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Siloxide and Triflate Gallium(III) Complexes Supported by the BDI Ligand

Malcolm H. Chisholm,* Diana Navarro-Llobet, and Judith Gallucci

Department of Chemistry, The Ohio State University,
Newman and Wolfrom Laboratories, 100 West 18th Avenue,
Columbus, Ohio 43210

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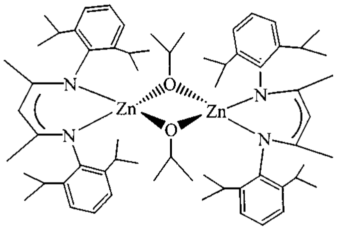
The ligand formed from deprotonation of 2-(2,6-diisopropylphenylamino)-4-(2,6-diisopropylphenyl-imino)-2-pentene, commonly called BDI, has already found an important position in single-site polymerization catalysis. For the later transition metals, it has been used in olefin polymerization catalysis,[1] and bonded to zinc[2] and magnesium,[3] it has been employed in lactide polymerization and the copolymerization of cyclohexene oxide.[1] The Coates' catalyst $[(BDI)Zn(O^iPr)]_2$, **I**, is remarkable in showing stereoselective polymerization of *rac*-lactide to give heterotactic PLA.[4] This presumably arises from end-group stereocontrol, for which the phenyl groups assist in creating a wedge in which the entering lactide and growing chain interact prior to the ring-opening event. This assumes that the reactive intermediate is a four-coordinate Zn or Mg complex, as depicted by **II**.



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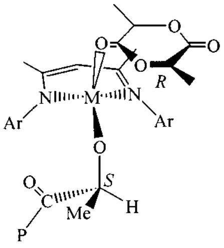

II

We were interested to see what influence the BDI ligand might exert in ROP of lactides at a five coordinate metal center. Prompted by these considerations, we turned our attention to group 13 elements, Al and Ga, with the intention of preparing (BDI)MX(OR) compounds, where X is an unreactive ancillary ligand, such as Cl, and OR represents a reactive group with respect to the ring-opening event. In our hands, we were unsuccessful in preparing a compound of this type for aluminum, although $(BDI)AlX_2$ compounds are known for X = Me,[5] Cl,[6] and I.[6] We describe here our findings for gallium. Since the inception of this work, others have reported the synthesis of $(BDI)Ga^{(I)}$,[7] $(BDI)GaX_2$, where X = Cl, I, and Me,[6] and (BDI)GaNAr′.[8]

Experimental Section

All syntheses were done under an argon atmosphere using standard Schlenk-line and drybox techniques. Toluene and ether were distilled from sodium benzophenone ketyl under nitrogen. Benzene and hexanes were distilled from potassium metal under nitrogen. $GaCl_3$ (Acros), potassium trimethyl-siloxide, and silver triflate (Aldrich) were used as purchased. The ligand BDI−H (2-(2,6-diisopropyl-phenylamino)-4-(2,6-diisopropylphenyl-imino)-2-pentene) was synthesized according to literature procedures,[9] as was Li(BDI)(THF). [9] $(BDI)GaCl_2$ was prepared from $GaCl_3$ and Li(BDI)(THF) in toluene.[6] PO was stirred over calcium hydride for 24 h and distilled under nitrogen. Lactide (Aldrich) was sublimed three times under nitrogen. Deuterated solvents were stored over 4 Å molecular sieves for 24 h prior to use.

^1H and ^{13}C NMR experiments were carried out with Bruker DPX-250 MHz and Bruker DPX-400 spectrometers operating at proton Lamour frequencies of 250 and 400 MHz, respectively. Their peak frequencies were referenced against benzene-d_6 at 7.15 ppm. ^{19}F NMR experiments were carried out on a Bruker DPX-250 MHz spectrometer and were referenced against 10% $CFCl_3$ in acetone-*d6* at 0 ppm. IR spectra were recorded in a Perkin-Elmer Spectrum GX FT-IR System.

Synthesis of $(BDI)GaCl(OSi(CH_3)_3)$. $(BDI)GaCl_2$ (0.2 g, 0.36 mmol) was dissolved in benzene. This solution was added to solid $KOSi(CH_3)_3$ (0.046 g, 0.36 mmol) at room temperature. The yellow solution was left stirring overnight, after which time, the solvent was evaporated under vacuum. The product was filtered from hexanes to give a yellow, clear solution, which was concentrated and recrystallized at −20 °C to give crystals suitable for X-ray diffraction. Yield: 0.18 g, 82%. E. A. Calcd: C, 62.80; H, 8.23; N, 4.58. Found: C, 62.68; H, 8.06; N, 4.53. IR (KBr, cm^{-1}): 3050, 2975, 2960, 2900, 1600, 1510, 1480, 1455, 1400, 1200, 1150, 925, 825, 800, 740. ^1H NMR (C_6D_6, ppm): δ 7.14, 7.12 (m, aromatic), 4.71 (s, 1H, *CH*), 3.59, 3.29 (heptet, 4H, $\mathit{CH}(CH_3)_2$), 1.52 (s, 6H, $(\mathit{CH_3})$), 1.515 (d, 6 H, $^3J_{H-H}$= 6.569 Hz, $CH(\mathit{CH_3})_2$), 1.45 (d, 6 H, $^3J_{H-H}$= 7.074 Hz, $CH(\mathit{CH_3})_2$), 1.17 (d, 6 H, $^3J_{H-H}$= 7.074 Hz, $CH(\mathit{CH_3})_2$), 1.065 (d, 6 H, $^3J_{H-H}$= 7.075 Hz, CH-$(\mathit{CH_3})_2$), 0.11 (s, 9H, $OSi(CH_3)_3$). ^{13}C NMR (C_6D_6, ppm): δ 170.8 (CH-*C*═N), 145.4, 144.0, 139.1, 125.1, 124.0 (aromatic), 96.2 (*C*H−C═N), 28.9 ($\mathit{CH_3}$−C═N), 28.1, 26.4, 24.8, 24.8 ($(\mathit{C}H_3)_2CH$), 24.2, 23.4 ($(CH_3)_2\mathit{C}H$), 2.8 ($OSi(\mathit{C}H_3)_3$).

Synthesis of $(BDI)GaCl(OSO_2CF_3)$. Ether was added to a flask containing $(BDI)GaCl_2$ (0.2 g, 0.36 mmol) and silver triflate (0.092 g, 0.36 mmol) at room temperature. The solution was left stirring overnight, after which time, a gray precipitate formed. After filtering, the resulting clear, colorless solution was evaporated under vacuum to give a white solid. Yield: 0.20 g, 83%. E. A. Calcd: C, 53.63; H, 6.15; N, 4.17. Found: C, 52.79; H, 6.19; N, 4.16. IR (KBr, cm^{-1}): 2964, 2871, 1530, 1465, 1438, 1375, 1204, 970, 810, 635. ^1H NMR (C_6D_6, ppm): δ 7.16, 7.13 (m, aromatic), 4.76 (s, 1H, *CH*), 3.32, 3.20 (heptet, 4H, $\mathit{CH}(CH_3)_2$), 1.46 (s, 6H, $(\mathit{CH_3})$), 1.485 (d, 6 H, $^3J_{H-H}$= 8.084 Hz, $CH(\mathit{CH_3})_2$), 1.355 (d, 6 H, $^3J_{H-H}$= 6.568 Hz, $CH(\mathit{CH_3})_2$), 1.09 (d, 6 H, $^3J_{H-H}$= 7.074 Hz, $CH(\mathit{CH_3})_2$), 1.05 (d, 6 H, $^3J_{H-H}$= 6.569 Hz, $CH(\mathit{CH_3})_2$). ^{13}C NMR (C_6D_6, ppm): δ 173.4 (CH-*C*═N), 144.6, 144.4, 137.1, 128.9, 125.1 (aromatic), 98.2 (*C*H−C═N), 28.8 ($\mathit{CH_3}$−C═N), 28.5, 25.5, 24.8, 24.7 ($(\mathit{C}H_3)_2CH$), 24.2, 23.5 ($(CH_3)_2\mathit{C}H$), OSO_2-CF_3 unresolved. ^{19}F NMR (C_6D_6, ppm): δ −75.5 (s, CF_3).

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* To whom correspondence should be addressed. chisholm@chemistry.ohio-state.edu.

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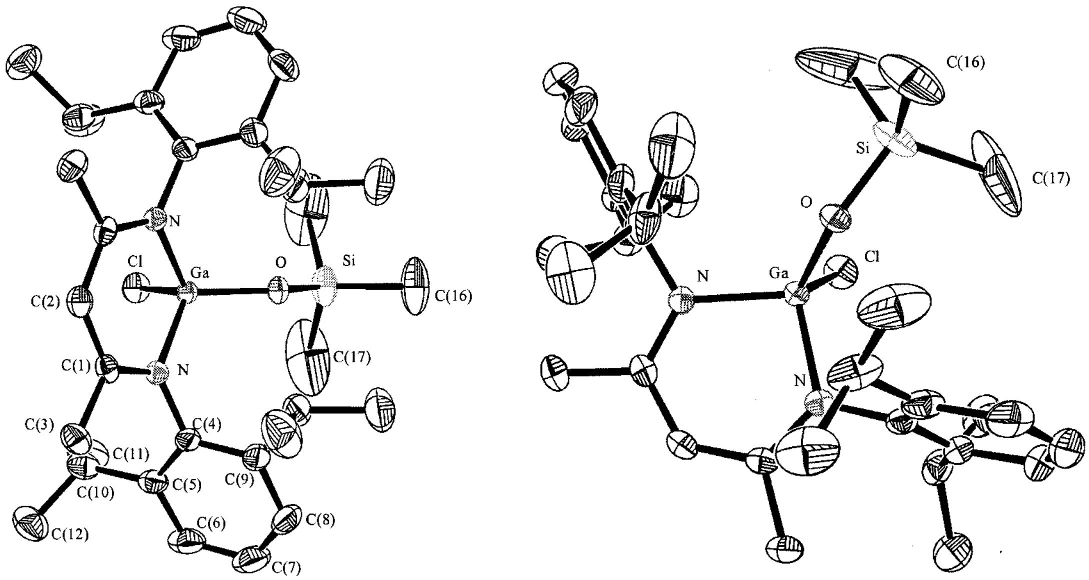

Figure 1. Two views of the compound (BDI)GaCl(OSiMe$_3$).

Table 1. Crystallographic Data for Compound (BDI)GaCl(OSiMe$_3$)

	BDIGaCl(OSiMe$_3$)
empirical formula	$C_{32}H_{50}ClGaN_2OSi$
fw	612.00
space group	*P21/m*
a (Å)	9.1113(1)
b (Å)	20.1484(2)
c (Å)	10.1963(1)
α (deg)	90.00(0)
β (deg)	115.313(1)
γ (deg)	90.00(0)
Temp (K)	150
Z	2
V (Å^3)	1692.10(3)
D_{calc} (mg/m^3)	1.201
λ (Å)	0.71073
μ (mm^{-1})	0.953
R_1 (*F*)	0.0373
*R*w (*F*)	0.0766

Polymerization Studies. Attempted polymerization reactions were done as follows: **(1) PO.** BDIGaClX (X=Cl, OSiMe$_3$) was added to PO monomer. The solution was left stirring for 3 days, after which time, the solvent was evaporated under vacuum. No polymerization occurred. **(2) L-Lactide.** Lactide (0.14 g, 0.97 mmol) was dissolved in benzene. The compound BDIGaClX (X = Cl, OSiMe$_3$, OSO$_2$CF$_3$, 0.020 mmol) was added to the solution. After stirring at 60 °C for 3 days, the solvent was evaporated under vacuum. No polymerization occurred.

PO/(BDI)GaCl(OSO$_2$CF$_3$). 1 mL of PO was mixed with 10 mg of catalyst and left stirring at room temperature. After 48 h, the excess monomer was evaporated under vacuum to give PPO. ^{1}H NMR (C$_6$D$_6$, ppm): δ 1.10, 1.14, 1.15, 1.16, 1.17, 1.18, 1.19 (m, CH$_3$), 3.36, 3.39, 3.40, 3.53, 3.54, 3.55, 3.56, 3.57 (m, CH and CH$_2$). ^{13}C NMR (C$_6$D$_6$, ppm): δ 16.8, 17.1, 17.7, 18.0, 18.3, 18.4, 18.8 (m, CH$_3$), 73.5, 73.8, 74.2, 74.7, 75.0, 75.2, 75.6, 75.7, 75.8, 76.2 (m, CH and CH$_2$). Yield: 40%.

Attempted Preparation of (BDI)Ga(X)(Y) Compounds. Equal molar quantities of (BDI)GaCl$_2$ or BDIGaCl(OSiMe$_3$) were mixed with one of LiNMe$_2$, LiN^{i}Pr$_2$, KO^{t}Bu, NaO^{t}Bu, or KOCH$_2$^{t}Bu. A solvent such as toluene, ether, THF, or hexanes was added. The reaction was left stirring overnight, after which time, the solvent was evaporated under vacuum. The remaining solid was washed with hexanes.

Results and Discussion

The challenge in the synthesis of a (BDI)GaX(OR) compound rests in the way in which the ligands are introduced to Ga. Initially, we employed the dimeric compound ClGa(NMe$_2$)$_2$[10] in reactions with BDI−H and (BDI)Li(THF). In the former case, we observed no reaction, and in the latter, mixtures were obtained. Starting with GaCl$_3$ and (BDI)Li(THF), we were able to obtain (BDI)GaCl$_2$ as a monomeric crystalline compound in a manner similar to that recently reported.[6] Attempted metathetic reactions involving (BDI)GaCl$_2$ and LiNMe$_2$, LiN^{i}Pr$_2$, KO^{t}Bu, NaO^{t}Bu, or KOCH$_2$^{t}Bu in benzene, toluene, Et$_2$O, and THF all failed to give single products of either mono- or disubstitution. The reactions proceeded slowly and always gave mixtures of products. Heating often displaced the BDI ligand as BDI−H. However, analogous reactions with KOSiMe$_3$ in benzene at room temperature did yield the desired product, (BDI)GaCl(OSiMe$_3$), as a white crystalline solid, which was soluble in common organic solvents (benzene, toluene, hexanes, etc).

The reaction between AgOSO$_2$CF$_3$ and (BDI)GaCl$_2$ in ether at room temperature was successful in yielding the triflate (BDI)GaCl(OSO$_2$CF$_3$), which was also a white crystalline solid. The solution NMR characterization of these compounds (Experimental Section) clearly identified the four-coordinate metal center as a compound of formula (BDI)GaX(Y). Specifically, the ^{i}Pr methyl signals appear as four sets of doublets. There is restricted rotation about the aryl C−N bonds and no C_2 axis of symmetry, which causes the ^{i}Pr groups to have diastereotopic methyl groups.

Solid State and Molecular Structure of (BDI)GaCl(OSiMe$_3$). A summary of crystallographic data is given in Table 1, and an ORTEP drawing of the molecule is given in Figure 1. A summary of selected bond distances and angles is given in Table 2 , where a comparison is also made with the related structures of (BDI)GaCl$_2$ and (BDI)Sn(O^{i}Pr). The latter compound involves a three-coordinate pyramidal Sn(II) center.[11] Formally, a lone pair could be viewed to occupy the fourth position at Sn(II). Its inclusion here is relevant, as this compound has been shown to be active in initiating the ROP of lactides.[11] The geometrical parameters for the two gallium compounds are not surprisingly similar with respect to the GaN$_2$Cl moiety. The Ga−O distance of 1.78 Å is short. The Ga−O−Si angle is 136°,

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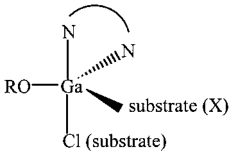
close to 120°, and it appears that the $SiMe_3$ group is constrained to lie over the Ga−Cl bond as a result of the steric interactions with the ${}^{i}Pr$ groups of the BDI ligand (see Figure 1).

The comparison with the Sn(II) compound reveals the notably larger radius of Sn(II) relative to Ga(III). Given the position of the two elements in the periodic table, this would seem to solely reflect the influence of charge on the metal center. The angles subtended at Sn(II) are all closer to 90°, in part in a reflection of the greater 4p element bonding. Conversely, in comparing the angles at Ga(III) and Sn(II), Ga employs more sp^3 character; for Sn(II), the 4s orbital is less involved as a result of the inert pair effect of the ns^2 valence configuration.

Inspection of Figure 1 and Table 2 allows one to anticipate the addition of a substrate to the Ga(III) center to form a five-coordinate adduct. The BDI ligand, which has a constrained N−Ga−N angle of less than 100°, would be expected to occupy an axial−equatorial site of a trigonal bipyramid. Based on considerations of trans influence and steric factors, we would anticipate the OR ligand to be equatorial, as depicted in **III**.



III

The position of the chloride and substrate could be either axial or equatorial, depending upon a variety of factors. In any event, the substrate and OR group would be cis, a requirement for migratory ring opening.

Attempted Polymerization Reactions. Despite the considerations above, we found that the $(BDI)GaCl(OSiMe_3)$ compound was inactive for ROP of L-lactide in benzene, even at 60 °C. [The $(BDI)GaCl_2$ and the triflate compound were similarly inactive, but based on our earlier studies they were not expected to be active].[12]

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(BDI)GaCl_2$,[a] $(BDI)GaCl(OSiMe_3)$, and $(BDI)Sn(O^{i}Pr)$[b]

	$(BDI)GaCl_2$	$(BDI)GaCl (OSiMe_3)$	$(BDI)Sn (O^{i}Pr)$
M−N	1.926(3) 1.906(3)	1.920(1)	2.206(4) 2.208(4)
M-Cl	2.228(1) 2.218(1)	2.1781(6)	
M−O		1.789(2)	2.000(5)
N−M−N	100.2(1)	98.34(8)	83.6(2)
Cl−M−X	110.20(4)	109.92(5)	
N−M−X			
X=O		112.36(5)	94.1(2) 92.5(2)
X=Cl	113.21 (4)[c] 110.09 (4)	111.74(4)	

[a] From ref 5. [b] From ref 11. [c] From our data.

Although the negative findings could be explained in a number of ways, we are inclined to the view that substrate uptake is rate limiting, i.e., lactide fails to bind significantly to this sterically demanding center.

From our previous work, we know that propylene oxide, PO, is a better ligand than lactide and competes with THF in binding to three coordinate Al(III) centers.[12] We therefore investigated the reactions of $(BDI)GaCl_2$, $(BDI)GaCl(OSiMe_3)$, and $(BDI)GaCl(OSO_2CF_3)$ with PO (see Experimental Section). Of those, only the triflate showed reactivity yielding highly regioirregular polypropylene oxide typical of Lewis acidic coordinate catalysis.[12]

Concluding Remarks

Although we were only successful in preparing one compound of formula (BDI)GaCl(OR), it seems likely that if other alkoxides are subsequently prepared they will be poor catalysts, if indeed effective at all, in the ROP of lactides.

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Supporting Information Available: CIF data for compounds $(BDI)GaCl_2$ and $(BDI)GaCl(OSiMe_3)$ are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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