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Article

Catalysis Design for Ring-Opening Polymerization of Cyclic Esters: 1. Group 1 Metal and Thallium(I) Trispyrazolylborate Complexes with Hemilabile Ligands[†]

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The synthesis of 3-(2-methoxy-1,1-dimethylethyl)pyrazole, pz*H is described together with its reactions with the borohydrides MBH_4, where M = Li, Na, and K, under melt conditions. At 180 °C, this procedure leads to a mixture of products for M = Li, and at higher temperatures, a derivative LiTp′pz*H, **1**, is isolated, wherein a B–H bond and a methyl group have been eliminated and a B–O bond has been formed. For M = Na, the reaction proceeds to give the tris-pyrazolylborate derivative NaTp*, **2**, but at higher temperatures the tetra-pyrazolylborate complex $NaB(pz^*)_4$, **3**, is obtained. The reactions involving KBH_4 and pz*H yield the dinuclear complex $K_2(Tp^*)_2pz^*H$, **4**. The reaction between NaTp* and TlOAc in CH_2Cl_2 at room temperature leads to the formation of TlTp*, **5**, along with NaOAc. Thallium **5** reacts with methyllithium in diethylether to give LiTp*, **6**, and thallium metal, and, similarly, **5** and KH react in tetrahydrofuran to give KTp*, **7** and Tl(0). **1**–**7** have been characterized by elemental analysis, NMR spectroscopy, and by single-crystal X-ray studies, the latter of which reveal the versatile modes of binding for this new ligand bearing hemilabile ether appendages.

Introduction

Ring-opening polymerization of cyclic esters derived from renewable resources is an attractive route to polyesters that find uses from bulk packaging materials to clothing, carpeting, and medicinal applications.[1] 1,4-dioxane-3,6-dimethyl-2,5-dione, lactide, LA and its polymers, PLAs, provide prime examples of a relatively new biobased bulk-commodity monomer and its polymer.[2] Polymer production can be brought about by enzymatic,[3] organic,[4] and metal-coordinate[5,6] catalysis, and the latter has attracted great attention within recent years because single-site catalysis can confer living polymerization status along with stereocontrol in the polymerization of meso-[7] and rac-LA.[8] The coordinate catalysis involves, in addition to the ring-opening event and propagation, a number of competing side reactions such as transesterification of the polymer chain (either intrachain to produce cycles or interchain) and chain transfer as shown in Scheme 1. Chain transfer can be achieved by the addition of an alcohol or by a bimolecular reaction of the catalyst. In addition, the presence of adventitious water can effect chain transfer and by a bimolecular reaction to oxo group formation and catalyst death. To avoid the latter, rigorously anhydrous conditions are often required along with triple sublimation of the substrate monomer.

In the development of coordinate catalysis, there is generally a trade-off between rates of reactivity and selectivity. Thus, in the use of the BDI ligand [BDI = $CH(CMeN\text{-}2,6\text{-}Pr^i_2\text{-}C_6H_3)_2$] that Coates et al.[8] have employed so effectively in the stereoselective polymerization of rac- and meso-LA with zinc alkoxide initiators, the metals magne-

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[†] Dedicated to S. Trofimenko in memoriam.

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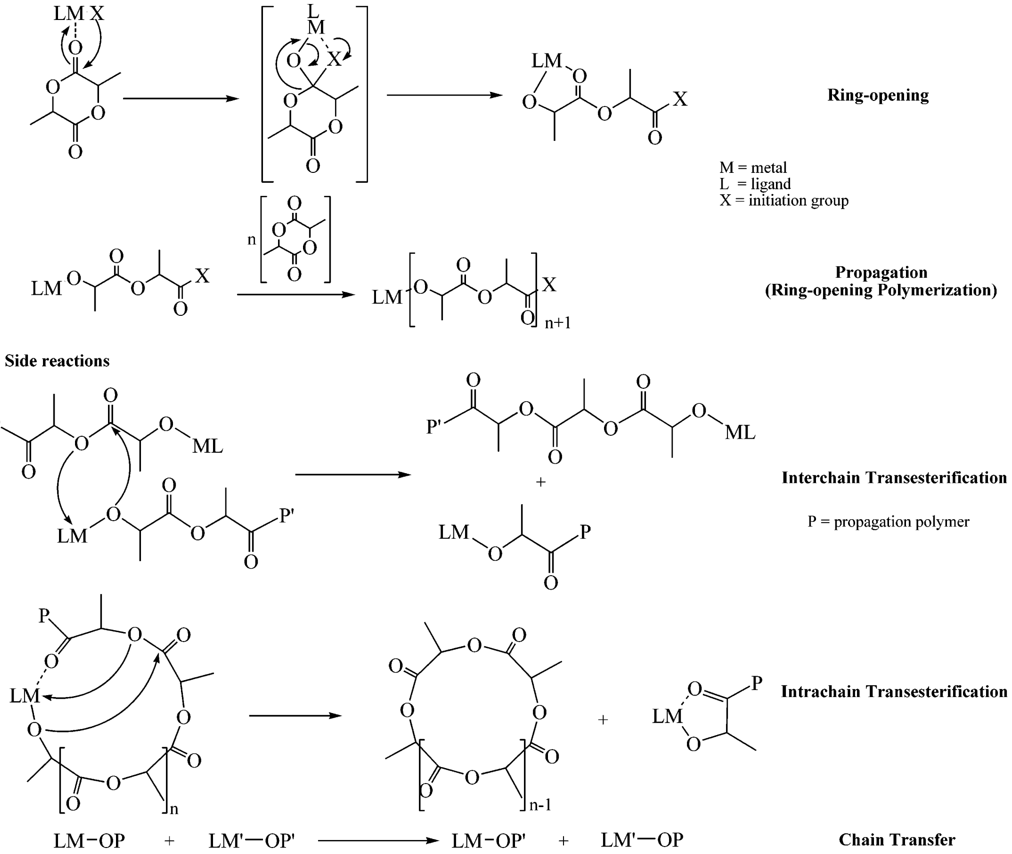
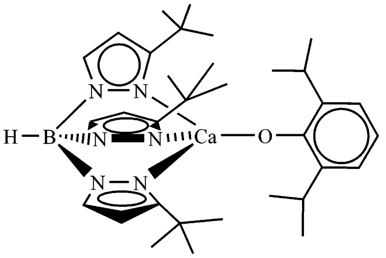
Scheme 1. Reactions Involved in Ring-opening Polymerization Employing a Coordinate Catalyst



sium[9] and calcium[10] show faster initial rates of ring-opening and ROP in the order Ca > Mg > Zn but also show less stereoselectivity, and with time the catalyst systems die, as a result of side reactions such as ligand scrambling by the Schlenk equilibrium: $2LMOR \rightleftharpoons L_2M + M(OR)_2$. To suppress the latter we employed the bulky tris-(3-tert-butylpyrazolyl)borate ligand with calcium.[10] This ligand allowed the isolation of discrete 4-coordinate complexes of calcium such as LCaO-C_6H_3-2,6-Me_2, shown in I below, and its THF adduct. These complexes initiated the rapid ROP of LA but they did not yield a living system.



We believed that the system died either because of ligand scrambling or adventitious water. To confer greater kinetic persistence to these most active of initiators, we reasoned that the introduction of hemilabile ether appendages to the bulky tris(3-tert-butylpyrazolyl)borate ligand would be desirable. The ether groups could act as solvent equivalents of THF, which had previously been found[11] to assist in the stabilization of magnesium-induced ROP involving the BDI ligand. In addition to stabilization against the Schlenk equilibrium, the ether groups could provide kinetic stabilization of a reactive Ca−OH group (formed by the presence of adventitious H_2O) by intramolecular hydrogen bonding.

To test this hypothesis, we needed to prepare an appropriate pyrazole and achieve its conversion to a metal trispyrazolyl borate complex, which could then act as a transfer agent for the ultimate formation of the desired LCaOR catalyst initiator. The ideal transfer agents via a metathetic reaction seemed to be one of MTp complexes where M = Li, Na, K, or Tl. We describe here our synthesis of these complexes and note that a preliminary communication of some aspects of this chemistry has appeared.[12]

Experimental Section

General Procedures. 1-Hydroxy-2,2-dimethylbutan-3-one and 2,2-dimethyl-1-methoxybutan-3-one were prepared according to literature procedures.[13] The manipulation of air-sensitive compounds employed standard Schlenk line techniques and involved the use of anhydrous solvents and dry, deoxygenated nitrogen. Ethyl formate, hydrazine hydrochloride, $LiBH_4$, $NaBH_4$, KBH_4, methyl lithium (LiMe), and thallium(I) acetate (TlOAc) were purchased

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Scheme 2. Synthesis of pz*H

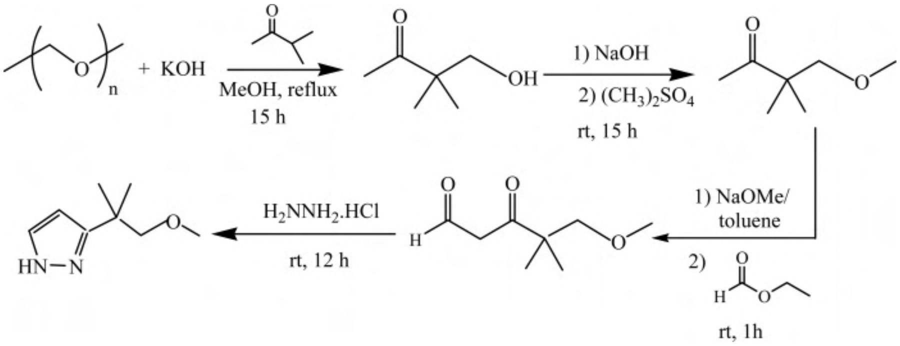

Table 1. Summary of Crystallographic Data for **1**−**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
empirical form	$C_{31}H_{50}BLiN_8O_4$	$C_{24}H_{40}BN_6NaO_3$	$C_{32}H_{52}BN_8NaO_4$	$C_{56}H_{94}B_2K_2N_{14}O_7$	$C_{24}H_{40}BN_6O_3Tl$	$C_{24}H_{40}BLi\ N_6O_3$	$C_{24}H_{40}BK\ N_6O_3$
fw	616.54	494.42	646.62	1175.28	675.80	478.37	510.53
cryst syst	monoclinic	cubic	monoclinic	triclinic	orthorhombic	cubic	cubic
a (Å)	11.365(2)	22.056(2)	13.3825(10)	13.163(1)	7.870(1)	21.864(1)	22.2678
b (Å)	14.028(2)		18.570(2)	13.629(1)	14.415(1)		
c (Å)	22.125(3)		14.715(2)	21.637(2)	24.533(3)		
α (deg)				75.219(4)			
β (deg)	103.156(8)		97.993(6)	78.293(5)			
γ (deg)				63.403(5)			
U (Å^3)	3434.8(9)	10729.5(17)	3621.3(7)	3338.3(5)	2783.2(5)	10452.6(8)	11041.6(2)
T (K)	200(2)	200(2)	150(2)	150(2)	150(2)	150(2)	150(2)
space group	$P2_1/n$	$\bar{I}43d$	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$	$I\bar{4}3d$	$I\bar{4}3d$
Z	4	16	4	2	4	16	16
μ (Mo−Kα) mm^{-1}	0.080	0.095	0.089	0.199	5.839	0.080	0.228
reflns measured	43 385	63 372	40 021	63 668	39 208	83 882	65 141
unique reflns rint	6056, 0.034	860, 0.046	6388, 0.031	11 749, 0.034	6330, 0.061	1077, 0.045	1635, 0.064
R1($I > 2\sigma I$)	0.0477	0.0269	0.0425	0.0444	0.0273	0.0415	0.0365
wR2 (all data)	0.1358	0.0701	0.1159	0.1193	0.0506	0.1183	0.0971

from Aldrich. Paraformaldehyde, 2,2-dimethyl-3-butanone, dimethylsulfate, and sodium methoxide were purchased from Acros. Potassium hydride was purchased from Strem Chemicals Inc. as 30−35% in oil and washed with hexanes five times prior to use. Elemental analyses for carbon, hydrogen, and nitrogen were performed by Atlantic Microlab, Inc.

Caution. Thallium metal and its salts are toxic. Extreme care must be employed in the handling of these materials and in disposing of their wastes.

Measurements. ^{1}H-, ^{11}B-, and ^{13}C{^{1}H}-NMR spectra were recorded in C_6D_6 and $CDCl_3$ on Bruker NMR spectrometers DPX-600, DPX-400, or DPX-250. Experiments for determining positive or negative ion Electron Spray Ionization mass spectra (ESI-MS) of the compounds were performed on a Bruker Esquire Ion Trap mass spectrometer (Bremen, Germany). Optimal ESI conditions were capillary voltage 3500 V, source temperature 250 °C, the ESI drying gas was nitrogen.

3-(2-Methoxy-1,1-dimethylethyl)pyrazole, pz*H. Sodium methoxide (62.5 g, 1.16 mol) was placed in a 500 mL round-bottom flask and then slurried in 70 mL of freshly distilled and degassed toluene under nitrogen. To this slurry was added dropwise 136 g (1.04 mol) of 2,2-dimethyl-1-methoxybutan-3-one, which yielded a pale-yellow slurry. Ethyl formate (93.5 mL, 85.7 g, 1.16 mol) was slowly added to this mixture at room temperature. The vigorous reaction was controlled using an ice−water bath. The mixture was allowed to stir for about an hour until it cooled down to room temperature. The volatile materials including toluene were removed under a vacuum and a thick dark-yellow paste was obtained. Ice−water (350 mL) was then added, and formation of a yellow aqueous layer and a white organic layer were noted. The organic layer was removed. An aqueous solution of 74.1 g (1.08 mol) of hydrazine monohydrochloride in 50 mL of distilled water was added dropwise to the aqueous layer. The reaction mixture was stirred at room temperature overnight. The product was extracted with dichloromethane (4 × 100 mL). The solvent was removed from the combined organic extracts by a rotary evaporator. Pure 3-(2-methoxy-1,1-dimethylethyl)pyrazole (151 g, 91% of theory) was obtained as a colorless oil upon vacuum distillation of the residue at 45 °C under a vacuum (∼10^{-4} atm). ^{1}H NMR (250 MHz, C_6D_6) δ: 10.68 (br, 1H, N−H), 7.40 (d, J = 3 Hz, 1H, H-5, pz), 6.06 (d, J = 3 Hz, 1H, H-4, pz), 3.19 (s, 2H, CH_2O), 3.03 (s, 3H, OMe), 1.32 (s, 6H, CMe_2). ^{13}C{^{1}H}-NMR (C_6D_6): 153.62 (C-3, pz), 134.87 (C-5, pz), 102.00 (C-4, pz), 82.01(CH_2O), 58.88 (OMe), 36.05 (*C*Me$_2$), 25.52 (C*Me*$_2$). GC-MS for $C_8H_{14}N_2O$: 154.33 g/mol. Anal. Calcd for $C_8H_{14}N_2O$: C, 62.31; H, 9.15; N, 18.17. Found: C, 62.20; H, 9.54; N, 17.45.

Lithium-(3-(2-methoxy-1,1-dimethylethyl)pyrazole)bis-[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl][5-(2-oxy-1,1-dimethylethyl)pyrazolyl]borate, LiTp′pz*H, 1. A mixture of 2.14 g (13.9 mmol) of pz*H and 0.0914 g (4.2 mmol) of ground $LiBH_4$ was heated to 230 °C for 16 h. Unreacted pyrazole was removed using a Kugelrohr distillation apparatus at 75 °C under a vacuum (∼10^{-4} atm). The residue was dissolved in *n*-hexane. Instead of lithium tris[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate, colorless crystals of **1** were obtained (0.36 g, 14%). 8.03 (d, J = 2 Hz, 2H, H-5, pz), 7.64 (br, 1H, H-5, pz), 7.48 (d, J = 2 Hz, 2H, H-5, pz), 5.97(d, J = 2 Hz, 1H, H-4, pz), 5.95 (d, J = 2 Hz, 3H, H-4, pz), 3.94 (br, 2 H, OMe), 3.32 (d, J = 9.5 Hz, 1H), 3.22 (s, 9H), 2.94 (d, J = 6.5 Hz, 1H), 2.84 (br, 6H), 1.26 (s, 6 H, CMe_2), 1.17 (s, 6 H, CMe_2), 1.04 (s, 12 H, CMe_2). ^{11}B-NMR (600 MHz, C_6D_6) δ: 0.528 (s). Anal. Calcd for $C_{31}H_{50}BLiN_8O_4$: C, 60.39; H, 8.17;

N, 18.17. Found: C, 59.21; H, 8.31; N, 17.72. Positive Ion ESI-MS for $[C_{23}H_{36}BLiN_6O_3]$-Li^+: 479.4.

Sodium tris[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate, NaTp*, 2. pz*H (10.2 g, 66.0 mmol) and $NaBH_4$ (0.757 g, 20.0 mmol) were mixed and heated to 180 °C until about 1.5 L (60 mmol) of hydrogen gas had been evolved. The reaction took about 4 h. A white solid was formed and was washed with toluene (3 × 20 mL) at 80−90 °C. **2** (7.81 g 79% of theory) was recrystallized from a 1:1 mixture of THF and chloroform as colorless crystals, upon the evaporation of the solvent mixture. Single crystals suitable for the X-ray study were also obtained from a concentrated solution of NaTp* in THF at −20 °C. ^1H NMR (400 MHz, C_6D_6) δ: 7.73 (d, J = 3 Hz, 3H, H-5, pz), 5.96 (d, J = 3 Hz, 3H, H-4, pz), 3.25 (s, 6 H, CH_2O), 3.18 (s, 9H, OMe), 1.19 (s, 18 H, CMe_2). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, J = 3 Hz, 3H, H-5, pz), 5.85 (d, J = 3 Hz, 3H, H-4, pz), 3.51 (s, 9H, OMe), 3.44 (s, 6H, CH_2O), 1.22 (s, 18 H, CMe_2). $^{13}C\{^1H\}$-NMR (250 MHz, $CDCl_3$) δ: 158.04 (C-3, pz), 134.24 (C-5, pz), 99.38 (C-4, pz), 83.63(CH_2O), 60.14 (OCH_3), 36.43 ($\mathit{C}Me_2$), 26.39 ($C\mathit{Me_2}$); ^{11}B-NMR (250 MHz, C_6D_6) δ: −2.21 (q). Positive Ion ESI-MS: 471.3 for H^+- $[HBC_{24}H_{39}N_6O_3]^-$. Anal. Calcd for $C_{24}H_{40}BN_6NaO_3$: C, 58.30; H, 8.15; N, 17.00. Found: C, 57.88; H, 8.14; N, 16.97.

Sodium tetrakis[3-(2-methoxy-1,1-dimethylethyl)pyrazoly]borate, $NaB(pz^*)_4$, 3. With an aim to increase the yield of the reaction yielding NaTp*, the reaction was run for 5 h, yielding sodium tris-[3-(2-methoxy-1,1-dimethylethyl)pyrazoly]hydroborate and sodium tetrakis[3-(2-methoxy-1,1-dimethylethyl)pyrazoly]borate in a 10:1 ratio. The latter compound was obtained as an over-reaction product, isolated by its superior solubility in toluene and recrystallized from a 1:5 mixture of hexanes/benzene solution at room temperature overnight. ^1H NMR (250 MHz, C_6D_6)δ: 7.89 (d, J = 2 Hz, 4H, H-5, pz), 6.09 (d, J = 2 Hz, 4H, H-5, pz), 3.26 (s, 8H, OCH_2), 3.10 (s, 12H, OMe), 1.26 (s, 24H, CMe_2). $^{13}C\{^1H\}$-NMR (250 MHz, C_6D_6) δ: 157.99 (C-3, pz), 135.28 (C-5, pz), 101.08 (C-4, pz), 83.68(CH_2O), 59.07 (OMe), 36.32 ($\mathit{C}Me_2$), 25.70($C\mathit{Me_2}$). ^{11}B-$\{^1H\}$-NMR (250 MHz, C_6D_6) δ: 1.13 (s). Positive Ion ESI-MS: 669.7 for $C_{32}H_{52}BN_8NaO_4{-}Na^+$. Negative Ion ESI-MS: 623.8 for $[C_{32}H_{52}BN_8O_4]^-$.

Dipotassiumbis{tris[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]-hydroborate}[3-(2-methoxy-1,1-dimethylethyl)pyrazole], $K_2Tp^*_2\cdot pz^*H$, 4. The aim of this reaction was to obtain KTp* by a melt reaction. However, only $K_2Tp^*_2\cdot pz^*H$ could be isolated from the residue of the reaction. A mixture of pz*H (6.69 g, 43.4 mmol) and potassium borohydride (0.585 g, 10.8 mmol) was heated to 180 °C. After 4 h at 180 °C, the reaction mixture was cooled to 60 °C, and *n*-hexane (2 × 15 mL) was added to extract unreacted 3-(2-methoxy-1,1-dimethylethyl)pyrazole. The mixture was centrifuged and decantated. The white precipitate was dried under a vacuum and redissolved in THF. The unreacted KBH_4 precipitated out and was removed by filtration. The supernatant solution was stripped to dryness, yielding a white solid (0.90 g, 18%). Single crystals of $K_2Tp^*_2\cdot pz^*H$ were obtained from a concentrated solution of THF at −20 °C. ^1H NMR (400 MHz, C_6D_6) δ: 7.44 (s, 3H, H-5, pz), 6.07 (s, 3H, H-4, pz), 3.29 (s, 6 H, CH_2O), 2.97 (s, 9H, OMe), 1.31 (s, 18H, CMe_2). Anal. Calcd for $C_{24}H_{40}BKN_6O_3$: C, 57.23; H, 8.06; N, 16.69. Found: C, 57.04; H, 8.24; N, 16.44. Negative ion ESI-MS: 471.8 for $[C_{24}H_{40}BN_6O_3]^-$. Positive ion ESI-MS: 701.7 for $C_{32}H_{52}BKN_8O_4{-}K^+$.

Thallium tris-[3-(2-methoxy-1,1-dimethylethyl)pyrazoly]hydroborate, TlTp*, 5. Sodium tris[1-(3-(2-methoxy-1,1-dimethyl)-pyrazolyl)]hydroborate (2.15 g, 4.34 mmol) and TlOAc (1.27 g, 4.83 mmol) were mixed under a nitrogen atmosphere. To this mixture was added 60 mL of dry dichloromethane. The mixture was stirred at room temperature overnight. Sodium acetate precipitated, and the solution was filtered and vacuum-stripped to dryness. TlTp* was obtained as an air-stable white powder (2.75 g, 94%). Colorless needles were obtained from the recrystallization of the product from a 3:1 mixture of toluene/diethyl ether through slow evaporation of the solvent mixture. The single crystals were also obtained from a concentrated THF solution of TlTp* at −20 °C. ^1H NMR (500 MHz, C_6D_6) δ: 7.64 (s, 3H, H-5), 6.06 (d, J = 12.5 Hz, 3H, H-4), 3.28 (d, J = 13.8 Hz, 6H, CH_2O), 3.06 (s, 9H, OMe), 1.41 (d, J = 11.8 MHz, 18H, CMe_2). $^{13}C\{^1H\}$-NMR (400 MHz, C_6D_6) δ: 159.93 (br, C-3, pz), 136.25 (C-5, pz), 102.21 (br, C-4, pz), 83.71(d, J = 100 Hz, CH_2O), 58.69 (OCH_3), 36.96 (s, $\mathit{C}Me_2$), 26.53 (d, J^4 = 173 Hz, $C\mathit{Me_2}$); ^{11}B-NMR (400 MHz, C_6D_6) δ: −0.08 (q). Anal. Calcd for $C_{24}H_{40}BN_6O_3Tl$: C, 42.66; H, 5.97; N, 12.44. Found: C, 42.72; H, 6.02; N, 12.53.

Lithium tris[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate, LiTp*, 6. A 1.6 M solution of LiMe in diethyl ether (1.46 mL, 2.33 mmol) was added dropwise to the solution of TlTp* (1.43 g, 2.12 mmol) in 50 mL of THF at room temperature. A gray, turbid reaction mixture was obtained as a result of deposition of thallium metal. The reaction was stirred for 2 h. All of the volatiles were removed under a vacuum. The gray solid residue was redissolved in 50 mL of diethyl ether to extract LiTp*. The solution was filtered to remove the gray precipitate, and a colorless solution was obtained. This solution was concentrated to 15 mL under a vacuum and then cooled to −15 °C. Colorless single crystals of LiTp* were obtained overnight (0.933 g, 92%). ^1H NMR (400 MHz, C_6D_6)δ: 7.61 (s, 3H, H-5, pz), 5.93 (s, 3H, H-4, pz), 3.33 (s, 6H, CH_2O), 3.20 (s, 9H, OMe), 1.32 (s, 18 H, CMe_2). $^{13}C\{^1H\}$-NMR (250 MHz, C_6D_6) δ: 158.28(C-3, pz), 134.52 (C-5, pz), 100.33 (C-4, pz), 83.44 (CH_2O), 60.01 (OCH_3), 36.83 ($\mathit{C}Me_2$), 25.88 ($C\mathit{Me_2}$). ^{11}B-NMR (C_6D_6, 250 MHz) $\delta = -2.53$ (d). Anal. Calcd for $C_{24}H_{40}BLiN_6O_3$: C, 60.00; H, 8.45; N, 17.63. Found: C, 60.26; H, 8.43; N, 17.57. Negative ion ESI-MS: 471.2 for $[C_{24}H_{40}BN_6O_3]^-$. Positive ion ESI-MS: 485.3 for $C_{24}H_{40}BLiN_6O_3{-}Li^+$.

Potassium tris-[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate, KTp*, 7. A solution of TlTp* (0.676 g, 1.00 mmol) in 15 mL of THF was added dropwise to a slurry of KH (0.0450 g, 1.10 mmol) in 15 mL of THF at room temperature. Formation of thallium metal as a gray precipitate was observed. The reaction mixture was stirred for 2 d. It was filtered through a fine glass frit with celite. The clear THF solution was concentrated to 10 mL and layered with 1 mL of pentane. Upon addition of the pentane, single crystals of KTp* formed at room temperature. A second crop of crystals was obtained from the mother liquor at −10 °C. The combined yield was 0.403 g, 79% on the basis of TlTp*. KTp* is air-sensitive and must be handled under inert conditions. ^1H NMR (400 MHz, C_6D_6)δ: 7.58 (H-5, pz*, s, 3H), 6.06 (H-4, pz*, s, 3H), 3.24 (s, 6H, CH_2O), 2.98 (s, 9H, OMe), 1.28 (s, 18 H, CMe_2). ^{13}C-$\{^1H\}$-NMR (400 MHz, C_6D_6) δ: 158.50 (C-3, pz), 134.48 (C-5, pz), 100.98 (C-4, pz), 83.48 (CH_2O), 58.93 (OCH_3), 36.63 ($\mathit{C}Me_2$), 26.18 ($C\mathit{Me_2}$). Anal. Calcd for $C_{24}H_{40}BKN_6O_3$: C, 56.46; H, 7.90; N, 16.46. Found: C, 54.47; H, 7.73; N, 15.67.

X-ray Structure Determinations. X-ray diffraction data were collected on a Nonius diffractometer equipped with a Kappa CCD detector, and crystal data, data collection, and refinement parameters are summarized in Table 1. All of the work was done at low temperature using an Oxford Cryosystems Cryostream Cooler. The structures were solved using direct methods and standard difference map techniques. Full-matrix least-squares refinements based on F^2

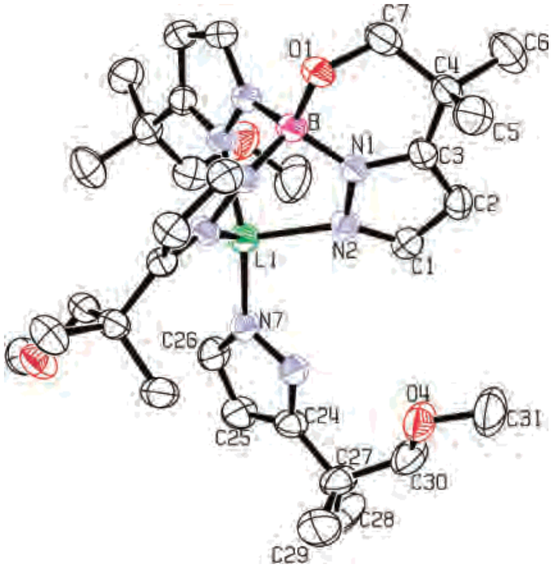

Figure 1. ORTEP drawing of LiTp′pz*H, **1**, with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths are Li−N(Tp*) = 2.06(2) Å (ave) and Li−N(pz*) = 2.042(3) Å.

were performed in *SHELXL-97*,[14] as incorporated in the *WinGX* package.[15] Hydrogen atoms on carbon were included in calculated positions.

Results and Discussion

Syntheses. 3-(2-Methoxy-1,1-dimethylethyl)pyrazole, pz*H. The synthesis of the ether-substituted pyrazole, pz*H, is shown in Scheme 2. The compound is purified by vacuum distillation and is obtained in ∼90% yield.

The reactions between the metal borohydrides, MBH_4 and pz*H, were then undertaken with the intent of preparing the metal tris[3-(2-methoxyl-1,1-dimethylethyl)pyrazolylhydroborates, MTp*, where M = Li, Na and K. However, as noted below, this method was only successful in the preparation of the sodium complex.

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) in the Single-Crystal X-ray Structure of LiTp′•pzH, **1**

N(2)−Li	2.033(4)	N(1)−N(2)−Li	108.17(14)
N(7)−Li	2.042(3)	N(8)−N(7)−Li	116.59(14)
O(1)−B	1.422(2)	N(2)−Li−N(4)	96.33(14)
N(1)−B	1.547(3)	N(7)−Li−N(4)	138.9(2)
N(7)−C(26)	1.318(2)	N(4)−Li−N(6)	91.16(13)
		O(1)−B−N(1)	109.9(2)
		N(2)−N(1)−B	123.60(14)

Lithium (3-(2-Methoxy-1,1-dimethylethyl)pyrazole)bis[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl][5-(2-oxy-1,1-dimethylethyl)pyrazolyl]borate, LiTp′pz*H, 1. The reaction between $LiBH_4$ and pz*H at 180 °C proceeded to give a mixture of products with the evolutions of H_2. Although the desired product LiTp* was among these, this method did not provide an efficient route to this compound, and the title complex, LiTp′pz*H, was the dominant species when the reaction was carried out at higher temperatures. In this complex, one pz*H ligand is complexed to lithium, and one pyrazolyl group has undergone a 3 to 5 isomerization and a further reaction, wherein the B−H bond and CH_3 group are eliminated with formation of the B−O bond, vide infra.

Sodium Tris[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate, NaTp*, 2. The reaction between $NaBH_4$ and pz*H at 180 °C proceeded to give the desired compound NaTp* within 4 h, with the evolution of 3 equiv of H_2. This white crystalline compound is prepared in this manner in ∼80% yield. With prolonged heating, however, further reaction occurs, to yield the sodium tetrakispyrazolylborate complex $NaB(pz^*)_4$, **3**. It is therefore important to monitor the evolution of H_2, with the intent of stopping the reaction when 3 equiv have been formed.

Dipotassium Bis[tris-{3-(2-methoxy-1,1-dimethylethyl)-pyrazolyl}hydroborate].(3-(2-methoxy-1,1-dimethylethyl)-pyrazole, $K_2(Tp^*)_2$·pz*H, 4. The equivalent reaction involving KBH_4 and pz*H at 180 °C proceeds to give the dipotassium complex with one coordinated molecule of the

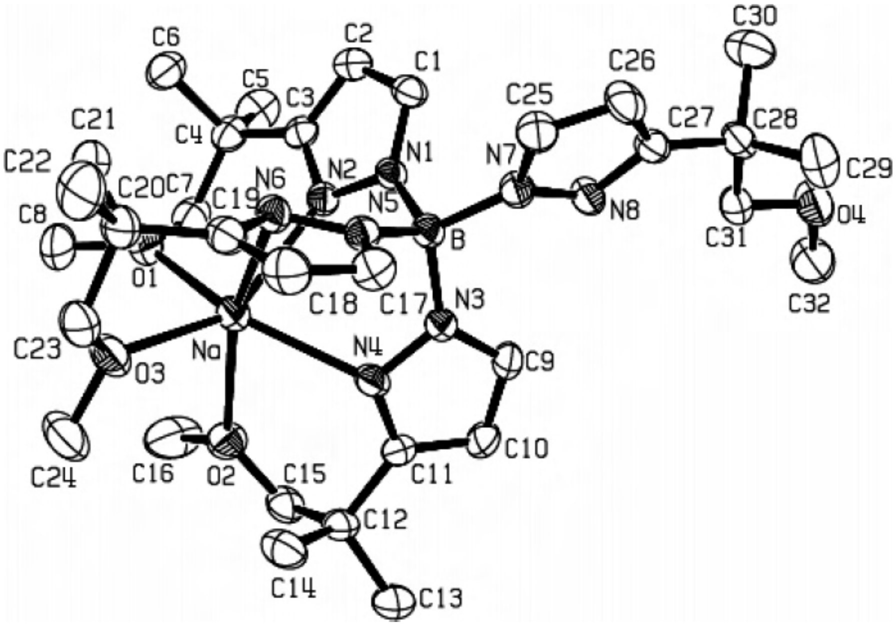

Figure 2. ORTEP drawing of $NaB(pz^*)_4$, **3**, with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

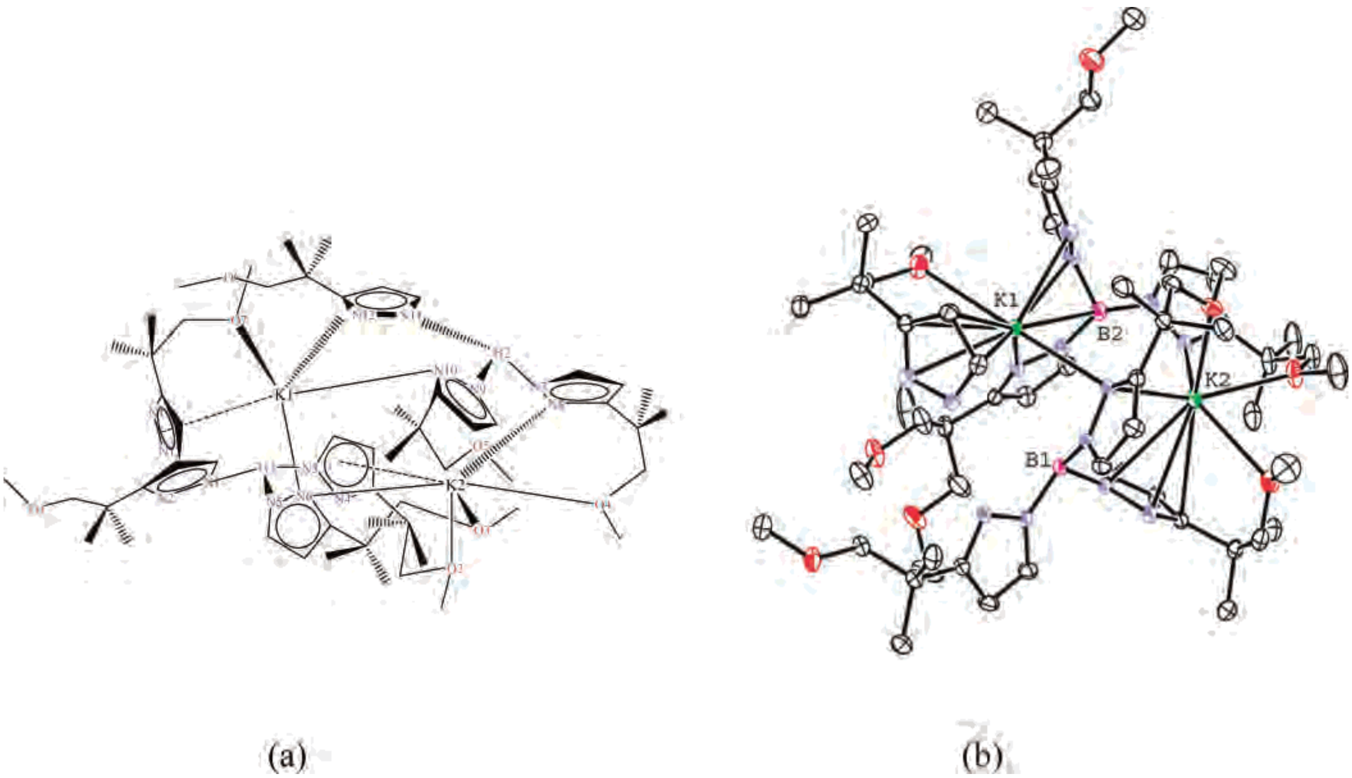

Figure 3. (a) ChemDraw and (b) an ORTEP drawing of **4**, with thermal ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Angstroms) and Angles (Degrees) in the Single-Crystal X-ray Structure of $NaB(pz^*)_4$, **3**

N(2)−Na	2.4653(15)	N(4)−Na−N(2)	82.49(5)
Na−O(1)	2.3747(15)	O(1)−Na−N(2)	77.15(5)
N(4)−Na	2.4244(16)	O(1)−Na−N(4)	148.55(6)
Na−O(2)	2.5218(14)	O(1)−Na−N(6)	112.07(5)
N(6)−Na	2.5199(16)	O(1)−Na−O(2)	88.35(5)
Na−O(3)	2.4478(15)	O(1)−Na−O(3)	94.03(5)
		N(1)−N(2)−Na	115.21(10)
		N(3)−N(4)−Na	115.59(10)
		N(5)−N(6)−Na	104.51(9)

pyrazole. This compound has a high crystallization tendency, and the pyrazole ligand cannot be readily removed under a vacuum.

Thallium Tris-[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate, TlTp*, 5. The thallium complex is prepared by the metathetic reaction involving NaTp* and thallium (I) acetate in dichloromethane at room temperature. After stirring for 12 h, the insoluble NaOAc is filtered off and TlTp*, **5**, is obtained as a white air- and moisture-stable (chemically persistent) crystalline solid in $\sim$90% yield.

Lithium Tris-[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate, LiTp*, 6. This lithium complex is best prepared from the reaction between methyllithium and TlTp* in ether/THF solutions. As the reaction proceeds, thallium metal is deposited and subsequently removed by filtration. Colorless/white crystals of LiTp*, **6**, are obtained by cooling a concentrated solution of the complex in THF at −15 °C.

Table 4. Selected Bond Lengths (Angstroms) and Angles (Degrees) in the Single-Crystal X-ray Structure of $K_2(Tp^*)_2 \cdot pz^*H$, **4**

C(51)−K(1)	3.217(2)	N(3)−B(1)−N(5)	109.61(15)
B(1)−N(3)	1.536(3)	O(7)−K(1)−N(12)	91.62(5)
B(2)−K(1)	3.260(2)	O(7)−K(1)−C(51)	95.36(5)
K(1)−N(12)	2.8863(17)	O(7)−K(1)−B(2)	109.33(5)
K(1)−O(7)	2.8251(15)	O(7)−K(1)−N(14)	68.06(4)
C(9)−K(2)	3.0807(19)	N(6)−K(1)−C(51)	68.53(5)
B(2)−N(9)	1.538(3)	N(9)−B(2)−N(11)	109.90(17)
K(2)−N(8)	2.8789(18)	O(3)−K(2)−N(8)	96.85(5)
K(2)−O(3)	2.7220(15)	O(3)−K(2)−O(4)	87.01(5)
		O(3)−K(2)−O(2)	103.99(5)
		O(2)−K(2)−C(11)	98.83(5)
		N(6)−K(2)−C(11)	83.53(5)

Potassium Tris-[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate, KTp*, 7. The potassium complex is prepared from the reaction between a slurry of KH in THF and TlTp*. As in the preparation of LiTp* above, a precipitate of thallium metal is formed and is removed by filtration. The white crystalline product, KTp*, is obtained in $\sim$90% yield upon crystallization from THF/pentane solutions.

Physico-Chemical Properties. All of the new compounds are chemically persistent in air for short periods of time. They are soluble in hydrocarbon and other organic solvents and yield molecular ions in the mass spectrometer. Elemental analytical and NMR spectroscopic data are given in the Experimental Section. The NMR data for sodium complex $NaB(pz^*)_4$, **3**, and thallium complex **5** reveal only one type of pz* arm, indicating the dynamic nature of Tp* ligand. ^{205}Tl-^{1}H and ^{205}Tl-^{13}C couplings in C_6D_6 were noted as it has been seen before for many TlTp complexes,[16] evidencing that the metal−ligand interaction is retained in solution and

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(15) *WinGX-Version 1.64.05*: Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837−838.

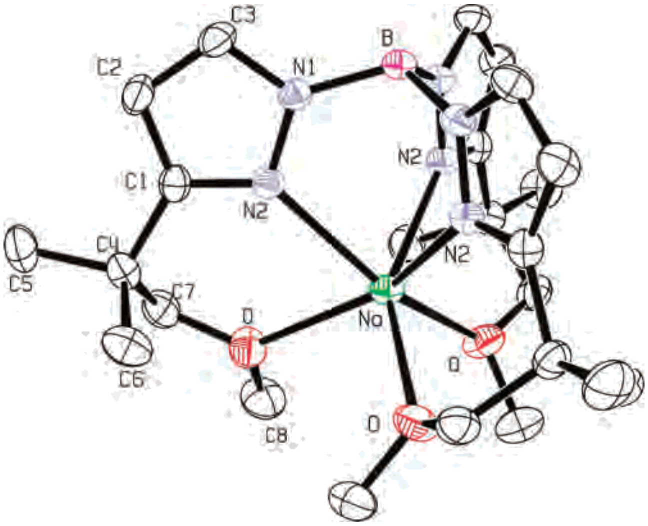

Figure 4. ORTEP drawing of **2**, with thermal ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Angstroms) and Angles (Degrees) in the Single-Crystal X-ray Structures of NaTp*(**2**), LiTp*(**6**), KTp*(7), and Tp*CaI (**8**)

	2	**6**	**7**	**8**
B−N(1)	1.5430(2)	1.541(2)	1.547(2)	1.542(5)
M−N(2)	2.4002(2)	2.144(5)	2.692(2)	2.384(4)
M−O	2.4723(1)	2.491(5)	2.639(2)	2.380(3)
N(2)−N(1)−B	122.13(2)	123.6(2)	121.3(2)	122.0(5)
N(1)−N(2)−M	117.49(1)	113.8(2)	119.05(1)	118.8(3)
N(2)#2−M−N(2)	80.84(6)	89.2(2)	74.21(7)	80.21(2)
cis-N(2)−M−O	74.49(5)	76.67(7)	68.82(6)	75.65(1)
trans-N(2)−M−O	147.56(5)	151.9(7)	138.30(6)	146.76(1)
O#1−M−O	97.05(5)	87.1(2)	108.16(5)	95.38(1)

that it is mainly covalent in character.[17] All of these complexes are fluxional on the NMR time-scale, even at low temperatures down to −80 °C.

Solid State and Molecular Structures. LiTp′pz*H, 1. The molecular structure of this over-reaction product is shown in Figure 1, and selected bond distances and bond angles are given in Table 2. The complex is seen to have four-coordinate lithium in a pseudo-tetrahedral geometry. The Li−N bond distances span a narrow range of 2.03−2.09 Å, and the N−Li−N angles involving the Tp′ ligand are less than the tetrahedral angle, falling between 91 and 99°. It is interesting to note that the lithium elects to bind to the nitrogen of a pyrazole ligand in preference to forming a bond to one (or more) of the ether oxygen atoms of the Tp′ ligand.

NaB(pz*)$_4$, 3. The molecular structure of this over-reaction product is shown in Figure 2, and selected bond distances and angles are given in Table 3. Three of the four pyrazolyl ligands coordinate to sodium and the fourth is left dangling. The Na−N and Na−O distances are very similar and fall in the range of 2.37−2.52 Å. The coordination about sodium approximates to a facial octahedral geometry with N−Na−N angles from 72−82° and trans N−Na−O angles from 146−160°. As can be seen from the view of the molecule shown in Figure 2, the pyrazolyl ring associated with N(6) is notably canted with respect to the N(6)−Na bond. The Na−N(6)-ring centroid angle is 120.2°, whereas the similar angles for N(2) and N(4) are 152.3 and 146.0°, respectively. It is thus perhaps not surprising that by NMR spectroscopy all four pyrazolyl ligands are undergoing rapid exchange at room temperature and even at low temperature.

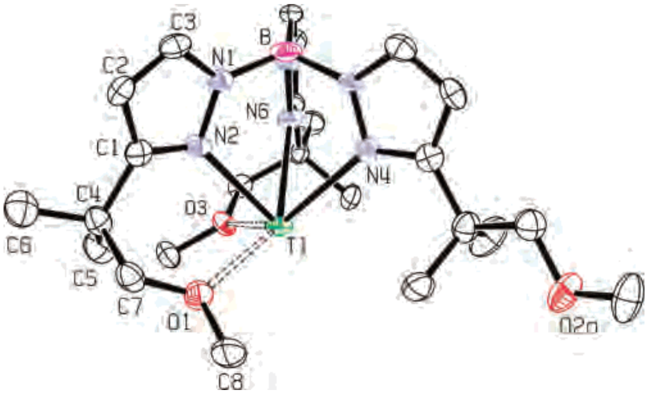

Figure 5. ORTEP drawing of TlTp*, **5**, with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

$K_2Tp*_2·pz*H$, 5. The structure of the dipotassium complex is shown in Figure 3 and reveals the diverse coordination modes of the Tp* ligand. Both Tp* ligands in this complex act as bridging ligands. The Tp* ligand that contains B(1) has one non-coordinating pz* arm and two that coordinate to K(2), one of which is η^5-bonded via the ring and oxygen-bound to the ether oxygen, whereas the other arm is nitrogen-bound to both K(2) and K(1) and oxygen-bound to K(1). The Tp* ligand that contains B(2) employs all three of its pz* arms in bonding. One is nitrogen and oxygen chelating to K(2); another is bonded to K(1) by both nitrogen atoms of the pz* ring, whereas the attendant ether group is left dangling, and the third arm just employs a single nitrogen donor atom to K(1). The coordination of K(1) is completed by the pz*H ligand which is η^5-ring bonded and oxygen-bonded. Selected bond distances and angles are given in Table 4.

NaTp*, 2; LiTp*, 6; and KTp*, 7. All three complexes crystallized in the same space group $I\bar{4}3d$, and each molecule has a crystallographically imposed C_3 axis of symmetry. The molecular structure of sodium complex **2** is shown in Figure 4, and the structural parameters for the three complexes are listed in Table 5 for an easy comparison. Also included in Table 5 are the structural parameters for the [Tp*Ca]$^+$ cation in the Tp*CaI salt that was previously reported in the preliminary communication. Several points warrant mention: (1) As expected, the M−N distances increase in the order Li < Na < K, consistent with the well-accepted group trends in ionic radii. (2) The Ca−N distance is 0.02 Å shorter than the Na−N distance, consistent with predictions based on six coordinated ions.[18] However, the Ca−O distances are notably shorter than the Na−O distance, and this implies that the increased positive charge on the calcium ion has a greater influence on the hemilabile ether donors. (3) Within each structure, the M−N and M−O distances are similar,

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Table 6. Selected Bond Lengths (Angstroms) and Angles (Degrees) in the Single-Crystal X-ray Structure of TlTp*, **5**

N(4)−Tl	2.703(3)	N(2)−N(1)−B	124.1(3)
N(6)−Tl	2.597(3)	N(1)−N(2)−Tl	117.8(2)
O1−Tl	3.109	N(6)−Tl−N(2)	77.20(11)
O3−Tl	3.050	N(1)−N(2)−Tl	117.8(2)
B−N(1)	1.534(5)	N(6)−Tl−O3	64.90
		O1−Tl−O3	120.97

as might be expected for dative bonds involving sp^2-hybridized nitrogen and sp^3 oxygen atoms, albeit for the minor differences noted in **2** above. However, the Li−N and Li−O distances differ by 0.35 Å, with the Li−O distances being longer than those in the sodium complex, **2**. This would seem to reflect the relative affinity of lithium toward nitrogen. (4) As the size of the metal ion increases, the bite angle of the N−O chelate decreases as does the N−M−N angle while the O−M−O angles increase. This is, of course, entirely consistent with expectations based on a hexadentate ligand binding to metals of differing size.

TlTp*, 5. The molecular structure of the thallium complex, **5**, is shown in Figure 5, and selected bond distances and angles are given in Table 6. The large and soft Tl$^+$ ion is bonded to three nitrogen atoms of the Tp* ligand, Tl−N $\sim$2.60 and very weakly to two of the ether oxygens, Tl−O $\sim$3.1 Å. Again, the difference between M−N and M−O is $\sim$0.4 Å, consistent with the soft nature of Tl$^+$ that has little affinity for the oxygen-donor ether. The Tl to O nonbonding distance is 6.3 Å.

Concluding Remarks

The preparation of a new scorpionate ligand adds to the ever-increasing number of Trofimenko-inspired ligands.[19] This is not the first hexadentate member of this family, and we note earlier work involving 3-{2-pyridyl)-[20] and {3-(2-methylsulfanyl)phenyl}-substituted ligands.[21] The present ligand, however, is well suited to provide coordination to the hard group 2 metals such as calcium, and this aspect of its chemistry and use as an ancillary ligand for the ROP of cyclic esters will be described in a further report.

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