Diterphenylgallium Alkyls and Hydride: Synthesis, Characterization, and Reactivity

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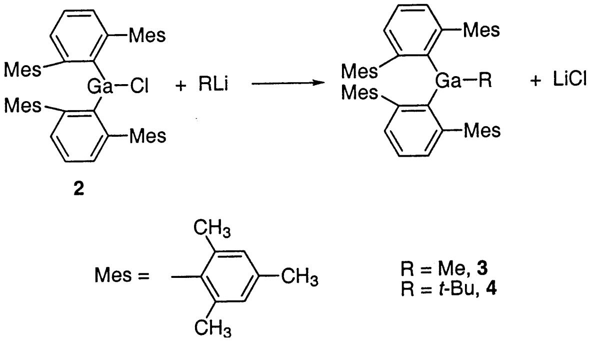
The reactions of $(2,6\text{-}Mes_2C_6H_3)_2GaCl$ (**2**) with LiMe, Li-*t*-Bu, and $LiHBEt_3$ afforded the bis(terphenyl)gallium compounds $(2,6\text{-}Mes_2C_6H_3)_2GaMe$ (**3**), $(2,6\text{-}Mes_2C_6H_3)_2Ga\text{-}t\text{-}Bu$ (**4**) and $(2,6\text{-}Mes_2C_6H_3)_2GaH$ (**5**). Hydrolysis of **2** and **3** gave the dimeric, hydroxide-bridged species $[2,6\text{-}Mes_2C_6H_3Ga(Cl)(\mu\text{-}OH)]_2$ (**6**) and $[2,6\text{-}Mes_2C_6H_3Ga(Me)(\mu\text{-}OH)]_2$ (**7**) via loss of the terphenyl substituent as $1,3\text{-}Mes_2C_6H_4$. Hydrolysis of **5** led to the loss of H_2 and the formation of the monomeric $(2,6\text{-}Mes_2C_6H_3)_2GaOH$ (**8**). The compounds were characterized by FTIR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and X-ray crystallography. The structural studies of the diterphenyl compounds **2**−**5** and **8** showed the highly flexible nature of these compounds, as expressed in the wide range of the $C_{Terph}-Ga-C_{Terph}$ angles from 113.23° in **4** to 153.5° in **2**. Methyl and hydride abstraction from **3** and **5** with the Lewis acids $[Ph_3C]^+[B(C_6F_5)_4]^-$ and $B(C_6F_5)_3$ afforded the ionic species $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+[B(C_6F_5)_4]^-$, $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+[MeB(C_6F_5)_3]^-$, and $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+[HB(C_6F_5)_3]^-$, all of which contain the linear two-coordinate cation $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$ ($\mathbf{1}^+$).

Introduction

Cationic aluminum compounds as potential transition-metal-free polymerization catalysts have been the focus of a series of recent research efforts by several groups.[1−4] As the high reactivity of low-coordinate cationic aluminum compounds has so far prevented a detailed analysis of their catalytic activity, we have begun to investigate the possible stabilization of these species by employment of sterically demanding and chemically robust *m*-terphenyl substituents.[5,6] In this context, we have recently prepared a linear two-coordinate bis(terphenyl)gallium cation, $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$ ($\mathbf{1}^+$), as a less reactive model compound for the above-mentioned alumenium ions.[7] This compound was obtained from a metathesis reaction of $(2,6\text{-}Mes_2C_6H_3)_2GaCl$ (**2**)[8] with 2 equiv of $Li[Al\{OCH(CF_3)_2\}_4]$.[9,10] Although successful, this approach was rather unusual for the preparation of cationic organometallic species. More common routes involve halide,[11] methide,[1] or hydride[12] abstraction with strong Lewis acids such as $AlCl_3$, $SbCl_5$, $[Ph_3C]^+[B(C_6F_5)_4]^-$, and $B(C_6F_5)_3$. To extend the scope of the formation of low-coordinate cationic gallium compounds, we have synthesized two new bis(terphenyl)gallium alkyls, $(2,6\text{-}Mes_2C_6H_3)_2GaMe$ (**3**) and $(2,6\text{-}Mes_2C_6H_3)_2Ga\text{-}t\text{-}Bu$ (**4**), and one bis(terphenyl)gallium hydride, $(2,6\text{-}Mes_2C_6H_3)_2GaH$ (**5**). Here we report their synthesis, their structural and spectroscopic characterization, and their reactivity toward the Lewis acids $Ph_3C^+[B(C_6F_5)_4]^-$ and $B(C_6F_5)_3$ and the weak Brønsted acid H_2O.

Results and Discussion

Synthesis and Characterization. The alkyl-substituted bis(terphenyl)gallium compounds $(2,6\text{-}Mes_2C_6H_3)_2GaMe$ (**3**) and $(2,6\text{-}Mes_2C_6H_3)_2Ga\text{-}t\text{-}Bu$ (**4**) were obtained by a metathesis reaction of **2**[8] with 1 equiv of LiMe or Li-*t*-Bu in benzene solution at 2−3 °C (eq 1).



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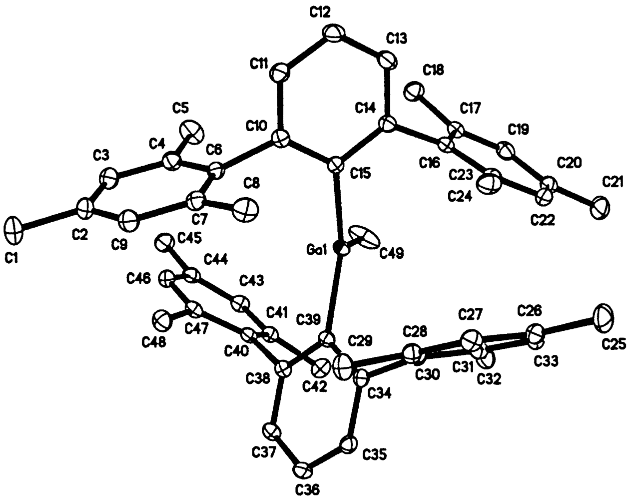
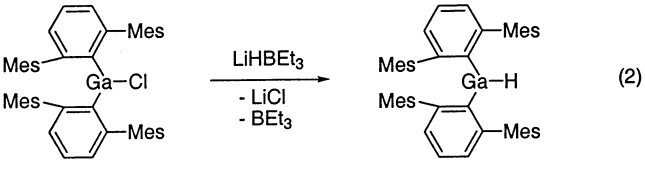


Figure 1. Thermal ellipsoid plot (30% probability ellipsoids) showing the molecular structure of **3**. Hydrogen atoms are omitted for clarity.

Similar to **2**, compound **3** is only slightly soluble in hexanes or Et_2O but highly soluble in benzene or toluene, whereas **4** is also soluble in hexanes. The formation of the *tert*-butyl derivative **4** was unexpected, since it had been observed previously that sterically hindered diarylaluminum or -gallium chlorides form the corresponding hydrides upon reaction with Li-*t*-Bu.[13] While the detailed mechanism for this latter reaction is not known, it is likely to proceed via a four-centered transition state involving the gallium center, the α- and β-carbons, and one of the β-hydrogens of the *tert*-butyl group. In the case of our reaction (eq 1) it seems plausible that the large steric requirements of two terphenyl substituents prevent the close approach of one of the β-hydrogens of the *tert*-butyl group to the gallium center. Compound **4** is surprisingly stable. No change is observed until its melting point at 262−268 °C, where it decomposes with gas evolution. Attempts to utilize this thermolysis reaction as a source for the hydride derivative $(2,6\text{-}Mes_2C_6H_3)_2GaH$ (**5**) were unsuccessful. However, **5** was eventually obtained in moderate yields by the reaction of **2** with Super-Hydride, $LiHBEt_3$ (eq 2).



2 **5** (2)

The crystal structure of the precursor $(2,6\text{-}Mes_2C_6H_3)_2$-GaCl (**2**) features an unusually wide C−Ga−C angle of 153.5(5)°.[8] To explore the influence of size and electronic properties of the substituent X on the structure of the bis(terphenyl)gallium compounds $(2,6\text{-}Mes_2C_6H_3)_2GaX$ (X = Cl (**2**), Me (**3**), *t*-Bu (**4**), H (**5**), OH (**8**)), the structures of **3**−**5** and **8** were determined by X-ray crystal structure analyses (for the synthesis of **8**, see below). The overall structural features of **3** (Figure 1), **4** (Figure 2), **5** (Figure 3), and **8** (Figure 4) are similar to those of the precursor **2**. The gallium center is three-coordinate in an unsymmetrical trigonal-planar environment, and the terphenyl substituents are arranged in a staggered fashion with respect to each other in order to minimize steric repulsion. However, there are

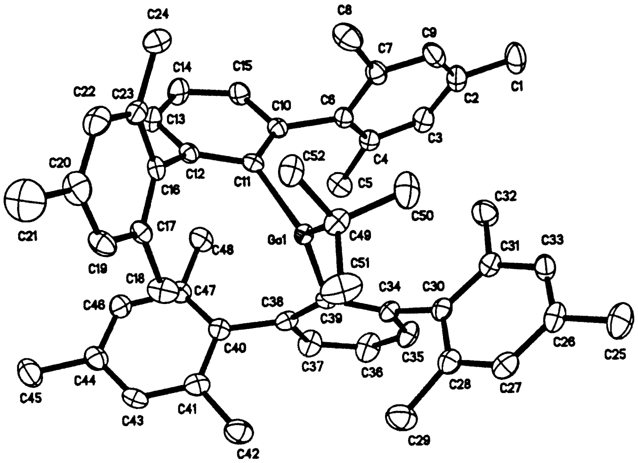


Figure 2. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **4**. Hydrogen atoms are omitted for clarity.

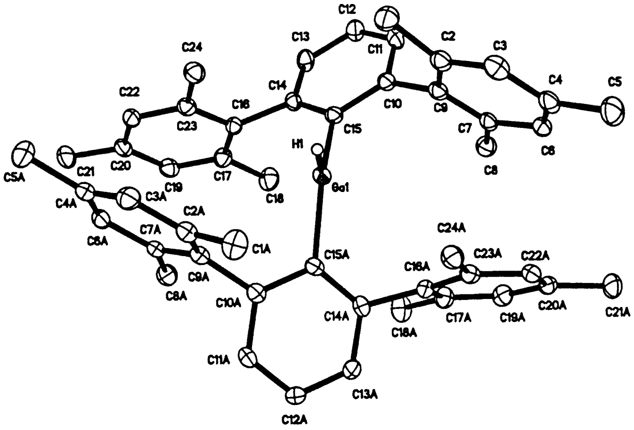


Figure 3. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **5**. Hydrogen atoms, with the exception of H(1), are omitted for clarity.

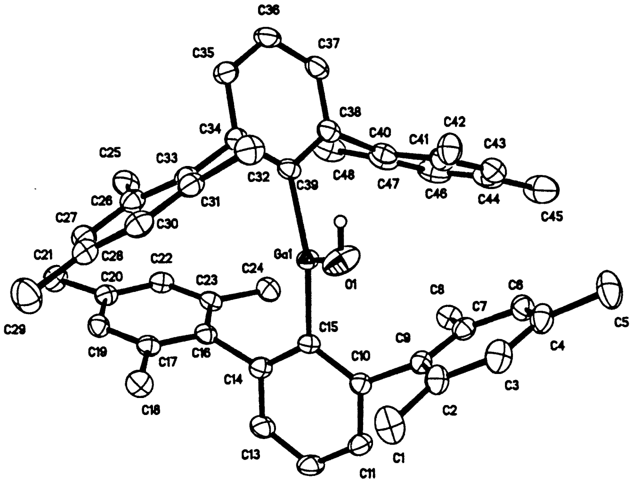


Figure 4. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **8**. Hydrogen atoms, with the exception of that bound to O(1), are omitted for clarity.

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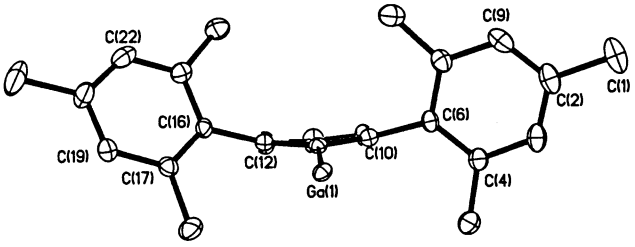

Figure 5. Thermal ellipsoid plot (50% probability ellipsoids) illustrating the distortions of one the terphenyl substituents in **4**. Hydrogen atoms are omitted for clarity.

significant variations in the $C_{Terph}-Ga-C_{Terph}$ angles, depending on the substituent X, with values of 135.08(7)° for **3**, only 113.23(14)° for **4**, 134.65(5)° for **5**, and 143.11(6)° for **8** (Table 2). This not only illustrates the high flexibility of the bis(terphenyl)gallium unit but may also be viewed as a reflection of a significant ionic (nondirectional) contribution to the character of the gallium−carbon bond. At first glance, the $C_{Terph}-Ga-C_{Terph}$ angles respond to the size of the substituents X in the order Cl < Me < *t*-Bu. However, the values for **5** and **8** do not fit this order, since both the hydride and the hydroxide are smaller than a chloride substituent,[14,15] and therefore a wider $C_{Terph}-Ga-C_{Terph}$ angle would be expected. An alternative rationalization includes the electronegativities[16] of the substituents: lower electronegativity ($\chi(CH_3) = 2.31$, $\chi(H) = 2.20$, Pauling scale) is correlated with smaller $C_{Terph}-Ga-C_{Terph}$ angles and vice versa ($\chi(Cl) = 3.16$, $\chi(OH) = 2.82-3.42$). In other words, a more polar Ga−X bond favors a widening of the $C_{Terph}-Ga-C_{Terph}$ angle, which approaches 180° for the two-coordinate cation. This is also reflected in the $Ga-C_{Terph}$ bond distances, which are shortest for X = Cl, OH with average values of 1.978 and 1.991 Å compared to 2.024 and 1.995 Å for X = Me, H, respectively. The large size of the *tert*-butyl substituent in **4** results in significant deviations from the above trends. The Ga−C distances are the longest (2.025 Å average), and the $C_{Terph}-Ga-C_{Terph}$ angle at 113.23(14)° is by far the narrowest in this group.

The crowded nature of the bis(terphenyl)gallium compounds also leads to distortions in the terphenyl substituents. In general, the flanking mesityl groups are pushed backward by 1.0−13.6°, and the central aryl rings are bent out of the GaC_2X plane by 3.3−13.8°. Similar distortions, but more severe, are observed in the very crowded structure of **4**. Both terphenyl substituents are severely bent. An illustration is given in Figure 5. The flanking mesityl groups are bent away from the plane of the central aryl ring by 10.2−16.4°. Similarly, the central aryl rings are bent out of the GaC_3 plane by 15.5° (C10−C15 ring) and 19.2° (C34−C39 ring). Further evidence for the steric crowding in **4** is found in the ^1H NMR spectra. Whereas the two terphenyl substituents are chemically equivalent in the ^1H NMR spectra of **2**, **3**, **5**, and **8**, the spectra of **4** display two sets of broadened signals for the *o*-Me groups, and the *m*-H signal of the mesityl groups is also broadened. The large size of the *tert*-butyl group apparently interferes with the motion of the aryl groups. A similar loss of chemical equivalence was observed for the cation $[(2,6\text{-}Mes_2C_6H_3)_2Ga\cdot pyridine]^+$.[7]

Reactivity. Our primary interest in the synthesis of the bis(terphenyl)gallium alkyls **3** and **4** and hydride **5** was the development of readily available precursors for the formation of cationic two-coordinate organometallic gallium species $[Terph_2Ga]^+$. One commonly used method for the generation of cationic organometallic species involves methide or hydride abstraction with trityl salts or strong Lewis acids. Most of the following experiments were performed in NMR tubes using about 10−20 mg of the gallium compound, and the progress of the reactions was monitored by ^1H and ^{19}F NMR spectroscopy. The reaction of $(2,6\text{-}Mes_2C_6H_3)_2GaMe$ (**3**) with $[Ph_3C]^+[B(C_6F_5)_4]^-$ at room temperature (eq 3) proceeded slowly, probably due to the low solubility of the trityl salt in C_6D_6.

$$(2,6\text{-}Mes_2C_6H_3)_2GaMe + [Ph_3C]^+[B(C_6F_5)_4]^- \rightarrow [(2,6\text{-}Mes_2C_6H_3)_2Ga]^+[B(C_6F_5)_4]^- + Ph_3CMe \quad (3)$$

In fact, many of these ionic organometallic compounds form dense phases, so-called clathrates,[12,17,18] in benzene solution. NMR spectra of these clathrates can be obtained if the sample is shaken vigorously and the data collection is completed before most of the dense phase has settled back to the bottom of the NMR tube. After 1 day, approximately half of the initial amount of **3** was consumed, and a new set of methyl signals was observed at δ 2.08 and 1.32 ppm in a ratio of 1:2. After 3 days more, ca. 75% of **3** was consumed, and the reaction was complete after 1 month. The C_6D_6 solution, which contained essentially only Ph_3CH, Ph_3CMe, and 1,3-$Mes_2C_6H_4$, was separated, and the remaining red oil was dissolved in C_6D_5Cl. The ^1H NMR spectrum clearly showed the presence of the cation $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$,[7] and the ^{19}F NMR spectrum is indicative of the uncoordinated $[B(C_6F_5)_4]^-$ anion.[19] The reaction of **3** and **5** with $B(C_6F_5)_3$ (eq 4) resulted in the separation of a colorless dense phase after approximately 20 h.

$$(2,6\text{-}Mes_2C_6H_3)_2GaR + B(C_6F_5)_3 \rightarrow [(2,6\text{-}Mes_2C_6H_3)_2Ga]^+[RB(C_6F_5)_3]^- \quad (4)$$
$$R = Me, H$$

NMR spectra of the upper C_6D_6 phase indicated that ca. 90% of the precursors were consumed. Removal of the C_6D_6 phase and dissolution of the dense clathrate in C_6D_5Cl or a 3:1 mixture of C_6D_6 and C_6D_5Cl gave clear colorless solutions whose ^1H and ^{19}F NMR spectra were in agreement with the formation of the ions $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$ [7] and $[MeB(C_6F_5)_3]^-$ [19] or $[HB(C_6F_5)_3]^-$.[20] No reaction was observed when $B(C_6F_5)_3$ was added to the crowded *tert*-butyl compound **4** in C_6D_6 solution.

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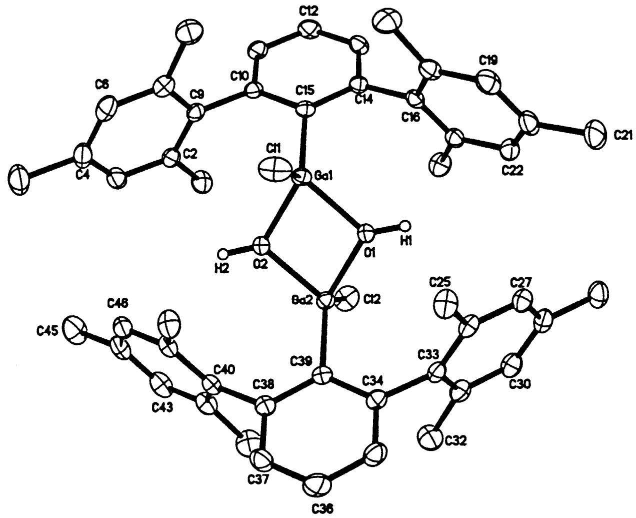

Figure 6. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **5**. Hydrogen atoms, with the exception of H(1) and H(2), are omitted for clarity.

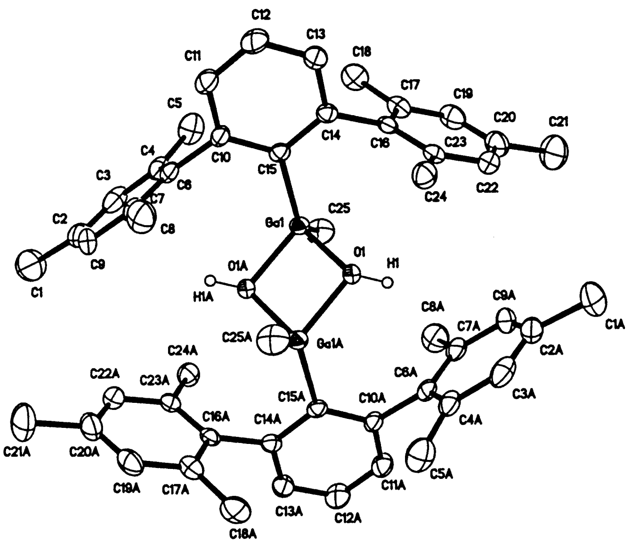

Figure 7. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of one of the two independent molecules of **5**. Hydrogen atoms, with the exception of H(1) and H(1a), are omitted for clarity.

Exposure of **2**, **3**, and **5** to moisture led to the formation of the hydroxide derivatives [2,6-$Mes_2C_6H_3$-Ga(Cl)(μ-OH)]$_2$ (**6**) [2,6-$Mes_2C_6H_3Ga(Me)(\mu\text{-}OH)]_2$ (**7**), and the unique $(2,6\text{-}Mes_2C_6H_3)_2GaOH$ (**8**), respectively (eqs 5 and 6).

$$(2,6\text{-}Mes_2C_6H_3)_2GaR + H_2O \rightarrow$$
$$^1/_2[2,6\text{-}Mes_2C_6H_3Ga(R)(\mu\text{-}OH)]_2 + 1,3\text{-}Mes_2C_6H_4 \quad (5)$$
$$R = Cl\ (\mathbf{6}),\ Me\ (\mathbf{7})$$

$$(2,6\text{-}Mes_2C_6H_3)_2GaH + H_2O \rightarrow$$
$$(2,6\text{-}Mes_2C_6H_3)_2GaOH + H_2 \quad (6)$$

It should be pointed out that the hydrolysis of **2** and **3** led to the loss of one terphenyl substituent, whereas the hydride substituent was eliminated in **8**. The crystal structures of **6** and **7** are similar (Figures 6 and 7). Both compounds consist of dimers connected by bridging hydroxides with a trans arrangement of the terphenyl substituents. Their overall structural features correspond closely to those of the related hydroxy-bridged $[2,6\text{-}Trip_2C_6H_3Ga(Cl)(\mu\text{-}OH)]_2$[21] and the chloride-bridged $[2,6\text{-}Mes_2C_6H_3M(Cl)(\mu\text{-}Cl)]_2$ (M = Al,[22] Ga[23]). The Ga−O and Ga−C_{Terph} distances in **6** are about 0.02 Å shorter than those in **7**, a possible reflection of the higher Lewis acidity of the chloride-containing compound **6**. The product of the hydrolysis of **5**, $(2,6\text{-}Mes_2C_6H_3)_2GaOH$ (**8**), is to date the only gallium hydroxide species that is monomeric in the solid state. The overall features of the structure of **8** have been discussed above. The Ga−O bond distance with a value of 1.7833(17) Å is less than those found previously for monomeric three-coordinate diorganogallium alkoxides (1.821(3) Å in $t\text{-}Bu_2GaOC_6H_3$-4-Me-2,6-t-Bu_2,[24] 1.831(4) Å in $t\text{-}Bu_2GaOCPh_3$,[25] and 1.843(2) Å in $[(Me_3Si)_2CH]_2GaOC_6F_5$[26]). The hydroxide hydrogen (H1a) was located in the C_2GaO plane.

Summary

Four new monomeric bis(terphenyl)-substituted gallium compounds have been obtained by metathesis reactions involving the precursor $(2,6\text{-}Mes_2C_6H_3)_2GaCl$ (**2**) and MeLi, t-BuLi, or $LiHBEt_3$ or by gentle hydrolysis of $(2,6\text{-}Mes_2C_6H_3)_2GaH$ (**5**). The structural investigation of these compounds illustrated the high flexibility of the bis(terphenyl)gallium system, as expressed in the C_{Terph}−Ga−C_{Terph} angles ranging from 113.23(14)° in **4** to 153.5(5)° in **2**. Methide or hydride abstraction from **3** or **5** by either $[Ph_3C]^+[B(C_6F_5)_4]^-$ or $B(C_6F_5)_3$ led smoothly to the formation of the unsolvated, linear, two-coordinate cation $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$ (**1**$^+$). Slow hydrolysis of **2** or **3** afforded the dimeric hydroxide-bridged compounds **6** and **7**, while the gallium hydride species **5** was cleanly transformed to the unique monomeric bis(terphenyl)-gallium hydroxide **8**. Studies involving other terphenyl substituents or the corresponding aluminum compounds are under way.

Experimental Section

General Procedures. All work was performed under anaerobic and anhydrous conditions by using either modified Schlenk techniques or an Innovative Technologies drybox. Solvents were freshly distilled under N_2 from sodium, potassium, or sodium/potassium alloy and degassed twice prior to use. *tert*-Butyllithium (1.5 M in pentane), methyllithium (1.5 M in Et_2O), Super-Hydride ($LiHBEt_3$; 1.0 M in THF), and $B(C_6F_5)_3$ were obtained from commercial suppliers. $(2,6\text{-}Mes_2C_6H_3)_2GaCl$ (**2**)[8] and $[Ph_3C]^+[B(C_6F_5)_4]^-$ [27] were synthesized according to literature methods. NMR spectra were recorded on a Varian Mercury 300 MHz or a Varian Unity Plus 400 MHz spectrometer, and ^1H NMR chemical shift values were determined relative to the residual protons in C_6D_6 as internal reference (δ 7.15 ppm). ^{13}C NMR spectra were referenced to the solvent signal (δ 128.0 ppm), and ^{19}F NMR

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spectra were referenced to an external solution of $C_6F_5CF_3$ in C_6D_6 (δ −63.72 ppm). Infrared spectra were recorded in the range 4000−200 cm^{-1} as either a Nujol mull or a thin film between CsI plates using a Nicolet Nexus 470 FTIR spectrometer. Melting points were determined in Pyrex capillary tubes (sealed under nitrogen) with a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed at Complete Analysis Laboratories Inc. in Parsippany, NJ, and Desert Analytics in Tucson, AZ.

$(2,6\text{-}Mes_2C_6H_3)_2GaMe$ (3). A solution of **2** (0.73 g, 1.0 mmol) in benzene (30 mL) was treated with a solution of MeLi in Et_2O (1.6 M, 0.66 mL, 1.05 mmol) via syringe at 2−3 °C. The ice bath was removed, and the reaction mixture was stirred at room temperature for 17 h. The fine colorless precipitate was allowed to settle, and the colorless supernatant liquid was decanted. Concentration to 1−2 mL under reduced pressure and subsequent cooling to 3−4 °C for 3 days gave well-shaped, colorless crystals of X-ray quality (0.1 g). A second batch (0.16 g) was obtained after concentration of the mother liquor to ca. 0.5−1 mL at room temperature for 2 days. Yield: 36%. Mp: 225−228 °C. Anal. Calcd for $C_{49}H_{53}Ga$: C, 82.70; H, 7.51. Found: C, 82.89; H, 7.35. ^1H NMR (400 MHz, C_6D_6): δ 7.05 (t, J = 7.6 Hz, *p*-H, 2H), 6.83 (s, *m*-H(Mes), 8H), 6.68 (d, J = 7.6 Hz, *m*-H, 4H), 2.23 (s, *p*-Me, 12H), 1.82 (s, *o*-Me, 24H), −0.12 (s, Ga−Me, 3H). $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6): δ 152.06, 148.42, 142.27, 137.01, 136.49, 128.94 (*m*-C(Mes)), 128.84, 128.79, 21.86 (*o*-Me), 21.20 (*p*-Me), 8.46 (Ga−Me).

$(2,6\text{-}Mes_2C_6H_3)_2Ga\text{-}t\text{-}Bu$ (4). *t*-BuLi (2.6 mL, 3.9 mmol, 1.5 M in pentane) was added dropwise to a solution of **2** (2.78 g, 3.8 mmol) in benzene (30 mL) at 2−3 °C. The reaction mixture was warmed to room temperature and stirred overnight. After removal of the solvent the colorless solid was extracted with hexanes (40 mL) and separated from the insoluble material by decanting. Concentration of the hexane solution to ca. 30 mL and subsequent cooling to −30 °C for 2 days afforded well-shaped, colorless crystals (0.85 g) of **4**$\cdot 0.5C_6H_{14}$. A second crop (0.75 g) was obtained after concentration of the mother liquor and cooling at −30 °C for 1 week. Yield: 56%. Mp: 262−268 °C with gas evolution. Anal. Calcd for $C_{55}H_{66}Ga$: C, 82.90; H, 8.35. Found: C, 81.92; H, 8.19. ^1H NMR (300 MHz, C_6D_6): δ 7.10 (t, J = 7.5 Hz, *p*-H, 2H), 6.80 (d, J = 7.5 Hz, *m*-H, 4H), 6.72 (s, br, $w_{1/2}$ = 4.3 Hz, *m*-H(Mes), 8H), 2.14 (s, *p*-Me, 12H), 1.93 (s, br, $w_{1/2}$ = 6.9 Hz, *o*-Me, 12H), 1.69 (s, br, $w_{1/2}$ = 7.4 Hz, *o*-Me, 12H), 0.47 (s, *t*-Bu, 9H). $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6): δ 153.98, 150.21, 143.19, 139.28 (br, $w_{1/2}$ = 50 Hz), 136.87, 136.11 (br, $w_{1/2}$ = 50 Hz), 129.84, 129.26, 129.01, 128, 58, 128.53, 31.89 ($C(CH_3)_3$), 29.13 ($C(CH_3)_3$), 22.63, (br, $w_{1/2}$ = 50 Hz, *o*-Me), 21.49 (br, $w_{1/2}$ = 50 Hz, *o*-Me), 20.85 (*p*-Me).

$(2,6\text{-}Mes_2C_6H_3)_2GaH$ (5). A solution of **2** (0.42 g, 0.57 mmol) in benzene (10 mL) was treated with $LiHBEt_3$ solution in THF (1.0 M, 0.7 mL) at room temperature and stirred for 23 h. The very fine colorless precipitate was allowed to settle for 2 days. After careful decanting of the clear colorless supernatant liquid, concentration to ca. 2 mL under vacuum, and cooling at 4 °C for 3 days, a small amount of feathery crystalline solid was obtained. Removal of the solvent under vacuum afforded a colorless solid which was recrystallized from benzene (1−2 mL) at 4 °C for 1 day to afford fine colorless needles of **5**. Yield: 38%. Crystals suitable for X-ray structure analysis were obtained by recrystallization of **5** (95 mg) from C_6D_6 (0.5 mL) at 4 °C. Mp: 230−234 °C with slight gas evolution. Anal. Calcd for $C_{55}H_{66}Ga$: C, 82.64; H, 7.37. Found: C, 80.85; H, 7.06. ^1H NMR (300 MHz, C_6D_6): δ 7.07 (t, J = 7.5 Hz, *p*-H, 2H), 6.83 (s, *m*-H(Mes), 8H), 6.71 (d, J = 7.5 Hz, *m*-H, 4H), 2.20 (s, *p*-Me, 12H), 1.82 (s, *o*-Me, 24H). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6): δ 148.76, 141.16, 136.52, 129.49, 128.87, 21.95 (*o*-Me), 21.43 (*p*-Me). FTIR (CsI plates, thin film): ν(GaH) 1890 (st) cm^{-1}.

$[2,6\text{-}Mes_2C_6H_3Ga(Cl)(\mu\text{-}OH)]_2$ (6). In an attempt to generate **5**, a solution of **2** (2.78 g, 3.8 mmol) and *n*-$OctSiH_3$ (2.78 g, 3.8 mmol) in C_6D_6 (0.9 mL) was put into an NMR tube, which was subsequently closed with a plastic cap and Teflon tape wrapped tightly around it. No reaction was observed after 1 day at 80 °C. The sample was kept in the NMR tube at room temperature for 1 month, during which time approximately 20% of the solvent evaporated, and a few well-shaped colorless crystals formed. The structure of **6** was determined by X-ray crystallography.

$[2,6\text{-}Mes_2C_6H_3Ga(Me)(\mu\text{-}OH)]_2$ (7). The solvent was removed under vacuum from the mother liquor of the second crop of **3**. The remaining colorless oil solidified after 2 h at room temperature. Hexanes (30 mL) was added, and the solution was stirred for 3 h, after which time most of the solid was dissolved. The fine colorless insoluble solid was allowed to settle for 3 days at room temperature. During this time a few well-shaped, long (2 mm) colorless needles formed (30 mg) which were of suitable quality for X-ray crystallography. Cooling of the supernatant liquid at −30 °C for 3 days afforded a second batch (20 mg). Mp: 278−280 °C with gas evolution. ^1H NMR (C_6D_6, 300 MHz): δ 7.22 (t, J = 7.2 Hz, *p*-H, 1H), 6.90 (d, J = 7.2 Hz, *m*-H, 2H), 6.83 (s, *m*-H(Mes), 4H), 2.33 (s, *p*-Me, 6H), 2.04 (s, *o*-Me, 12H), 0.14 (s, OH, 1H), −0.46 (s, GaMe, 3H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.45 MHz): δ 148.16, 147.70, 141.64, 136.20, 136.14, 128.80, 128.45, 126.81, 21.76 (*p*-Me), 21.38 (*o*-Me), −4.14 (GaMe). FTIR (CsI plates, Nujol): ν(OH) 3640 (w), 3627 (w) cm^{-1}.

$(2,6\text{-}Mes_2C_6H_3)_2GaOH$ (8). The solvent was removed under vacuum from the mother liquor of the crystals of **5**, and the remaining colorless solid was stirred with hexanes at room temperature for 1 h, during which time most of the solid dissolved. Decanting from the small amount of insoluble solid followed by concentration to 3−4 mL under vacuum and cooling to −40 °C for 2 days afforded a few small colorless crystals (50 mg), which were analyzed by ^1H NMR spectroscopy as a mixture of **5** and **8** in an approximate 1:2 ratio. Alternatively, **8** was obtained by slow diffusion of moisture into an NMR tube over a period of 2 weeks containing a solution of **5** (10 mg) in C_6D_6 (0.8 mL). ^1H NMR (C_6D_6, 300 MHz): 7.05 (t, J = 7.5 Hz, *p*-H, 2H), 6.84 (s, *m*-H(Mes), 8H), 6.67 (d, J = 7.5 Hz, *m*-H, 4H), 2.22 (s, *p*-Me, 12H), 1.91 (s, *o*-Me, 24H). FTIR (CsI plates, thin film): ν(GaH) 3620 (st) cm^{-1}.

Reaction of 3 with $[Ph_3C]^+[B(C_6F_5)_4]^-$. In a glovebox $[Ph_3C]^+[B(C_6F_5)_4]^-$ (23 mg, 0.025 mmol) was added to a solution of **3** (18 mg, 0.025 mmol) in C_6D_6 (1.0 mL) in a resealable NMR tube to afford an orange solution, from which a dense red liquid phase separated after a few minutes. A ^1H NMR spectrum taken after 3 h showed the appearance of a new signal at 1.32 ppm, which can be assigned to the *o*-Me hydrogens in $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$. The sample was shaken occasionally to better mix the two phases, and the progress of the reaction was monitored by ^1H NMR and ^{19}F NMR spectroscopy. After 4 days, approximately 80% of **3** was consumed. The upper C_6D_6 layer was carefully separated, and the dense red phase was dissolved in C_6D_5Cl. The C_6D_6 layer contained only 1,3-$Mes_2C_6H_4$, Ph_3CMe, and Ph_3CH according to ^1H NMR spectroscopy. The ^1H NMR and ^{19}F NMR spectra of the C_6D_5Cl solution were in excellent agreement with those reported for the “free” $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$ and $[B(C_6F_5)_4]^-$ ions.[7,19] ^1H NMR (C_6D_5Cl, 300 MHz): δ 7.27 (t, J = 7.8 Hz, *p*-H, 2H), 6.83 (s, *m*-H(Mes), 8H), 6.76 (d, J = 7.8 Hz, *m*-H, 4H), 2.18 (s, *p*-Me, 12H), 1.55 (s, *o*-Me, 24H). ^{19}F NMR (C_6D_5Cl, 282.34 MHz): δ −133.5 (s, 8F), −161.6 (t, J = 20.7 Hz, 4F), −165.8 (s, 8F).

Reaction of 3 with $B(C_6F_5)_3$. In a glovebox $B(C_6F_5)_3$ (16 mg, 0.031 mmol, 30% excess) was added to a solution of **3** (17 mg, 0.024 mmol) in C_6D_6 (1.0 mL) in a resealable NMR tube. A ^1H NMR spectrum taken after 1 h showed the appearance of a new signal at 1.32 ppm, which can be assigned to the *o*-Me hydrogens in $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$. After 20 h at room temperature a clear colorless dense phase formed, and the ^1H NMR spectrum showed the consumption of ca. 90% of **3**. The remaining amount of **3** was completely consumed after 1 week. The upper C_6D_6 layer was carefully separated, and the dense red phase was dissolved in C_6D_5Cl. The ^1H NMR and ^{19}F NMR

Table 1. Crystal Data and Structural Refinement for Compounds 3−8

	3	**4**·0.5 C_6H_{14}	**5**	**6**	**7**	**8**
empirical formula	$C_{49}H_{53}Ga$	$C_{55}H_{66}Ga$	$C_{48}H_{51}GaO_{0.3}$	$C_{48}H_{52}Cl_2Ga_2O_2$	$C_{50}H_{58}O_2Ga_2$	$C_{48}H_{51}GaO_{0.7}$
formula wt	711.63	796.80	702.41	871.24	830.40	708.81
T, K	173(2)	173(2)	97(2)	120(2)	173(2)	120(2)
wavelength, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	triclinic	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$Fdd2$	$Pbca$	$P2_1/c$	$P2_12_12_1$
a, Å	10.3920(16)	11.755(4)	20.7761(10)	18.1341(10)	21.965(2)	11.8097(8)
b, Å	11.269(2)	12.046(4)	42.558(2)	20.0259(11)	9.087(3)	15.7004(11)
c, Å	17.060(2)	18.668(6)	8.3874(4)	23.7470(13)	24.186(3)	20.7826(15)
α, deg	87.299(12)	95.977(18)	90	90	90	90
β, deg	80.598(12)	104.66(2)	90	90	114.337(7)	90
γ, deg	82.705(17)	114.229(9)	90	90	90	90
V, Å^3	1954.4(5)	2266.5(12)	7416.1(6)	8623.8(8)	4398.3(14)	3853.4(5)
Z	2	2	8	8	4	4
D_{calcd}, Mg/m^3	1.209	1.168	1.258	1.342	1.254	1.222
μ(Mo Kα), mm^{-1}	0.736	0.642	0.776	1.411	1.262	0.748
F(000)	756	854	2979	3616	1744	1502
cryst size, mm^3	0.46 × 0.42 × 0.36	0.48 × 0.46 × 0.42	0.22 × 0.06 × 0.02	0.42 × 0.36 × 0.28	0.52 × 0.46 × 0.28	0.16 × 0.14 × 0.12
cryst color and habit	colorless prism	colorless prism	colorless plate	colorless prism	colorless plate	colorless prism
2θ_{max}, deg	1.82−25.00	1.97−25.00	1.91−25.99	1.72−27.14	1.85−25.00	1.96−27.00
no. of observns	6892	7868	3553	9505	7715	8397
no. of variables	463	521	242	509	511	468
R1^a ($I > 2\sigma(I)$)	0.0333	0.0535	0.0305	0.0259	0.0430	0.0289
wR2^b ($I > 2\sigma(I)$)	0.0881	0.1290	0.0798	0.0684	0.1020	0.0760
goodness of fit on F^2	1.036	1.146	0.998	1.036	1.042	1.049
largest diff peak, e Å^{-3}	0.408	0.787	1.008	0.511	0.406	0.406

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

Table 2. Bond Distances (Å) and Angles (deg) of the Monomeric $(2,6\text{-}Mes_2C_6H_3)_2GaX$ Complexes 2−5 and 8

	X = Cl, **2**	X = Me, **3**	X = t-Bu, **4**	X = H, **5**	X = OH, **8**
Ga−C$_{Terph}$	1.956(16)	2.023(2)	2.039(3)	1.9953(9)	1.9876(15)
	2.001(16)	2.024(2)	2.020(4)	1.9953(9)	1.9940(14)
Ga−X	2.177(5)	1.968(2)	2.016(4)	1.417(3)	1.7833(17)
C$_{Terph}$−Ga−C$_{Terph}$	153.5(5)	135.08(7)	113.23(14)	134.65(5)	143.11(6)
C$_{Terph}$−Ga−X	103.2(4)	112.49(9)	115.88(14)	112.67(3)	104.82(7)
	103.4(4)	112.44(9)	130.17(14)	112.67(3)	111.93(7)

Table 3. Bond Distances (Å) and Angles (deg) of 6 and One of the Two Independent Molecules of 7

Compound **6**			
Ga(1)−O(1)	1.9119(9)	Ga(2)−O(2)	1.9110(9)
Ga(1)−O(2)	1.9127(9)	Ga(2)−O(1)	1.9193(9)
Ga(1)−C(4)	1.9458(13)	Ga(2)−C(5)	1.9490(13)
Ga(1)−Cl(1)	2.1756(4)	Ga(2)−Cl(2)	2.1659(4)
O(1)−Ga(1)−O(2)	78.57(4)	C(5)−Ga(2)−Cl(2)	123.28(4)
C(4)−Ga(1)−Cl(1)	122.92(4)	Ga(1)−O(1)−Ga(2)	101.36(4)
O(2)−Ga(2)−O(1)	78.43(4)	Ga(2)−O(2)−Ga(1)	101.64(4)
Compound **7**			
Ga(1)−O(1)	1.938(2)	Ga(1)−C(15)	1.977(3)
Ga(1)−O(1A)	1.942(2)	Ga(1)−C(25)	1.952(4)
O(1)−Ga(1)−O(1A)	79.29(10)	Ga(1)−O(1)−Ga(1A)	100.71(10)
C(25)−Ga(1)−C(15)	127.98(15)		

spectra of the C_6D_5Cl solution were in excellent agreement with those reported for the "free" $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$ and $[MeB(C_6F_5)]^-$ ions.[7,19] ^{1}H NMR (C_6D_5Cl, 300 MHz): δ 7.27 (t, J = 7.8 Hz, p-H, 2H), 6.83 (s, m-H(Mes), 8H), 6.76 (d, J = 7.8 Hz, m-H, 4H), 2.18 (s, p-Me, 12H), 1.55 (s, o-Me, 24H), 1.25 (s Me-B, 3H). ^{19}F NMR (C_6D_5Cl, 282.34 MHz): −132.2 (d, J = 19.5 Hz, 8F), −164.7 (t, J = 20.7 Hz, 4F), −167.0 (m, 8F).

Reaction of 5 with $B(C_6F_5)_3$. In a glovebox $B(C_6F_5)_3$ (13 mg, 0.025 mmol) was added to a solution of **5** (19 mg, 0.027 mmol) in C_6D_6 (1.0 mL) in a resealable NMR tube. After 20 h at room temperature a clear colorless dense phase formed, and the ^{1}H NMR spectrum showed the consumption of ca. 90% of **5**. The upper C_6D_6 layer was carefully separated, and the dense red phase was dissolved in a 3:1 mixture of C_6D_6 and C_6D_5Cl. The ^{1}H NMR spectrum of this solution was in excellent agreement with those observed for the "free" $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$ ion in C_6D_6/C_6D_5Cl mixtures. ^{1}H NMR (3:1 C_6D_6/C_6D_5Cl, 300 MHz): δ 7.05 (t, J = 7.5 Hz, p-H, 2H), 6.71 (s, m-H(Mes), 8H), 6.54 (d, J = 7.5 Hz, m-H, 4H), 2.09 (s, p-Me, 12H), 1.44 (s, o-Me, 24H). ^{19}F NMR (3:1 C_6D_6/C_6D_5Cl, 282.34 MHz): −138.3 (m, 8F), −159.8 (m, 4F), −164.4 (m, 8F).

X-ray Crystallography. Crystals were removed from the Schlenk tube under a stream of N_2 gas and immediately covered with a layer of hydrocarbon oil. Crystals of **6** were removed from the NMR tube inside a nitrogen-filled drybox and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream.[28] The data for **3**, **4**·0.5C_6H_{14}, and **7** were collected at 173(2) K on a Siemens P4 diffractometer and those for **5**, **6**, and **8** at 97(2), 120(2), and 120(2) K on a Bruker Apex diffractometer using Mo Kα (λ = 0.710 73 Å) radiation. The data were corrected for Lorentz and polarization effects. Absorption corrections based on ψ scans were applied for **3**, **4**·0.5C_6H_{14}, and **7**, and a multiscan method from equivalent reflections was used for **5**, **6**, and **8**. The structures were solved by direct methods using the SHELXTL program suite, version 5.1[29] for **3**, **4**·0.5C_6H_{14}, and **7** and version 6.12 for **5**, **6**, and **8**, and refined by full-matrix least squares on F^2 including all reflections. Unless stated otherwise, all the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were included in the refinement with idealized parameters. The crystals of **5** were nonmerohedral twins. The structure of **5** was refined with three different

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(28) Hope, H. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 10.

(29) SHELXTL Version 5.1; Bruker AXS, Madison, WI, 1997.

component crystals. In addition, the crystal chosen for the X-ray structure determination was found to be a mixture of approximately 70% **5** and 30% **8**. Similar mixtures have been observed previously in X-ray structure studies of organoaluminum hydrides.[22] The hydroxide hydrogen atoms in **6** and **7** were located in the difference map and refined isotropically. The structure of **7** contains two independent half-molecules in the asymmetric unit. The complete molecules are centrosymmetric. The structure of **8** was found to be a mixture of **5** and **8** and was refined with split occupancies of 70% for the hydroxide in **8** and 30% for the hydride in **5**. Some details of the crystal data and refinement are given in Table 1, and selected bond distances and angles are listed in Tables 2 and 3. Further details are given in the Supporting Information.

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Supporting Information Available: Crystallographic tables, numbering schemes, and unit cell plots for compounds **3**−**8** (these data are also given as CIF files) and ^{1}H NMR spectra of the compounds **3**−**5**, **7**, **8**, $[(2,6\text{-Mes}_2C_6H_3)_2Ga]^+$-$[B(C_6F_5)_4]^-$, and $[(2,6\text{-Mes}_2C_6H_3)_2Ga]^+[RB(C_6F_5)_3]^-$ (R = Me, H). This material is available free of charge via the Internet at http://pubs.acs.org.

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