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1,2-Dimetalated Benzene Derivatives $(1,2\text{-}C_6H_4MCH_3)_n$ of Group 13 (M = Al, Ga, In)

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Reaction of (*o*-phenylene)magnesium (**1**) with CH_3MCl_2 (**2**; M = Al, Ga, In) gave access to the corresponding methyl(*o*-phenylene)metal compounds **3** ($(1,2\text{-}C_6H_4MCH_3)_n$). These novel 1,2-dimetalated benzene derivatives of group 13 were characterized by their spectral data and, in the case of **3b** (M = Ga, n = 2), by a single-crystal X-ray structure determination.

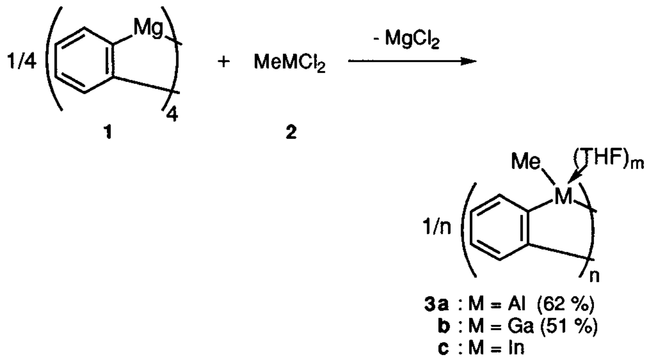
Introduction

The chemistry of the group 13 metals has benefited much from the pioneering work of Karl Ziegler, and many organometallic derivatives of these elements have been described since.[1] In contrast, 1,2-dimetalated benzene derivatives of group 13 have been investigated less extensively (with the exception of indium derivatives, vide infra).

After having achieved the synthesis of 1,2-disubstituted benzene derivatives of group 14, in particular of 9,10-dimetallatriptycenes,[2] from (*o*-phenylene)magnesium (**1**) and the corresponding metal halides, we wanted to extend this approach to group 13 metals. In this paper we report the preparation of methyl(*o*-phenylene)aluminum, -gallium, and -indium (**3**, $(1,2\text{-}C_6H_4MCH_3)_n$; **a**, M = Al; **b**, M = Ga; **c**, M = In) from **1** and the methylmetal dichlorides CH_3MCl_2 (**2**). The novel compounds **3** were characterized via their spectral data and, in the case of the gallium derivative **3b**·Pyr, by a single-crystal X-ray structure determination.

Results and Discussion

Scheme 1



Synthesis of Methyl(*o*-phenylene)metal Compounds 3a−c. When a THF solution of (*o*-phenylene)magnesium[3] (**1**; Scheme 1) was treated at −10 °C with CH_3MCl_2 (**2**; M = Al, Ga, In) and the reaction mixture was warmed to room temperature, a turbid solution was obtained. Evaporation of the solvent and extraction of the residue with toluene afforded a clear yellow solution and a white precipitate; the latter is magnesium chloride, which was found to be insoluble in toluene. The clear solution was isolated by careful decantation and evaporated to dryness to afford a solid residue that was subjected to ^1H and ^{13}C NMR spectroscopic analysis (Table 1). The spectra obtained indicated the total disappearance of the starting materials and the formation of products **3**, which contained one methyl substituent per *o*-phenylene group, in addition to at least one coordinated THF (Scheme 1, m = 1); an excess of presumably free but rapidly exchanging THF was found in the solutions of **3b** and **3c**. In the case of **3a** and **3b**, the yields were 62% and 51%, respectively, as determined by titration of the corresponding M^{3+} ion with EDTA of a sample of the toluene solution after hydrolysis. For **3c**, the yield could not be determined via titration, and attempts to determine the purity of the obtained toluene solution via ^1H NMR spectroscopy failed because the resonances were rather broad.

From Table 1, it follows that the ^1H and ^{13}C NMR chemical shifts of **3** are in good agreement with those reported for related compounds such as $(C_6H_5)_3Al·THF$[4]

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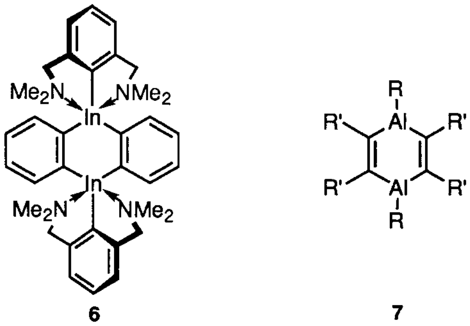
Table 1. ^{1}H and ^{13}C NMR Data ($\delta(^1H)/\delta(^{13}C)$) of Compounds 3−6

	$C(M)_{ipso}$	$C(H)_{ortho}$	$C(H)_{meta}$	$CH_3(M)$
3a (M = Al)[a]	−/162.7	8.00/136.6	7.47/126.4	0.00/−12.2
3b (M = Ga)[a]	−/[b]	8.02/[b]	7.50/[b]	0.41/[b]
3b·Pyr[c]	−/162.8	7.91/136.8	7.36/125.7	0.29/−9.9
3c (M = In)[a]	−/162.5	7.91/138.9	7.29/126.9	0.26/−1.6
$(C_6H_5)_3Al\cdot THF$ (**4**)[a,d]	−/147.4	7.96/138.7	7.40/127.7	
$(C_6H_5)_3Ga$ (**5**)[e]	−/147.3	7.73/137.9	7.28/128.2	
6 (M = In)[c,f]	−/170.6	7.38/138.9	7.07/126.4	

[a] C_6D_6. [b] Not measured. [c] [D_8]toluene. [d] Reference 4. [e] ^{1}H NMR in [D_8]toluene, ^{13}C NMR in C_6D_6.[5] [f] See Figure 1.[8b]



6 **7**

Figure 1.

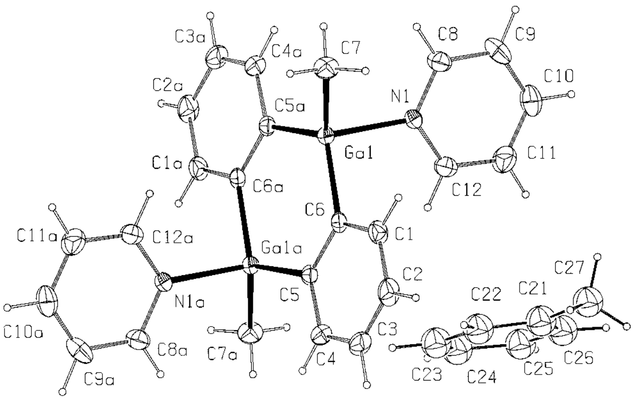


Figure 2. ORTEP plot of **3b**·Pyr with ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (deg): Ga1−N1 = 2.096(3), Ga1−C6 = 1.982(3), Ga1−C7 = 2.002(3), Ga1−C5a = 1.978(3), C5−C6 = 1.419(4); N1−Ga1−C6 = 100.50(11), N1−Ga1−C7 = 100.43(13), N1−Ga1−C5a = 101.62(12), C6−Ga1−C7 = 115.97(13), C6−Ga1−C5a = 115.94(12), C7−Ga1−C5a = 117.72(13), Ga1−C6−C1 = 119.0(2), Ga1−C6−C5 = 122.5(2).

(**4**), $(C_6H_5)_3Ga$[5] (**5**), and the 9,10-dihydro-9,10-diindaanthracene derivative **6**[9b](Figure 1). However, some differences can be observed. For example, the ^{13}C NMR chemical shift of the $C(M)_{ipso}$ atom of **3a** (δ 162.7 ppm) and **3b** (δ 162.8 ppm) are rather deshielded in comparison to those of **4** (δ 147.4 ppm) and **5** (δ 147.3 ppm). For the ^{13}C NMR chemical shift of $C(Mg)_{ipso}$ of the bifunctional organomagnesium compound **1** (δ 189.1 ppm)[3] and of the monofunctional organomagnesium compound $(C_6H_5)_2Mg\cdot 2THF$ (δ 169.9 ppm),[6] the same trend is observed. Therefore, the relatively deshielded shift of $C(M)_{ipso}$ in **3a** and **3b** is attributed to the close proximity of the second carbon-to-metal bond.

To obtain more information on the oligomeric nature of **3a** and **3b**, we attempted to grow crystals suitable for a single-crystal X-ray structure determination from the obtained toluene extracts. In the case of **3a**, our efforts were frustrated by the fact that the colorless crystals, obtained by slowly cooling the toluene extracts to −10 °C, crumbled upon drying, and a white powder was obtained after pumping off the crystals overnight under high vacuum. This white powder was only sparingly soluble in C_6D_6, and ^{1}H NMR analysis of a sample revealed that now **3a** had only one molecule of THF coordinated per *o*-phenylene unit. Apparently the excess of THF present in the residues obtained from the toluene extracts is only loosely bound and can be removed in vacuo. Unfortunately, all attempts to prepare crystals from the dried product were unsuccessful due to its low solubility.

In the case of **3b** the combined toluene extracts were concentrated in vacuo to furnish a brown residue. Recrystallization of this residue from THF yielded yellow crystals which were dissolved in toluene. The addition of 1 equiv of pyridine to the toluene solution thus obtained (by diffusion via the gas phase) instantaneously afforded colorless crystals. The solubility of these crystals was poor, but ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopic analysis established that the coordinated THF of **3b** had been displaced by pyridine to furnish **3b**·Pyr.

Single-Crystal X-ray Structure Determination of 3b·Pyr. The molecular structure of **3b**·Pyr is depicted in Figure 2. The compound is dimeric in the crystalline state; i.e., it is 9,10-dimethyl-9,10-dihydro-9,10-digallaanthracene. There is one pyridine molecule coordinated to each of the two gallium atoms, and these pyridine molecules reside on opposite sides of the practically planar central six-membered ring formed by C(5), C(6), Ga(1), C(5a), C(6a), and Ga(1a).

The crystal lattice contains one disordered toluene molecule per dihydroanthracene residue. The geometry of the gallium centers in **3b**·Pyr can be described as distorted tetrahedral: Ga(1) is situated 0.374(1) Å out of the plane defined by C(6), C(7), and C(5a) (sum of the angles around Ga(1) 349.6(2)°), with N(1) perpendicular to this plane. Deviations from an ideal tetrahedral environment around the metal centers are substantial, as the observed C−Ga−C angles (115.94(12)−117.72(13)°) are larger than 109.4°, while the observed

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N−Ga−C angles (100.43(13)−101.62(13)°) are smaller. The Ga−C_{aryl} distances (Ga(1)−C(6) = 1.982(3) Å, Ga(1)−C(5a) = 1.978(3) Å) and the Ga−C_{alkyl} distance (Ga(1)−C(7) = 2.002(3) Å) are in good agreement with those reported for other triorganylgallium compounds (Ga−C_{aryl} = 1.957(7) Å,[7a] 1.968(4) Å,[7b] 1.972(11) Å,[7c] 1.991(2) Å,[7d] Ga−C_{alkyl} = 1.967(2) Å,[7e] 1.978(3) Å,[7d] 1.998(4) Å[7f]).

While in principle the possibility of ligand exchange in organometallic compounds of group 13 might give rise to a number of different oligomers of **3** ranging from monomeric to polymeric (cf. Scheme 1: $n = 1, 2, 3, ..., \infty$), the dimeric structure actually observed for **3b**·Pyr is in line with that of many 9,10-dimetalla-9,10-dihydroanthracenes known in this group. Thus, several examples have been reported for boron[8] and indium.[9] In the case of aluminum, X-ray structures of this type are unknown, but 1,4-dialumina-2,5-cyclohexadienes **7** (Figure 1), analogues of **3** which lack the double benzoannelation at the central six-membered ring, have been described;[10] it is of interest that, in this category, tetrameric structures have sometimes been encountered as well,[11] while the analogous derivative of zinc occurs as a dimer in the crystalline state but as a trimer in THF solution.[12] Nevertheless, the dimeric dihydroanthracene structure (**3**, $n = 2$) appears to be dominant; it probably represents the normally best compromise between the excessive strain in the monomeric metallabenzocyclopropene (**3**, $n = 1$), which has only been suggested as a short-lived intermediate,[1d,10b,11] and the unfavorable entropy going along with association to form higher homologues. Therefore, we assume that **3a** and **3c** have an analogous dimeric structure.

As in **3b**·Pyr, a (nearly) planar (or a boat-shaped) geometry of the central ring is frequently encountered in 9,10-dihydro-9,10-dimetallaanthracenes.[8,9,13] Chairlike geometries of this ring have been reported only twice: for the diindaanthracene **6**[9b] (Figure 1) and for one[14] of the many representatives of the disilaanthracenes.[9]

Conclusions

(*o*-Phenylene)magnesium (**1**) allows access to novel 1,2-dimetalated benzene derivatives, as demonstrated by the preparation of the methyl(*o*-phenylene)aluminum, -gallium, and -indium species **3a**−**c**. **3b**·Pyr is the first 1,2-digallobenzene derivative to be structurally characterized.

Experimental Section

General Methods. All manipulations involving organometallic compounds were performed in fully sealed glassware ("full glass") using standard high-vacuum techniques[15] unless stated otherwise. Amounts of "total" base and Mg^{2+} in organomagnesium samples were determined after hydrolysis of a sample by titration with HCl and EDTA, respectively.[15] Amounts of Al^{3+} in organoaluminum samples or Ga^{3+} in organogallium samples were determined after hydrolysis of a sample by titration with EDTA.[16] For NMR, the following resonances were found for the various solvents used. ^{1}H NMR: [D_6]DMSO, δ_H 2.50; C_6D_6, δ_H 7.17; [D_8]toluene, δ_H 2.03. ^{13}C NMR: C_6D_6, δ_C 128.0; [D_8]toluene, δ_C 20.5. ^{27}Al NMR: C_6D_6 as solvent, $Al(H_2O)_6^{3+}$ as an external reference. ^{1}H chemical shifts and coupling constants were determined by NMR spectral simulation using the gNMR program.[17] Solvents were predried over KOH and then dried by distillation from liquid Na/K alloy. Magnesium was sublimed twice prior to use. (*o*-Phenylene)magnesium[3] (**1**) and its precursor (*o*-phenylene)mercury[18] (**8**, $(1,2\text{-}C_6H_4Hg)_3$) were prepared via adapted literature procedures.

(*o*-Phenylene)mercury (8). In a conical flask under an N_2 atmosphere, a solution of 1,2-dibromobenzene (14.85 g, 62.7 mmol) in Et_2O (70 mL) was added over 1.5 h to a stirred Na/Hg alloy, which had been prepared by dissolving Na (4.3 g, 187 mmol) in Hg (30 mL, 400 g, 2 mol). After it was stirred for 4 days at room temperature, the reaction mixture was quenched with cold water (100 mL) and transferred into a separatory funnel to remove excess mercury. The resulting mixture was filtered over a glass frit, and the gray residue was dried in vacuo. The crude product was purified via Soxhlet extraction (300 mL of DMF/190 °C/7 days) to furnish 7.6 g of a white solid, which was identified by ^{1}H NMR spectroscopy as pure **8**. Yield: 9.2 mmol (44.0%, lit.[18b] yield 52%). ^{1}H NMR (200 MHz, [D_6]DMSO): δ 7.50 (m, $^{3}J_{HH} = 7.3$ Hz, $^{4}J_{HH} = 1.3$ Hz, $^{5}J_{HH} = 1.0$ Hz, 2H; $C(H)_{ortho}$), 7.02 (m, $^{3}J_{HH} = 8.2$ Hz, $^{3}J_{HH} = 7.3$ Hz, $^{4}J_{HH} = 1.5$ Hz, 2H; $C(H)_{meta}$).

(*o*-Phenylene)magnesium (1). Magnesium (1.73 g, 71 mmol), **8** (3.79 g, 13.7 mmol of the formal monomeric unit C_6H_4-Hg), and mercury (0.1 mL) were stirred in THF (180 mL) for 5 days at room temperature and then for 10 h at 70 °C. A pale yellow solution with a fine black precipitate was obtained. The solution was separated from the excess magnesium amalgam and the black precipitate by careful decantation. Crystallization, induced by distilling off most of the solvent and slowly cooling the remaining solution to −10 °C, afforded colorless crystals which were isolated by careful decantation and dissolved in THF (180 mL). A sample of the THF solution thus obtained was evaporated to dryness, and the resulting solid residue was identified by ^{1}H and ^{13}C NMR spectroscopy as pure **1**. Yield: 11.6 mmol (84.7%, lit.[3b] yield 68%) of the formal monomeric unit C_6H_4Mg (based upon titration ("total base" and Mg^{2+}) of an aliquot of the obtained THF solution after hydrolysis). ^{1}H NMR (200 MHz, C_6D_6): δ 8.33 (m, $^{3}J_{HH} = 6.7$ Hz, $^{4}J_{HH} = 1.5$ Hz, $^{5}J_{HH} = 1.0$ Hz, 2H; $C(H)_{ortho}$), 7.41 (m, $^{3}J_{HH} = 7.4$ Hz, $^{3}J_{HH} = 6.7$ Hz, $^{4}J_{HH} = 1.5$ Hz, 2H; $C(H)_{meta}$), 3.34 (bs; H_{THF}), 1.19 (m; H_{THF}). ^{13}C NMR (50 MHz, C_6D_6): δ 189.1 (bs; $C(M)_{ipso}$), 140.9 (dd, $^{1}J_{CH} = 150.9$ Hz; $C(H)_{ortho}$), 124.6 (dd, $^{1}J_{CH} = 151.2$ Hz; $C(H)_{meta}$)), 68.2 (t, $^{1}J_{CH} = 140$ Hz; C_{THF}), 25.5 (t, $^{1}J_{CH} = 125$ Hz; C_{THF}).

Methyl(*o*-phenylene)aluminum (3a). At −10 °C, **2a** (0.27 mmol in 2.7 mL of *n*-hexane) was added over 5 min to **1** (0.27 mmol of the formal monomeric unit C_6H_4Mg in 10.0 mL of THF). After the mixture had been stirred for 1.5 h, it was warmed to room temperature overnight. The solvent was evaporated in vacuo, and the residue was extracted with

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toluene (3 × 10 mL). The combined organic layers were filtered over a glass frit, and a sample of the clear filtrate was evaporated to dryness. The solid residue obtained was identified by ^{1}H and ^{13}C NMR spectroscopy as **3a** with approximately 2.0 equiv of coordinated THF per *o*-phenylene unit. Yield: 0.17 mmol (62%; based upon EDTA titration of Al^{3+} of an aliquot of the toluene solution after hydrolysis). Crystallization induced by slowly cooling a saturated toluene solution of the compound to −5 °C afforded brittle colorless crystals which crumbled on drying. ^{1}H NMR (200 MHz, C_6D_6): δ 8.10 (m, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.3 Hz, 2H; C$(H)_{ortho}$), 7.57 (m, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.3 Hz, 2H; C$(H)_{meta}$), 3.38 (bs, 4H; H_{THF}), 0.76 (m, 4H; H_{THF}), 0.00 (s, 3H; CH_3(M));. ^{13}C NMR (50 MHz, C_6D_6): δ 162.7 (bs; $C(M)_{ipso}$), 136.6 (dd, $^1J_{CH}$ = 153.2 Hz, $^3J_{CH}$ = 5.2 Hz; $C(H)_{ortho}$), 126.4 (dd, $^1J_{CH}$ = 148.5 Hz, $^3J_{CH}$ = 2.9 Hz; $C(H)_{meta}$), 70.9 (t, $^1J_{CH}$ = 152 Hz; C_{THF}), 24.5 (t, $^1J_{CH}$ = 134 Hz; C_{THF}), −12.2 (bs; CH$_3$(M)). ^{27}Al NMR (104 MHz, C_6D_6): δ 162.7 (bs).

Methyl(*o*-phenylene)gallium (3b) was prepared from **2b** (3.94 mmol in 79.0 mL of Et_2O) and **1** (3.86 mmol of the formal monomeric unit C_6H_4Mg in 130.0 mL of THF) as described for **3a**. The solid residue obtained after extraction with toluene and evaporation of the solvent was recrystallized from THF to afford yellow crystals which were dissolved in toluene (50 mL). A sample of the toluene solution was evaporated to dryness, and the residue was dissolved in C_6D_6. The ^{1}H NMR spectrum showed the presence of **3b** with approximartely 4 mol equiv of rapidly exchanging THF per *o*-phenylene unit. Yield: 1.0 mmol (51%; based upon EDTA titration of Ga^{3+} of an aliquot of the toluene solution after hydrolysis). ^{1}H NMR (200 MHz, C_6D_6): δ 8.02 (m, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.4 Hz, 2H; C$(H)_{ortho}$), 7.50 (m, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.4 Hz, 2H; C$(H)_{meta}$), 3.59 (bs, 4H; H_{THF}), 1.25 (m, 4H; H_{THF}), 0.41 (s, 3H; CH_3(M)).

3b·Pyr. Slow diffusion of pyridine (0.16 mL, 0.158 g, 2.0 mmol) from the gas phase into the toluene solution of **3b** afforded colorless crystals which, after drying, were suitable for a single-crystal X-ray structure determination. A sample of the crystals obtained was subjected to ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. ^{1}H NMR (400 MHz, [D_8]toluene): δ 8.11 (bd, $^3J_{HH}$ = 4.8 Hz, 2H; H_{pyr}), 7.91 (m, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.5 Hz, $^5J_{HH}$ = 0.6 Hz, 2H; C$(H)_{ortho}$), 7.36 (m, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.5 Hz, 2H; C$(H)_{meta}$), 6.51 (bt, $^3J_{HH}$ = 7.6 Hz, 1H; H_{pyr}), 6.11 (bt, $^3J_{HH}$ = 6.8 Hz, 2H; H_{pyr}), 0.29 (s, 3H; CH_3-(M)). ^{13}C{^{1}H} NMR (100 MHz, [D_8]toluene): δ 162.8 (bs; $C(M)_{ipso}$), 148.1 (s; C_{pyr}), 136.4 (s; C_{pyr}), 126.8 (s; $C(H)_{ortho}$), 125.7 (s; $C(H)_{meta}$), 124.3 (s; C_{pyr}), −9.9 (bs; CH$_3$(M)).

Methyl(*o*-phenylene)indium (3c). At −10 °C, **1** (0.37 mmol of the formal monomeric unit C_6H_4Mg in 9.30 mL of THF) was added over 20 min to a suspension of **2c** (0.075 g, 0.37 mmol) in THF (2 mL). After the mixture had been stirred for 1 h at −10 °C and for 1 h at 5 °C, it was warmed to room temperature overnight. The solvent was evaporated in vacuo, and the residue was suspended in C_6D_6. ^{1}H and ^{13}C NMR spectroscopic analysis revealed the presence of **3c** with approximately 2.5 equiv of rapidly exchanging THF per *o*-phenylene unit. ^{1}H NMR (200 MHz, C_6D_6): δ 7.91 (bm, 2H; C$(H)_{ortho}$), 7.29 (bm, 2H; C$(H)_{meta}$), 3.73 (bs, 4H; H_{THF}), 1.36 (bs, 4H; H_{THF}), 0.26 (bs, 3H; CH_3(M)). ^{13}C NMR (50 MHz, C_6D_6): δ 138.9 (d, $^1J_{CH}$ = 157.6 Hz; $C(H)_{ortho}$), 126.9 (d, $^1J_{CH}$ = 156.1 Hz; $C(H)_{meta}$), 69.3 (t, $^1J_{CH}$ = 148 Hz; C_{THF}), 25.3 (t, $^1J_{CH}$ = 133 Hz; C_{THF}), −1.6 (q, $^1J_{CH}$ = 129.0 Hz; CH$_3$(M).

Table 2. Crystal Data and Details of the Structure Determination of 3b·Pyr

empirical formula	$C_{24}H_{24}Ga_2N_2 \cdot C_7H_8$
fw	572.03
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a (Å)	9.0867(8)
b (Å)	9.2953(8)
c (Å)	9.7569(8)
α (deg)	112.454(7)
β (deg)	104.350(7)
γ (deg)	101.820(7)
V (Å^3)	695.36(12)
Z	1
D(calcd) (g cm^{-3})	1.366
F(000)	294
μ(Mo Kα) (mm^{-1})	2.0
cryst size (mm)	0.12 × 0.35 × 0.38
temp (K)	150
radiation (Å)	Mo Kα; 0.710 73
θ_{min}, θ_{max} (deg)	2.4, 27.5
scan (type & range) (deg)	0.54 + 0.35 tan θ
total and unique no. of data; R(int)	5189, 3193; 0.047
no. of obsd data ($I > 2.0\sigma(I)$)	2767
N_{ref}, N_{par}	3193, 152
R, R_w,[a] S	0.0396, 0.0996, 1.03
max and av shift/error	0.00, 0.00
min and max resd dens (e Å^{-3})	−0.90, 0.93

[a] $w = 1/(\sigma^2(F_o^2) + (0.047P)^2 + 0.083P)$, where $P = (F_o^2 + 2F_c^2)/3$.

X-ray Crystallographic Data for 3b·Pyr. X-ray data (Table 2) were collected on an Enraf-Nonius CAD4T diffractometer (rotating anode) for a colorless transparent crystal, covered with an inert fluor-oil at 150 K. The data were corrected with PLATON/DELABS[19] for absorption. The structure was solved by automated Patterson techniques using DIRDIF[20] and refined on F^2 with SHELXL96.[21] A disorder model was used for the toluene molecule disordered over an inversion center. Hydrogen atoms were taken into account at calculated positions, riding on their carrier atoms.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra of **3a**−**c** and tables giving crystal data and data collection details, positional and thermal parameters, and bond distances and angles for **3b**·Pyr. This material is available free of charge via the Internet at http://pubs.acs.org.

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