of stoichiometric amounts of the ligand salts with CH_3InCl_2 (eq 12). Compound 8 can also be prepared by the reaction

$$2CH_3InCl_2 + 2K[H_2B(pz)_2] + 2Na(O_2CCH_3) \rightarrow \underset{8}{\{[H_2B(pz)_2]In(CH_3)(O_2CCH_3)\}_2} + 2KCl + 2NaCl \quad (12)$$

of 6 and CH_3CO_2H (eq 13). Compound 8 is a relatively low-melting solid that is freely soluble in aromatic solvents and halocarbon solvents and sparingly soluble in saturated hydrocarbon solvents. It is also stable in air as a solid and in solution. Molecular weight studies show that this complex is a dimer in benzene solution. In contrast, the analogous gallium compound is a monomer in solution.[2b]

$$2[H_2B(pz)_2]In(CH_3)_2 + 2CH_3CO_2H \rightarrow \{[H_2B(pz)_2]In(CH_3)(O_2CCH_3)\}_2 + 2CH_4 \quad (13)$$

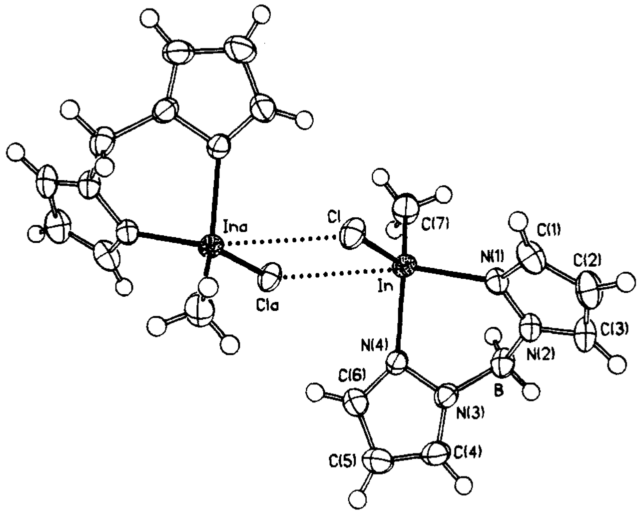

Figure 1. Molecular structure and labeling scheme for 5 drawn with 40% thermal ellipsoids. One of two independent molecules is shown. Each of the molecules is Cl-bridged through a crystallographic inversion center.

Molecular Structures of 5 and 6. An ORTEP drawing of 5 is shown in Figure 1; selected bond distances and angles are shown in Table IV. There are two crystallographically independent, but very similar, half-dimers, with each half of the dimeric unit related by an inversion center. The dimer is held together by a pair of very asymmetrically bonded chlorine atoms. The short In–Cl bond of 2.410 (1) Å (molecule A) is at the low end of the range typically

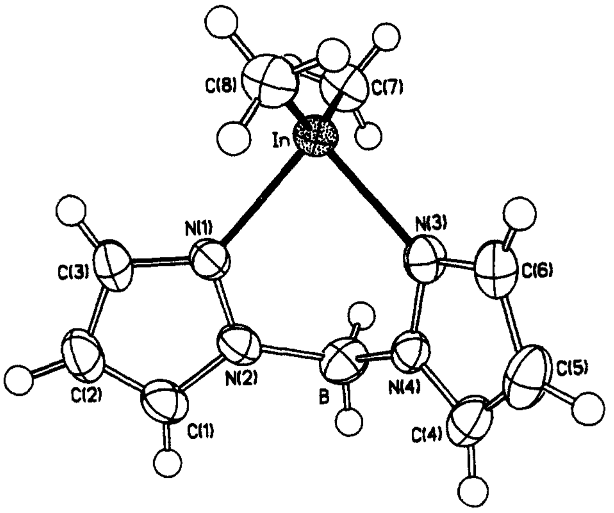

Figure 2. Molecular structure and labeling scheme for 6 drawn with 40% thermal ellipsoids.

found in other In(μ-Cl)$_2$In units (2.40–2.82 Å).[11,12] The second In–Cl bond (3.203 (1) Å) appears to be the longest yet observed for this bridging unit (it is shorter in molecule B, 3.066 (1) Å, the only major difference in bond distances between the two independent molecules). The same In–Cl distance of 3.203 (2) Å is observed in the polymeric structure of CH_3InCl_2 as well as a longer distance of 3.799 (3) Å.[13] Another long In–Cl distance of 3.450 (9) Å is reported in the polymeric structure of $(CH_3)_2InCl$.[14]

The geometry about the indium atom is best described as a distorted trigonal bipyramid with the axial positions occupied by the bridging chlorine atom with the long In–Cl bond (Cl(a)) and N(1) of the dihydrobis(pyrazolyl)borate ligand. The N(1)–In–Cl(a) bond angle of 162.9 (1)° is fairly close to the 180° angle expected for a trigonal bipyramid. The three equatorial bond angles (119.2 (1), 128.0 (1), and 104.7 (1)°) are also close to the expected angle of 120°. The largest distortion is the C(7)–In–N(1) bond angle of 113.6 (2)°, considerably different from the expected 90° axial–equatorial angle.

The nitrogen donor atoms of the dihydrobis(pyrazolyl)borate ligand occupy an axial and equatorial position of the trigonal bipyramid, as observed previously in the structure of $[H_2B(pz)_2]_2GaCl$[2a] and as expected for the 86.3 (1)° N(1)–In–N(4) angle formed by this chelate ligand. This angle formed by the dihydrobis(pyrazolyl)borate ligand is within 1° of that observed for the analogous angles in the other two dihydrobis(pyrazolyl)borate–indium structures.

The unusual five-coordinate arrangement observed for 5 is similar to that recently reported for the polymeric structure of $[In(CH_2C(CH_3)_3)Cl_2]_x$.[12b] For this complex, the In(μ-Cl)$_2$In units are also asymmetric with the axial In–Cl bonds (2.700 (6)–2.821 (6) Å) longer than the equatorial bonds (2.393 (6)–2.452 (5) Å). While this bonding is distorted, the degree of distortion is much greater in 5. The origins of the distortions in the bridging unit of 5 do not appear to be intramolecular crowding, as there are no unusual nonbonding contacts.

The structure of 6, the dimethyl analogue of 5, is shown in Figure 2. In this case the molecule is clearly a four-coordinate monomer with no close intermolecular contacts. The donor atoms are arranged in a distorted-tetrahedral geometry. The natural bite angle of the dihydrobis(pyrazolyl)borate ligand restricts the N(1)–In–N(3) angle to 85.2 (1)°. The C–In–N angles are fairly close to the tetrahedral angle, but the C(7)–In–C(8) angle is extremely large at 141.1 (1)°. While it is reasonable to expect that this angle would open up somewhat in response to the low N(1)–In–N(3) angle opposite to it, the distortion is greater than would be expected from this alone. Large C–In–C angles are a structural feature that seem to be general for four-coordinate $In(CH_3)_2$ structures, where a range of values from 126.1 (2) to 152.2 (6)° has been observed previously.[15] Even in the anion $In(CH_3)_2Br_2^-$, which does not have any geometrical restraints imposed by chelate rings, the angle is 135.0 (6)°.[15b]

In the structures of 3,[5] 5, and 6, the InN_4B ring formed by the dihydrobis(pyrazolyl)borate ligand is in the typical shallow boat configuration.[16] The B···In distances are 3.462 (4), 3.516 (4), and 3.606 (4) Å in 3,[5] 3.216 (2) and 3.281 (2) Å in the two independent molecules in the structure of 5, and 3.399 (2) Å in 6. While these show a surprising range, they are all long enough to demonstrate that there is not an agostic interaction of a B–H group with the indium. This type of interaction has been observed previously with the dihydrobis(pyrazolyl)borate ligand[17] in transition-metal complexes, and C–H agostic interactions have been suggested recently for main-group metals.[12a,18] We had anticipated that four-coordinate 6 could have a B–H···In agostic interaction.

Summary

We have been able to prepare the complete series of dihydrobis(pyrazolyl)borate complexes of the general formula $[H_2B(pz)_2]_mInCl_n(CH_3)_p$ ($m + n + p = 3$), analogous to those of gallium reported earlier.[2] A difference between the two metals is that the reaction of $InCl_3$ with 1 equiv of $K[H_2B(pz)_2]$ yields $[H_2B(pz)_2]InCl_2$ (1), whereas the analogous reaction with $GaCl_3$ yields $\{[H_2B(pz)_2]_2Ga\}GaCl_4$. With the exception of 1, these complexes are stable to air in both the solid and solution state and are thermally stable to their melting points. $[H_2B(pz)_2]In(CH_3)Cl$ can also be formed in the exchange reaction of $[H_2B(pz)_2]_2InCl$ and $(CH_3)_2InCl$.

As observed in the gallium chemistry, acetic acid will cleave a dihydrobis(pyrazolyl)borate ligand from 3 to form 7. In contrast, 7 is also formed from 4 and acetic acid with release of CH_4, whereas $[H_2B(pz)_2]_2GaCH_3$ does not react with this weak acid. Another difference between indium and gallium is that 8 is dimeric in solution whereas $[H_2B(pz)_2]Ga(CH_3)(O_2CCH_3)$ is monomeric.

The solid-state structure of 5 shows that it is dimeric with a highly asymmetric In(μ-Cl)$_2$In bridging unit and a distorted-trigonal-bipyramidal geometry about the indium.

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The solid-state structure of **6** shows that it is monomeric with a distorted-tetrahedral geometry about indium.

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Supplementary Material Available: Tables of positional parameters of H atoms, anisotropic thermal parameters, and bond distances and angles (8 pages); listings of structure factor amplitudes (41 pages). Ordering information is given on any current masthead page.

Carbanions. 25. Phenyl Migration during Reactions of Triphenylmethane, 1,1,1-Triphenylethane, Tetraphenylmethane, and 3,3-Diphenyl-1-butene with Cesium–Potassium–Sodium Alloy[1]

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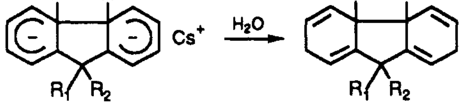
Both 3,3-diphenyl-1-butene and triphenylmethane react with excess Cs–K–Na alloy in THF at −75 °C to give a red dianion of unique structure involving [1,2]-phenyl migration into an adjacent benzene ring, according to structural characterization of the products of protonation and deuteration. The dianion from the butene is assigned the structure dicesium 6-(*cis*-1′-methyl-2′-propen-1′-id-1′-yl)-6-phenylcyclohexa-2,4-dien-1-ide (**6**) and that from triphenylmethane dicesium 6-(phenylmethanidyl)-6-phenylcyclohexa-2,4-dien-1-ide (**4f**). Tetraphenylmethane evidently undergoes a similar reaction with Cs–K–Na alloy, but the product of [1,2]-phenyl migration largely undergoes fragmentation prior to or following protonation. In contrast 1,1,1-triphenylethane reacts with Cs–K–Na alloy at −75 °C to give an ortho-cyclized dianion, dicesium 9-methyl-9-phenyl-*cis*-4a,4b-dihydrofluoren-2,5-diide (**2a**), which on protonation affords 9-methyl-9-phenyl-*cis*-2,4a,4b,7-tetrahydrofluorene (**3a**). The geometry of **3a** was established by X-ray crystallography. At higher temperatures, additional products are formed from 1,1,1-triphenylmethane and Cs–K–Na alloy via both [1,2]-phenyl migration and phenyl cleavage.

Introduction

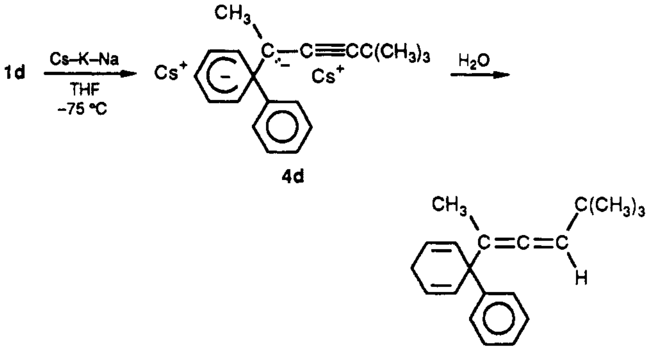
In previous work 1,1,1-triphenylethane, 1,1,1-triphenylpentane, and 2,2-diphenylpropane were reported[2] to react with Cs–K–Na alloy in tetrahydrofuran (THF) at −60 to −70 °C to give dianions (apparently **2a–c**) that upon protonation gave tetrahydrofluorene derivatives (**3a–c**).

1a: R$_1$ = Ph, R$_2$ = CH$_3$
b: R$_1$ = Ph, R$_2$ = n-C$_4$H$_9$
c: R$_1$ = CH$_3$, R$_2$ = CH$_3$
d: R$_1$ = CH$_3$, R$_2$ = C≡CC(CH$_3$)$_3$
e: R$_1$ = CH$_3$, R$_2$ = CH═CH$_2$
g: R$_1$ = Ph, R$_2$ = Ph
h: R$_1$ = H, R$_2$ = Ph



2a–c **3a–c**

In contrast, 5,5-dimethyl-2,2-diphenyl-3-hexyne (**1d**) was found[3] to react under similar conditions to give the product **5** of a [1,2]-phenyl migration, evidently via the rearranged dianion **4d**.



4d **5**

Since the rearrangement of a phenyl group to the ipso position on a benzene ring under reducing conditions is, to our knowledge, without precedent and since the powerful reducing agent eutectic Cs–K–Na alloy has been little studied in organic chemistry, the present work was un-

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(1) Presented in part at the International Symposium on Chemistry of Carbanions, University of Durham, Durham, U.K., July 1984.

(2) Grovenstein, E., Jr.; Beres, J. A.; Chen, Y.-M.; Pegolotti, J. A. *J. Org. Chem.* **1972**, *37*, 1281–1292.

(3) Grovenstein, E., Jr.; Chiu, K.-W.; Patil, B. B. *J. Am. Chem. Soc.* **1980**, *102*, 5848–5859. For some related [1,2]-anionic rearrangements, especially the "Zimmerman–Grovenstein" rearrangement, see: Eisch, J. J.; Kovacs, C. A.; Chobe, P. *J. Org. Chem.* **1989**, *54*, 1275–1284 and references therein.