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Dialkylgallium Complexes with Alkoxide and Aryloxide Ligands Possessing N-Heterocyclic Carbene Functionalities: Synthesis and Structure

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Supporting Information

ABSTRACT: Methods for the synthesis of dialkylgalium compounds with alkoxide or aryloxide ligands possessing N-heterocyclic carbene functionalities have been established. As a result, the synthesis of a series of dialkylgallium complexes $Me_2Ga(O,C)$ (1, 3-5), and $Me_2Ga(O,C) \cdot Me_3Ga$ (2, 6) is described, where (O,C) represents an alkoxide or aryloxide monoanionic chelate ligand with an N-heterocyclic carbene functionality. All complexes have been fully characterized using spectroscopic and X-ray techniques. The presence of a strongly basic NHC functionality in alkoxide or aryloxide ligands resulted in the formation of monomeric $Me_2Ga(O,C)$ species. The reaction of those complexes with the Lewis acid



 Me_3Ga leads to $Me_2Ga(O,C)$ · Me_3Ga adducts (2 and 6) with a strong Me_3Ga-O dative bond. The effect of (O,C) ligands with various steric and electronic properties on the structure of obtained $Me_2Ga(O,C)$ and $Me_2Ga(O,C)$ · Me_3Ga has been discussed on the basis of spectroscopic data. Finally, the bond valence vector model has been used to estimate the effect of a chelating (O,C) ligand on strains in complexes 1–6 on the basis of X-ray data.

■ INTRODUCTION

Transition-metal complexes with N-heterocyclic carbenes (NHCs) have been widely applied as catalysts in various areas of chemistry.¹ Although the strongly basic properties of NHCs allow their use as ligands for the synthesis of maingroup-metal complexes, the number of well-characterized maingroup-metal complexes with N-heterocyclic carbenes is limited.² For instance, among main-group-metal alkoxides and aryloxides widely investigated in both catalysis and material chemistry, there are only a few reports concerning structurally characterized $Zn_{,}^{3}$ Ga $,^{4}$ and Ge⁵ alkoxides and aryloxides and boron alkoxides⁶ with NHCs. Of the former, zinc complexes were found to be highly active catalysts for the controlled and stereoselective polymerization of rac-lactide^{3a,c} as well as ε caprolactone and cyclohexyl oxide.^{3b} Recently we have shown that dialkylgallium alkoxides with NHCs are highly active and isoselective catalysts in the polymerization of rac-LA under mild conditions and allow for a facile stereoselectivity switch.⁴ The latter, supported by the promising catalytic properties of gallium complexes in the ring-opening polymerization (ROP) of cyclic esters,⁷ indicates the need for construction of new gallium catalysts and encouraged us to investigate whether it is possible to synthesize gallium complexes with alkoxide or aryloxide ligands possessing NHC functionalities. It is noteworthy that Ti and Zr bisaryloxides with NHC functionalities were active and stereoselective in the polymerization of racLA.⁸ Although they showed no stereoselectivity, Zn and Mg⁹ as well as Y and Ti¹⁰ complexes with alkoxide ligands possessing NHC functionalities were also active in the polymerization of lactide. Despite the fact that Li,¹¹ Na,¹² K,¹³ Mg,^{10,12} and Zn¹⁰ complexes with alkoxide- or aryloxide-linked NHC ligands (NHC-alkoxide or NHC-aryloxide) have been synthesized and characterized, there is still a paucity of data concerning the structure and methods of synthesis of main-group-metal complexes with such ligands. To our knowledge, no gallium or other group 13 element complexes with NHC-alkoxide or -aryloxide ligands have been reported so far. Here we report the synthesis and structure of a series of Me₂Ga(O,C) complexes, where (O,C) is a monoanionic alkoxide or aryloxide ligand possessing an N-heterocyclic carbene functionality.

RESULTS AND DISCUSSION

We used two strategies for the synthesis of $Me_2Ga(O,C)$ complexes. The first one, presented in Scheme 1, included the reaction of an NHC salt possessing an alkoxide or aryloxide group ($[H_2L]X$) with Me_3Ga in order to obtain a dimethylgallium alkoxide or aryloxide with an imidazolinium salt functionality: [$(Me_2Ga(HL))X$]. Subsequent reaction with potassium hydride was performed in order to form the N-

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Scheme 1. First Approach to the Synthesis of Me₂Ga(O,C) Complexes



heterocyclic carbene functionality and the desired $Me_2Ga(O,C)$ complexes.

In the second approach (Scheme 2) the alkoxide or aryloxide salt $[H_2L]X$ was first treated with KH, resulting in the formation of the cyclic compound [HL], which was further reacted with Me₃Ga.

Scheme 2. Second Approach to the Synthesis of Me₂Ga(O,C) Complexes



While the second method has been already described in the literature and used for the synthesis of Mg and Zn complexes,¹⁰ the first approach, as far as we are concerned, has not been described for the synthesis of metal alkoxides or aryloxides. The low tendency of dimethylgallium alkoxides for (i) exchange reactions with the halogen anions and (ii) reactions with the acidic proton of e.g. an imidazolinium functionality¹⁴ should allow for the isolation of $[(Me_2Ga(HL))X]$ and further formation of Me₂Ga(O,C) due to the reaction of $[(Me_2Ga-(HL))X]$ with KH (Scheme 1). Therefore, we developed methods for the synthesis of a series of imidazolinium salt derivatives of alcohols and phenols ($[H_2L]X$) (Scheme 3), which were further used as substrates for the synthesis of the desired gallium complexes.

Synthesis and Structure of Alkoxide Complexes. The reaction of $[H_2L^1]I$ with Me_3Ga in a 1:1 molar ratio resulted in the evolution of methane and formation of a white solid that is

insoluble in common organic solvents: e.g., CH₂Cl₂, toluene, and *n*-hexane (Scheme 4). Further reaction with 1 equiv of KH in toluene was carried out at room temperature in the presence of a catalytic amount of KO^tBu acting as a proton transfer agent and required due to essential insolubility of both [(Me2Ga- (HL^1) X] and KH in toluene. The final product Me₂GaL¹ (1) was crystallized by slow addition of *n*-hexane to the toluene solution to give colorless crystals in moderate yield. The X-ray diffraction analysis revealed monomeric species with the coordination sphere of gallium atoms adopting a distortedtetrahedral geometry (Figure 1). The presence of the strongly basic NHC functionality coordinated to gallium, resulting in the six-membered chelate ${\rm GaO}{\cdots}{\rm C}_{\rm carbene}$ ring, caused a decrease of gallium acidity and therefore prevented association to e.g. dimeric species via Ga-O-Ga bridges. ¹H and ¹³C NMR spectroscopy in CD₂Cl₂ revealed higher field shifts of signals corresponding to Me groups, at -0.88 and -2.5 ppm, respectively, in comparison with dimethylgallium alkoxides,¹ which indicates the strong coordination of carbene carbon to gallium in solution. Similarly to 1, such a higher field shift was observed for $Me_2GaOR(SIMes)$ (SIMes = 1,3-bis(2,4,6trimethylphenyl)imidazolin-2-ylidene; OR = methoxide, (S)methyl lactate) monomeric complexes recently reported by us.⁴ Finally, a single set of signals in ¹H NMR, similarly to the case for Me₂GaOR(SIMes), was in line with the monomeric structure of 1 in solution. The presence of monomeric species due to a strong Ga– $C_{\rm carbene}$ interaction is not surprising in light of the structure of Me₂GaOR(SIMes).⁴ However, it must be noted that examples of monomeric dialkylgallium alkoxides are rare, due to the strong tendency of dialkylgallium alkoxides to form Ga-O-Ga bridges, which results most often in the formation of dimeric species.¹⁴ Except for monomeric Me₂GaOR(SIMes),⁴ only recently we reported the dialkylgal-

Scheme 3. Imidazolinium Salts [H₂L]X Used in the Study^a



 a [H₂L⁵]Cl has been reported in the literature.¹⁵ [H₂L¹]I and [H₂L²]I were synthesized according to the method proposed in the literature for the synthesis of asymmetric NHC salts.¹⁶ [H₂L³]Cl and [H₂L⁴]Cl were synthesized according to the method described in the literature for the synthesis of similar compounds.¹⁷

Scheme 4. Synthesis of $Me_2GaL^1(1)$





Figure 1. Molecular structure of 1 with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)-C(1) 2.0789(10), Ga(1)-C(4) 1.9792(11), Ga(1)-C(5) 1.9790(11), Ga(1)-O(1) 1.8946(8); C(5)-Ga(1)-C(4) 120.50(5), O(1)-Ga(1)-C(1) 92.60(4), O(1)-Ga(1)-C(4) 109.84(4), O(1)-Ga(1)-C(5) 108.26(4), C(4)-Ga(1)-C(1) 111.00(4), C(5)-Ga(1)-C(1) 111.03(5), N(2)-C(1)-N(1) 108.90(9).

lium alkoxide, which adopts a monomeric structure exclusively due to the increased basicity of the alkoxide ligand functionality.^{7b} In the latter case the presence of the alkoxide ligand with an organosuperbase functionality resulted in the formation of a strong Ga-N bond. The other monomeric dialkylgallium species were isolated only in the cases where the basicity of alkoxide oxygen is decreased by (i) conjugation with the ligand,¹⁸ (ii) electron-withdrawing substituents,¹ and (iii) the engagement of oxygen in hydrogen bonding.²⁰

As a result of the reaction between $[H_2L^2]I$ and Me₃Ga in a 1:1 molar ratio, the ionic compound $[(Me_2Ga(HL^2))I]$ was obtained in essentially quantitative yield. ¹H NMR confirmed the formation of this salt due to the reaction of the OH group of $[H_2L^2]I$ with Me₃Ga, while the proton of the imidazolinium ring remained unreacted. We were, however, unable to crystallize the obtained compound for X-ray analysis, as any attempts at crystallization led to the formation of a heterophase system, most probably due to its ionic nature. Although in the next step the obtained $[(Me_2Ga(HL^2))I]$ initially reacted with KH in the presence of a catalytic amount of KO^tBu, the reaction ceased after several minutes and even after heating to

90 °C for 24 h further evolution of gas was not observed. ¹H NMR analysis revealed a complex mixture of products, from which we were unable to crystallize $[Me_2GaL^2]$ or any other pure product. Therefore, in this case we applied the second strategy for the synthesis of $Me_2Ga(O,C)$ complexes, which is presented in Scheme 2. [H₂L²]I was initially reacted with potassium hydride, which resulted in the formation of cyclic $[HL^2]$ in the form of a pale yellow oil, in essentially quantitative yield (Scheme 5). The structures of such products have already been confirmed by X-ray diffraction studies and reported in the literature.²¹ The reaction of [HL²] with Me₃Ga (1:1) in toluene proceeded, as evidenced by evolution of methane gas, after heating of the reaction mixture to about 50 °C. Surprisingly, after crystallization from a toluene/n-hexane solution colorless crystals of the adduct Me₂GaL² Me₃Ga (2), rather than the expected Me₂GaL², were isolated in high yield. X-ray diffraction analysis revealed monomeric species with the Me₃Ga coordinated to the alkoxide oxygen of Me_2GaL^2 (Figure 2). The coordination sphere of gallium in the Me_2GaL^2 moiety adopts a distorted-tetrahedral geometry. The coordination of the NHC functionality to gallium resulted in the formation of a seven-membered $GaO \cdots C_{carbene}$ ring. Notably, the coordination of Me₃Ga to the alkoxide oxygen resulted in significant lengthening of the Me₂Ga(1)-O bond (1.9414(8) Å) in comparison with that in 1 (1.8946(8) Å). The strong coordination of Me₃Ga to alkoxide oxygen in solution, and the lack of exchange of Me groups between gallium centers, was further confirmed by ¹H NMR spectroscopy in toluene- d_{s_1} which revealed two sharp singlets at -0.40 and 0.02 ppm corresponding to Me₂Ga and Me₃Ga protons, respectively. This lack of exchange of Me groups between the gallium centers of Me₂GaL²·Me₃Ga is in sharp contrast to analogous dialkylaluminum alkoxides with Me₃Al coordinated to alkoxide oxygen, for which exchange of methyl groups between aluminum centers was observed, resulting in one broad signal for the Al-Me protons.²² The formation of 2 can be explained by the coordination of Me₃Ga present in solution to in situ formed Me_2GaL^2 and therefore a decrease of reactivity of Me_3Ga in adduct 2 toward HL^2 . The reaction of 2 with HL^2 was not observed up to 100 °C. This can be explained by the impeded coordination of Me₃Ga to HL² due to strong coordination of Me₃Ga to the alkoxide oxygen of Me₂GaL². It is worth noting that among main-group metals there is only one example of a similar compound, namely a monomeric Li complex bearing an







Figure 2. Molecular structure of 2 with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)-C(1) 2.0865(10), Ga(1)-C(4) 1.9697(12), Ga(1)-C(5) 1.9745(12), Ga(1)-O(1) 1.9414(8), Ga(2)-O(1) 2.0003(8), Ga(2)-C(22) 1.9945(12), Ga(2)-C(23) 1.9799(13), Ga(2)-C(24) 1.9904(12); C(5)-Ga(1)-C(4) 122.01(6), O(1)-Ga(1)-C(1) 95.66(4), O(1)-Ga(1)-C(4) 106.69(5), O(1)-Ga(1)-C(5) 107.93(4), C(4)-Ga(1)-C(1) 113.34(5), C(5)-Ga(1)-C(1) 107.83(5), N(2)-C(1)-N(1) 109.03(9), Ga(1)-O(1)-Ga(2) 123.63(4).

alkoxide ligand with an NHC functionality with a coordinated Lewis acid ($Sc(CH_2SiMe_3)_3$) to alkoxide oxygen.²³ Interestingly, a search of the CSD^{24} revealed that **2** is the only example of a structurally characterized gallium alkoxide with Me₃Ga coordinated to alkoxide oxygen.

The reactivity of Me₃Ga toward Me₂GaL², resulting in the formation of 2, is noteworthy in light of the reaction of $Me_2Ga(O,O')(SIMes)$ ((O,O') = (S)-methyl lactate) with Me₃Ga in an equimolar ratio (Scheme 6). The latter resulted in the formation of a $[Me_2Ga(O,O')]_2$ and $Me_3Ga(SIMes)$ adduct, due to the reaction of Me₃Ga with the SIMes ligand bonded to gallium, rather than the alkoxide oxygen of $Me_2Ga(O,O')$ (SIMes). $Me_3Ga(SIMes)$ is the second example of a crystallographically characterized Me₃Ga adduct with NHC²⁵ and the first with a saturated N-heterocyclic carbene. Colorless crystals of Me₃Ga(SIMes) were obtained from a toluene/hexane solution, and X-ray analysis revealed a monomeric complex with tetrahedral gallium (Figure 3). Interestingly, the ¹³C NMR shifts of the carbon signals of $Me_2Ga(O,O')$ (SIMes) (199.3 ppm)⁴ and $Me_3Ga(SIMes)$ (206.1 ppm) revealed a weaker Ga…C_{carbene} bond in the case of Me₃Ga(SIMes). In this case the reactivity of Me₃Ga toward the carbene carbon of SIMes bonded to the gallium of Me2Ga-

Scheme 6. Reaction of $Me_2Ga(O,O')(SIMes)$ with Me_3Ga



Figure 3. Molecular structure of $Me_3Ga(SIMes)$ with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)-C(1) 2.121(3), Ga(1)-C(4) 2.001(3), Ga(1)-C(5) 1.994(3), Ga(1)-C(6) 2.002(3); C(4)-Ga(1)-C(1) 106.02(12), C(5)-Ga(1)-C(1) 108.70(11), C(6)-Ga(1)-C(1) 107.41(12).

(O,O')(SIMes) is more likely due to the formation of dimeric dialkylgallium alkoxide. Therefore, the presence of a chelating (O,C) ligand in Me₂GaL² is one of the main reasons for the different reactivity of Me₂Ga(O,C) with Me₃Ga, in comparison with Me₂GaOR(NHC).

Synthesis and Structure of Aryloxide Complexes. The first approach (Scheme 1) was applied for the synthesis of dimethylgallium aryloxides with N-heterocyclic carbene functionalities. In the first step, reactions of $[H_2L^3]Cl$, $[H_2L^4]Cl$, and [H₂L⁵]Cl with Me₃Ga in 1:1 molar ratios led to the formation of the dimethylaryloxide salts $[(Me_2Ga(HL^{3-5}))Cl]$ with imidazolinium functionalities (Scheme 7). ¹H NMR spectra of obtained complexes were indicative of the presence of an imidazolinium salt functionality, which showed that methane formation was exclusively due to the reaction of Me₃Ga with phenol groups of [H₂L³⁻⁵]Cl. Similarly to $[(Me_2Ga(HL^2))I]$, attempts to crystallize $[(Me_2Ga(HL^{3-5}))-$ Cl] led to the formation of heterophase liquid systems, which did not give monocrystals suitable for X-ray studies. The reactions of [(Me₂Ga(HL³⁻⁵))Cl] with 1 equiv of KH in toluene at room temperature resulted in the formation of Me_2GaL^{3-5} (3-5), which were crystallized from toluene/nhexane solution to give colorless crystals in moderate to high yields. X-ray diffraction analysis revealed monomeric species with the coordination sphere of gallium adopting a distortedtetrahedral geometry (Figures 4–6). The $Ga-C_{carbene}$ interaction led to the formation of a six-membered (5) or sevenmembered (3, 4) GaO… $C_{carbene}$ ring. The formation of monomeric dialkylgallium aryloxides with NHC functionalities (3-5) is in accordance with the weaker basicity of phenolate oxygen in comparison with alkoxides and therefore the lower tendency for the formation of e.g. dimeric dimethylgallium aryloxides. Particularly for dimethylgallium aryloxides with



Scheme 7. Synthesis of Me_2GaL^{3-5} (3-5)





Figure 4. Molecular structure of 3 with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)-C(1) 2.0802(11), Ga(1)-C(4) 1.9762(12), Ga(1)-C(5) 1.9725(12), Ga(1)-O(1) 1.9137(8); C(5)-Ga(1)-C(4) 124.06(5), O(1)-Ga(1)-C(1) 100.45(4), O(1)-Ga(1)-C(4) 103.28(4), O(1)-Ga(1)-C(5) 105.28(4), C(4)-Ga(1)-C(1) 108.53(5), C(5)-Ga(1)-C(1) 112.11(5), N(2)-C(1)-N(1) 108.83(9).



Figure 5. Molecular structure of 4 with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)-C(1) 2.0664(13), Ga(1)-C(4) 1.9787(15), Ga(1)-C(5) 1.9700(14), Ga(1)-O(1) 1.9045(10); C(5)-Ga(1)-C(4) 119.45(6), O(1)-Ga(1)-C(1) 99.23(5), O(1)-Ga(1)-C(4) 107.13(6), O(1)-Ga(1)-C(5) 107.42(5), C(4)-Ga(1)-C(1) 106.96(6), C(5)-Ga(1)-C(1) 114.52(5), N(2)-C(1)-N(1) 109.14(11).

Lewis base functionalities, such as amines and Schiff bases, dimers with weakened Ga–O–Ga bridges²⁶ or monomeric species²⁷ are reported. For 3-5 ¹H NMR revealed in each case one set of signals, in agreement with the presence of monomeric species. The shifts of Ga–Me protons in toluene d_8 of -0.34 ppm (3), -0.35 ppm (4), and -0.21 ppm (5) were similar to that of the alkoxide derivative 2 (-0.40 ppm), indicating the strong coordination of the NHC functionality to gallium. The latter was also confirmed by ¹³C NMR shifts of 198.4 and 198.2 ppm for the carbene carbons of 3 and 4,



Figure 6. Molecular structure of 5 with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)-C(1) 2.0559(12), Ga(1)-C(4) 1.9596(13), Ga(1)-C(5) 1.9857(13), Ga(1)-O(1) 1.9209(9); C(5)-Ga(1)-C(4) 121.50(6), O(1)-Ga(1)-C(1) 88.30(4), O(1)-Ga(1)-C(4) 110.05(5), O(1)-Ga(1)-C(5) 106.49(5), C(4)-Ga(1)-C(1) 114.33(5), C(5)-Ga(1)-C(1) 110.79(5), N(2)-C(1)-N(1) 109.43(11).

respectively, which were similar to those of 1, 2, and $Me_2GaOR(SIMes)$.⁴ The ¹³C NMR shift of 193.9 ppm in the case of 5 was indicative of even stronger coordination of NHC to gallium in comparison with the complexes mentioned above.

Despite the weaker basicity of aryloxide oxygen, we examined whether Me₂Ga may coordinate to the aryloxide oxygen of $Me_2Ga(O,C)$ strongly enough to form complexes analogous to 2. The reaction between 4 and Me_3Ga (1:1) at ambient temperature led to the formation of Me₂GaL⁴·Me₃Ga (6) as a white crystalline solid in essentially quantitative yield. Monocrystals of the toluene solvate of 6 were obtained by crystallization from a toluene/n-hexane solution. X-ray diffraction analysis revealed a monomeric species essentially isostructural with 2, with the Me₃Ga coordinated to the aryloxide oxygen (Figure 7). The weaker basicity of aryloxide oxygen of 6 was reflected by much longer Me₃Ga-O bonds of 2.0678(14) and 2.0622(14) Å for the two independent molecules of the asymmetric unit in comparison with the analogous bond in the alkoxide derivative 2 (2.0003(8) Å). ¹³C NMR of coordinated Me₃Ga was indicative of the same trend in solution and revealed signals shifted to higher field at -3.2and -1.9 ppm for 2 and 6, respectively. The strong coordination of Me₃Ga to aryloxide oxygen in solution and the lack of exchange of Me groups between gallium atoms was shown by ¹H NMR, which revealed a sharp singlet for Me₃Ga. For 6 the presence of a broad signal of Me_2Ga , along with benzylic CH₂, should be interpreted in terms of slow exchange, on the NMR time scale, between two asymmetric isomers of the Me₂GaL⁴ unit, which is associated with the conformation of



Figure 7. Molecular structure of one of two unique molecules of 6 with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)-C(1) 2.0701(19), Ga(1)-C(4) 1.967(2), Ga(1)-C(5) 1.964(2), Ga(1)-O(1) 1.9637(14), Ga(2)-O(1) 2.0678(14), Ga(2)-C(25) 1.984(2), Ga(2)-C(26) 1.982(2), Ga(2)-C(27) 1.983(2), C(5)-Ga(1)-C(4) 123.38(10); O(1)-Ga(1)-C(1) 98.27(7), O(1)-Ga(1)-C(4) 107.26(8), O(1)-Ga(1)-C(5) 105.68(8), C(4)-Ga(1)-C(1) 104.59(9), C(5)-Ga(1)-C(1) 114.62(9), N(2)-C(1)-N(1) 109.10(17), Ga(1)-O(1)-Ga(2) 121.13(7).

the chelate ring (vide supra). Interestingly, a search of the CSD^{22} revealed only one example of a structurally characterized complex in which Me₃Ga is coordinated to a gallium aryloxide moiety.²⁸

The weaker bonding of Me_3Ga to aryloxide oxygen in comparison with alkoxide oxygen, as demonstrated for compounds **6** and **2**, respectively, encouraged us to verify the possibility of using the second strategy presented in Scheme 2 for the synthesis of **3** and **4**. In both cases the reactions of $[H_2L^3]Cl$ and $[H_2L^4]Cl$ with 1 equiv of KH resulted in the formation of $[HL^3]$ and $[HL^4]$, respectively, and in both cases colorless oils were obtained in essentially quantitative yield, as evidenced by ¹H NMR spectroscopy. The X-ray structure of an analogous compound has been reported in the literature.²⁹ A subsequent reaction of $[HL^3]$ with Me_3Ga proceeded after heating of the reaction mixture to 80 °C with evolution of methane. After the reaction ceased, the ¹H NMR analysis of the reaction mixture revealed the presence of two signals of Ga-Me at -0.02 and -0.36 (corresponding to 3), in a 1:1.7 ratio (Figure S32, Supporting Information). Subsequent recrystallizations led to the isolation of colorless crystals of 3 in about 15% yield. Although the first approach (Scheme 1) was more efficient for the synthesis of 3, the experiment described above shows that the second approach may be used for the synthesis of dialkylgallium aryloxide derivatives with NHC functionalities (Scheme 8). However, some limitations of this approach were shown by the lack of reactivity of [HL⁴] toward Me₃Ga even at elevated temperatures up to 100 °C.

Discussion and Bond Valence Vector Analysis. We have analyzed the structure of compounds 1-6 in order to demonstrate how the steric and electronic parameters of (O,C) ligands influence the structure of discussed complexes. In order to analyze the role of the NHC functionality in an alkoxide chelate ligand, the simple dimethylgallium alkoxide with the NHC Me₂GaOMe(SIMes)⁴ served as a reference.

As indicated above, a strong Ga-C_{carbene} bond has considerable influence on the structure of the investigated complexes and is responsible for their monomeric structure both in solution and the solid state. An analysis of bond lengths for 1-6 on the basis of X-ray crystallography revealed important information on the coordination of the (O,C) ligand containing an NHC functionality to gallium. For 1-6 the Ga-C_{carbene} bond length decreased in comparison with the analogous bond in Me2GaOMe(SIMes) (2.1007(13) Å) by 0.014-0.045 Å and was greater than for GaCl₃(NHC)³⁰ (2.023-2.027 Å) with a saturated NHC. In solution the strength of the carbene carbon interaction with the metal center can be estimated on the basis of the ¹³C NMR carbene carbon signal.³¹ Although similar chemical shifts of carbene carbons for 1-4, 6, and the reference complex Me₂GaOMe(SIMes) (198.2-200.5 ppm) indicate strong coordination of gallium with the carbene carbon, they do not in all cases correlate with the length of the Ga $-C_{carbene}$ bond. However, for 5 ¹³C NMR analysis revealed the carbone carbon signal at 193.9 ppm, which correlates well with the shortest Ga $-C_{carbene}$ bond (2.0559(12) Å). The stronger coordination of the NHC functionality for 1-6 in comparison with that for $Me_2GaOMe(SIMes)$ is expected to be the result of a chelate effect. It should be noted that stronger coordination of the NHC functionality due to a chelate effect could be responsible for the reactivity of Lewis acids with Me₂Ga(O,C) at oxygen rather than the carbene carbon. In comparison with the Ga-O bond of Me₂GaOMe-(SIMes) (1.8778(11) Å) the length of the Ga-O bond was slightly increased for alkoxide derivative 1 (1.8946(8) Å) and

Scheme 8. Synthesis of Me_2GaL^3 (3) and Me_2GaL^4 (4) via the Second Approach



Table	1 Walnes	of Salactad	Bond Distance	and Angles	for Compounds	1-6 and Ma	$C_{0}OM_{0}(SIM_{00})^{4}$
I able	L. Values	of Selected	Donu Distance	s and Angles	for Compounds	$1-0$ and Me_2	GaOme(Simes)

compound	$Ga-C_{carbene}$ (Å)	Ga–O (Å)	Ga–C (Å)	Ga–C (Å)	yaw angle (deg)	pitch angle (deg)	O-Ga- $C_{carbene}$ (deg)
1	2.0789(10)	1.8946(8)	1.9792(11)	1.9790(11)	5.8	4.9	92.60(4)
2	2.0865(10)	1.9414(8)	1.9697(12)	1.9745(12)	3.6	4.0	95.66(4)
3	2.0802(11)	1.9137(8)	1.9762(12)	1.9725(12)	6.2	6.7	100.45(4)
4	2.0664(13)	1.9045(10)	1.9787(15)	1.9700(14)	5.1	2.8	99.23(5)
5	2.0559(12)	1.9209(9)	1.9596(13)	1.9857(13)	6.6	1.3	88.30(4)
6 ^{<i>a</i>}	2.0701(19)	1.9637(14)	1.967(2)	1.964(2)	4.1	2.9	98.27(7)
	2.0782(19)	1.9667(14)	1.967(2)	1.955(2)	5.9	5.4	97.65(7)
Me ₂ GaOMe(SIMes)	2.1007(13)	1.8778(11)	1.9798(17)	1.9838(16)	4.5	4.3	101.99(5)
^{<i>a</i>} For two unique mo	olecules of 6.						

aryloxide derivatives 3 (1.9137(8) Å), 4 (1.9045(10) Å), and 5 (1.9209(9) Å). The coordination of Me₃Ga to the alkoxide oxygen of 2 and 6 resulted in a more significant elongation of the Me₂Ga-O bond, which was found to be 1.9414(8) Å for 2 and 1.9637(14) and 1.9667(14) Å for 6. It is worth noting that in the latter case the elongation of the Me₂Ga-O bond did not result in shortening of the Ga-C_{carbene} bond, and a comparison of 4 and 6 serves as a good example. No major modification of the Ga-C_{carbene} bond was compensated by the shorter Ga-C(Me) bonds (the difference is greater than 3σ) with subsequent widening of the C(Me)-Ga-C(Me) angle. As the Ga-C_{carbene} bond was shorter and the Ga-O bond longer for 1-6 in comparison with Me₂GaOMe(SIMes), we used the bond valence model³² to calculate Ga-C_{carbene} and Ga-O bond valencies in order to evaluate the relationship between these bonds. For 1 (1.27), 3 (1.24), 4 (1.28), 5 (1.28), and $Me_2GaOMe(SIMes)$ (1.26) the sum of $Ga-C_{carbene}$ and Ga-Obond valencies (in valence units) were essentially the same within method accuracy. For 2(1.19) and 6(1.19, 1.17) the coordination of Me₃Ga to alkoxide or aryloxide oxygen resulted in a decrease of 0.1 (see the Supporting Information).

While the latter analysis concerns the strength of the (C,O) ligand coordination to gallium, the strains resulting from the chelate GaO- $C_{carbene}$ ring can be reflected by selected angles. The strains should be mainly seen by the deformations around carbene and gallium centers. Yaw (in plane tilting) and pitch (out of plane tilting) angles are usually used for the description of the former.³³ For compounds **1**–**6** and Me₂GaOMe-(SIMes)⁴ pitch angles are less than 7° (Table 1). Similarly low values for yaw angles (Scheme 9, Table 1) for Me₂GaOMe(SIMes) and investigated Me₂Ga(O,C) complexes indicate that the binding mode for **1**–**6** should not be affected considerably by chelate effects.^{29,34} On the other hand, OGaC_{carbene} bite angles were analyzed as a possible indication

Scheme 9. Coordination Sphere of Me₂Ga(O,C) Complexes



of the chelating ring strain. For 3 $(100.45(4)^{\circ})$ the value of the OGaC_{carbene} angle is closest to the analogous angle in Me₂GaOMe(SIMes) $(101.99(5)^{\circ})$. Smaller angles are observed for compounds 4 $(99.23(5)^{\circ})$, 6 $(98.27(7)^{\circ}$ and $97.65(7)^{\circ})$, 2 $(95.66(4)^{\circ})$, 1 $(92.60(4)^{\circ})$, and 5 $(88.30(4)^{\circ})$. The smallest OGaC(NHC) angles for 1 and 5 may indicate higher ring strains for complexes with six-membered OGa…C(NHC) rings.

An alternative method we used to estimate the strains at the gallium center was the bond valence vector model (BVVM) proposed by Zachara.³⁵ The bond valence vector model was shown to be a convenient tool for the estimation of constraints of the geometry of the coordination sphere, which was demonstrated for five-coordinate aluminum organometallic complexes, four-coordinate phosphate derivatives, and threecoordinate carbonates.³¹ Such constraints were shown to correlate with the resultant bond valence vector, which is the sum of individual valence vectors of all Ga-X bonds, where X is the ligating atom in the coordination sphere. For compounds 1-6 and Me₂GaOMe(SIMes) the resultant bond valence vectors were calculated according to the method proposed in the literature³¹ (for details see the Supporting Information). In the case of 1 and 5 with six-membered $\text{GaO}{\cdots}\text{C}_{\text{carbene}}$ rings the resultant bond valence vectors are the longest and are equal to 0.077 and 0.108 vu (valence units), respectively. They are directed toward the (O,C) ligand, as depicted in Figure 8, therefore indicating the largest strains caused by the chelate ring. The strain magnitude was smaller for 2 (0.036 vu), 3 (0.066 vu), 4 (0.039 vu), 6 (0.059 and 0.040 vu), and Me₂GaOMe(SIMes) (0.043 vu), as evidenced by the resultant bond valence vectors. It must be noted that the large strains revealed by the BVV model for 1 and 5 are in line with the smallest O–Ga– $C_{carbene}$ bite angles observed for these complexes, which indicates that the latter is a good measure for the estimation of ring strain in metal alkoxides with NHC functionalities.

Another cause of conformational differences for **1–6** is the presence of a large substituent on the N(2) atom. The most pronounced changes concern the arrangement of a mesityl or $C_6H_4{}^iPr_2$ substituent vs Me groups bonded to gallium, which results in a twist of the Me₂GaO entity around the Ga- $C_{carbene}$ bond. The orientation of Me₂GaO can be described by the O(1)-Ga-C(1)-N(1) torsion angle. In the case of **1** (12.41(9)°) and **3** (-18.72(10)°) with mesityl substituents the low values indicate an essentially symmetric arrangement, as demonstrated in Figure 9a for **3**. The switch from mesityl to $C_6H_4{}^iPr_2$ caused the asymmetrization of **4** (47.46(12)°), **5** (-35.45(10)°), and **6** (41.17(19)°, 43.82(19)°), which is demonstrated in Figure 9b for **4**. Interestingly, the coordination of GaMe₃ to the alkoxide oxygen in **2** resulted in the increase of the analyzed torsion angle to -37.42(9)° despite the presence



Figure 8. Resultant bond valence vector at the gallium center (in purple) for (a) 1 and (b) 5. For the graphical presentation it was assumed that 1 vu is equal to 10 Å.



Figure 9. Molecular structures (views along the $Ga-C_{carbene}$ bond) and space-filling diagrams of (a) 3 transformed by a glide plane and (b) 4.

of the sterically less demanding mesityl substituent. The latter shows that electronic changes at the alkoxide substituent may lead to asymmetrization. In solution the fast exchange between asymmetric conformers led to one sharp signal corresponding to $GaMe_2$ protons, as shown by ¹H NMR. Only in the case of **6** is the exchange slow on NMR time scale, which results in the broadening of the signal for $GaMe_2$ protons. In this case such behavior in solution is the result of a more difficult inversion due to (i) coordination of alkoxide oxygen to Me_3Ga and (ii) the presence of a more sterically demanding $C_6H_4^{~i}Pr_2$ substituent.

CONCLUSIONS

In summary, we have focused on the synthesis of dialkylgallium alkoxides and aryloxides with alkoxide or aryloxide ligands possessing N-heterocyclic carbene functionalities and developed two approaches for their synthesis. The most important features of obtained complexes include a monomeric structure due to the presence of a N-heterocyclic carbene with strongly Lewis basic properties, despite the high tendency of dialkylgallium alkoxides and aryloxides to form aggregates with an increase of coordination number. The role of the chelating ligand possessing an NHC functionality was revealed in the reaction of $Me_2Ga(O,C)$ with Me_3Ga , a Lewis acid, which occurred at the alkoxide or aryloxide oxygen rather than at the carbene carbon of the N-heterocyclic carbene functionality, leading to $Me_2Ga(C,O)$ · GaMe₃ adducts. Finally, the obtained complexes constitute a platform of compounds which can serve as substrates for the further synthesis of gallium catalysts for the polymerization of heterocyclic monomers, which is the topic of our current research.

EXPERIMENTAL SECTION

General Procedures. The synthesis of gallium complexes was carried out under dry argon using standard Schlenk techniques. Solvents and reagents were purified and dried prior to use. Solvents were dried over potassium (toluene, n-hexane) or calcium hydride (methylene chloride). Me₃Ga was purchased from STREM Chemicals, Inc., and used as received. N¹-Mesitylethane-1,2-diaminium chloride was prepared according to the literature.¹⁶ Potassium hydride (50% in paraffin) was used, and the paraffin was washed out with n-hexane before the reaction. ¹H and ¹³C NMR spectra were recorded on Agilent 400-MR DD2 400 MHz and Varian UnityPlus 200 MHz spectrometers with shifts given in ppm according to the deuterated solvent shift. Visualization of TLC plates was performed by UV light with either KMnO₄ or I₂ stain. Flash chromatography was performed using silica gel 60 (230-400 mesh). Melting points were recorded on an OptiMelt SRS instrument with a heating rate of 10 °C/min. Highresolution electrospray mass spectra (HRMS) were recorded on a Quattro LC (triple-quadrupole mass spectrometer). The mass spectrometer was calibrated with an internal standard solution of sodium formate in MeOH. Elemental analysis was performed on a Vario EL III instrument (Heraeus).

Synthesis of NHC Salts. Synthesis of $[H_2L^1]I$ and $[H_2L^2]I$. N^1 -Mesitylethane-1,2-diaminium chloride (5.0 g, 20.0 mmol) was refluxed in 15 equiv of trimethyl orthoformate for 6 h. Then, the volatiles were removed under reduced pressure. The residue was dissolved in DCM (100 mL) and precipitated by the addition of diethyl ether (250 mL). The precipitate was dissolved in EtOH (50 mL) and stirred with 1.05 equiv of KOH for 30 min. Then, the solvent was removed and toluene (100 mL) was added, and the resulting solution was filtered through a Büchner funnel. Finally toluene was removed under vacuum to give 1mesityl-4,5-dihydro-1H-imidazole as a white solid in 93% yield (3.50 g). Spectral data are in agreement with those reported in the literature.³⁶ A mixture of 1-mesityl-4,5-dihydro-1H-imidazole (1.88 g, 10.0 mmol) and 1.1 equiv of 2-iodoethanol (0.8 mL, 10.0 mmol) or 3iodo-1-propanol (1.0 mL, 10.0 mmol) in toluene (20 mL) was stirred at 80 °C for 16 h in a pressure flask. After the solution was cooled to room temperature, the solvent and volatiles were removed under vacuum. The residue was dissolved in DCM (20 mL) and precipitated by the gradual addition of diethyl ether (100 mL) to give a white crystalline solid. This operation was repeated three times. The final precipitate of 3-(2-hydroxyethyl)-1-mesityl-4,5-dihydro-1H-imidazolinium iodide (2.34 g, 65%) or 3-(3-hydroxypropyl)-1-mesityl-4,5dihydro-1H-imidazolinium iodide (3.07 g, 8.2 mmol, 82%) was dried under vacuum.

3-(2-Hydroxyethyl)-1-mesityl-4,5-dihydro-1H-imidazolinium iodide ($[H_2L^1]I$): MS (ESI) m/z 233.5 $[M - I]^+$. ¹H NMR (400 MHz, CDCl₃) 2.25 (s, 3H, CH₃), 2.30 (s, 6H, CH₃), 3.83–3.96 (m, 4H, CH₂), 4.05 (br t, 1H, OH), 4.22 (dd, ${}^{3}J(H,H) = 12.5$, 9.2 Hz, 2H, CH₂), 4.44 (dd, ${}^{3}J(H,H) = 12.5$, 9.2 Hz, 2H, CH₂), 6.89 (d, ${}^{3}J(H,H) = 0.5$ Hz, 2H, CH_{Ar}), 8.56 (s, 1H, CH); ${}^{13}C$ NMR (100 MHz, CDCl₃) 18.7, 21.1, 48.8, 50.6, 51.2, 56.8, 130.0, 130.5, 135.5, 140.3, 158.7.

3-(3-Hydroxypropyl)-1-mesityl-4,5-dihydro-1H-imidazolinium iodide ($[H_2L^2]I$): MS (ESI) m/z 247.6 $[M - I]^+$. ¹H NMR (400 MHz, CDCl₃) 1.95–2.05 (m, 2H, CH₂), 2.26 (s, 3H, Mes-CH₃), 2.30 (s, 6H, CH₃), 2.98 (br, 1H, OH), 3.76 (t, ³J(H,H) = 5.4 Hz, 2H, CH₂), 3.97 (t, ³J(H,H) = 6.2 Hz, 2H, CH₂), 4.18 (dd, ³J(H,H) = 12.6, 9.2 Hz, 2H, CH₂), 4.38 (dd, ³J(H,H) = 12.6, 9.2 Hz, 2H, CH₂), 6.87–6.92 (m, 2H, CH₂), 8.85 (s, 1H, CH); ¹³C NMR (100 MHz, CDCl₃) 18.6, 21.1, 29.0, 46.8, 49.6, 51.0, 59.1, 130.0, 130.6, 135.5, 140.3, 158.5.

Synthesis of [H₂L³]Cl. In a 100 mL round-bottomed flask N¹-(2,4,6trimethylphenyl)- N^2 -(2-hydroxybenzyl)-1,2-diaminoethane (2.0 g, 7.03 mmol) was dissolved in 50 mL of Et₂O. Then HCl (10 mL, 2.5 equiv) 1 M in dioxane was added (dropwise), and the mixture was stirred for 2 h. Next, the white precipitate was filtered and washed with cold Et₂O, triethyl orthoformate (5.23 mL, 5 equiv) was added, and the resulting mixture was stirred for 12 h at 100 °C. After that, the reaction mixture was cooled to room temperature and the resulting beige precipitate was filtered through the Schott filter and washed with cold *n*-hexane, giving the desired product [H₂L³]Cl as white crystals which were dried in vacuo (1.8 g, 77%); mp 249-251 °C; MS (ESI) m/z 295.2 [M - Cl]⁺; HRMS calcd 295.1810, found 295.1801; ¹H NMR (400 MHz, C₂D₆SO, 100 °C) 2.24 (s, 6H, CH₃), 2.27 (s, 3H, CH₃), 3.87-4.20 (m, 4H, CH₂), 4.72 (s, 2H, CH₂), 6.80-6.89 (m, 1H, CH_{Ar}), 7.03–7.07 (m, 3H, CH_{Ar}), 7.19–7.34 (m, 2H, CH_{Ar}), 9.02 (s, 1H, CH), 10.37 (br, 1H, OH); 13 C NMR (100 MHz, C₂D₆SO, 100 °C) 17.2, 20.5, 47.7, 50.4, 115.7, 119.1, 129.3, 130.1, 130.7, 131.2, 135.5, 139.2, 156.4, 159.3.

Synthesis of [H₂L⁴]Cl. In a 100 mL round-bottomed flask N¹-(2,6diisopropylphenyl)- N^2 -(2-hydroxybenzyl)-1,2-diaminoethane (1.8 g, 5.51 mmol) was dissolved in 50 mL of Et₂O. Then HCl (8.27 mL, 3 equiv) 1 M in dioxane was added (dropwise), and the mixture was stirred for 2 h. Next the white precipitate was filtered and washed with cold Et₂O, triethyl orthoformate (4.7 mL, 5 equiv) was added, and the resulting mixture was stirred for 12 h at 100 °C. After that the reaction mixture was cooled to room temperature and the resulting beige precipitate was filtered through the Schott filter and washed with cold *n*-hexane, giving the desired product $[H_2L^4]Cl$ as white crystals which were dried in vacuo (1.75 g, 85%): mp 282-284 °C; MS (ESI) m/z 337.2 [M - Cl]⁺; HRMS calcd 337.2280, found 337.2264; ¹H NMR (400 MHz, C₂D₆SO) 1.12-1.27 (m, 12H, CH₃); 2.87-2.97 (m, 1H, CH), 3.95-4.16 (m, 4H, CH₂),), 4.75 (s, 2H, CH₂), 6.85 (td, 1H, ${}^{3}J(H,H) = 8.4, 1.2 \text{ Hz}, \text{CH}_{Ar}), 7.08-7.14 \text{ (m, 1H, CH}_{Ar}), 7.25 \text{ (td, 1H, })$ ${}^{3}J(H,H) = 9.2, 1.6, CH_{Ar}), 7.28-7.38 (m, 3H, CH_{Ar}), 7.46-7.52 (m, 3H, CH_$ 1H, CH_{Ar}), 9.18 (s, 1H, CH), 10.34 (br, 1H, OH); ¹³C NMR (100 MHz, C₂D₆SO) 23.9, 25.1, 28.2, 47.7, 48.2, 53.4, 116.1, 119.3, 119.4, 124.9, 130.5, 130.8, 130.9, 131.0, 146.8, 156.9, 159.2.

Synthesis of $[H_2L^5]Cl$. N^1 -(2,6-Diisopropylphenyl)- N^2 -(2-hydroxybenzyl)-1,2-diaminoethane (1.7 g, 5.21 mmol) was dissolved in 4.3 mL (5 equiv) of triethyl orthoformate in a 25 mL round-bottomed flask, and then 2.86 mL (2.2 equiv) of 4 M HCl in dioxane was added and the resulting mixture was stirred for 12 h at 100 °C. After that, the reaction mixture was cooled to room temperature and the resulting beige precipitate was filtered through the Schott filter and washed with cold *n*-hexane, giving white crystals which were dried in vacuo. The resulting NHC salt was used in the next step without purification. A 100 mL Schlenk was equipped with a stirring bar, and then the imidazolinium salt (1.43 g, 3.85 mmol) was dissolved in 20 mL of CH₂Cl₂ (DCM, dry) under an Ar atmosphere and the resulting solution was cooled to 0 °C. BBr₃ (7.71 mL, 1 mol/L in n-hexane, 2 equiv) was added dropwise and the mixture was stirred for 30 min. After that, the ice bath was removed and the resulting mixture was stirred at room temperature. Control of the reaction was carried out by TLC (DCM/MeOH 9/1). After 6 h a saturated solution of aqueous sodium bicarbonate was added (100 mL). The CH₂Cl₂ layer was separated, and the aqueous layer was washed with EtOAc (2×20 mL). The combined organic phases were dried over anhydrous MgSO₄, filtered, and concentrated. Purification of the crude mixture by

silica gel chromatography (c-Hex/EtOAc, 3/7) yielded the product $[H_2L^5]Cl$ as a white powder which was dried in vacuo (1.2 g, 64%, over two steps). Spectral data for $[H_2L^5]Cl$ are in agreement with data reported in the literature.¹⁵

Synthesis of Gallium Complexes. Synthesis of 1. A stirred solution of $[H_2L^1]I$ (774.0 mg, 2.15 mmol) in CH_2Cl_2 (10 mL) was cooled to -70 °C, and 1 mL of a CH₂Cl₂ solution of Me₃Ga (247.0 mg, 2.15 mmol) was added dropwise. After addition, the cooling bath was removed and the reaction mixture was warmed. Before the reaction mixture reached room temperature, the evolution of gas and formation of a white precipitate was observed. Then, the reaction mixture was stirred for 1 h and the solvent and volatile residues were removed under vacuum to give a white crystalline solid, essentially insoluble in common organic solvents, which was assumed on the basis of other results (see below) to be [(Me₂Ga(HL¹))I]. Next, [Me₂Ga(S-1)] (692 mg, 1.51 mmol) and KH (60.5 mg, 1.151 mmol) were placed in a Schlenk vessel and toluene (35 mL) was added at room temperature. After subsequent addition of around 5 mol % of KO^tBu the evolution of gas was observed and the reaction mixture was stirred for 2 h until gas evolution essentially ceased. The solution was filtered through a $0.45 \ \mu m$ hydrophobic syringe filter, and the solvent and volatile residues were then removed under vacuum to give a white crystalline solid. Crystallization from CH₂Cl₂/toluene solution resulted in the formation of colorless crystals of 1 (190 mg, 38%). Anal. Calcd for 1, C16H25GaN2O: C, 58.04; H, 7.61; N, 8.46. Found: C, 58.08; H, 7.80; N, 8.46. ¹H NMR (CD₂Cl₂, 400 MHz): -0.88 (s, 6H, GaCH₃), 2.18 (s, 6H, CH₃), 2.29 (s, 3H, CH₃), 3.35 (m, 2H, CH₂), 3.70 (m, 2H, CH₂), 3.85 (m, 2H, CH₂), 4.08 (m, 2H, CH₂), 6.93 (s, 2H, CH_{Ar}). $^{13}\text{C}\{^{1}\text{H}\}$ NMR (CD_2Cl_2, 50 MHz): –2.5 (GaMe_3), 18.2, 21.1, 49.4, 49.7, 51.2, 130.2, 130.3, 130.8, 135.7, 140.9, 158.6, 177.3. Because of its intensity, the signal at 177.3 ppm should not be interpreted as a carbene carbon signal. The carbene carbon signal, expected at around 200 ppm, was not observed despite long measurement times.

Synthesis of $[(Me_2Ga(HL^2))I]$. A stirred solution of $[H_2L^2]I$ (810.1 mg, 2.16 mmol) in CH_2Cl_2 (10 mL) was cooled to -70 °C, and 1 mL of a CH_2Cl_2 solution of Me_3Ga (248.0 mg, 2.16 mmol) was added dropwise. After addition, the cooling bath was removed and the reaction mixture was warmed. Before the reaction mixture reached room temperature, the evolution of gas and formation of a white precipitate was observed. Then the reaction mixture was stirred for 1 h and the solvent and volatile residues were removed under vacuum to give $[(Me_2Ga(HL^2))I]$ as a white crystalline solid in essentially quantitative yield. ¹H NMR (CD_2Cl_2 , 400 MHz): -0.17 (s, 6H, $GaCH_3$), 1.97 (m, 2H, CH_2), 2.30 (s, 3H, CH_3), 2.32 (s, 6H, CH_3), 3.79 (br, 2H, CH_2), 3.95 (br t, 2H, CH_2), 4.16–4.30 (m, 4H, CH_2), 6.97 (s, 2H, CH_{Ar}), 9.23, 9.43 (br, 1H, CH).

Synthesis of 2. [H₂L²]I (200.0 mg, 0.53 mmol) and KH (21.4 mg, 0.53 mmol) were placed in a Schlenk vessel, and toluene (20 mL) was added at room temperature. After subsequent addition of around 5 mol % of KO^tBu the evolution of gas was observed and the reaction mixture was stirred for 3 h until gas evolution essentially ceased. The solution was filtered through a 0.45 μ m hydrophobic syringe filter, and the solvent and volatile residues were then removed under vacuum to give a pale yellow oil of [HL²] in 92% yield (120 mg). ¹H NMR (toluene-d₈, 200 MHz): 0.58 (m, 1H, CH₂), 1.70 (m, 1H, CH₂), 2.15 (s, 3H, CH₃), 2.41 (s, 6H, CH₃), 2.70-2.85 (m, 2H, CH₂), 2.98-3.45 $(m, 5H, CH_2)$, 3.76 $(m, 2H, CH_2)$, 3.85 $(m, 2H, CH_2)$, 5.05 $(s, 1H, CH_2)$ CH), 6.78 (s, 2H, CH $_{\rm Ar}).$ To a stirred solution of $[\rm HL^2]$ (110.0 mg, 0.45 mmol) in toluene (5 mL) was added Me₃Ga (50 mg, 0.44 mmol) at $-70\,$ °C. The reaction mixture was warmed, but no gas evolution was observed until room temperature. Heating to around 50 °C resulted in gas evolution, which ceased after 30 min. Next, the solvent and volatile residues were removed under vacuum to give a crystalline solid, which was subsequently crystallized from toluene/n-hexane to give a white crystalline solid (70 mg) in 88% yield, based on Ga content. Anal. Calcd for 2, C₂₀H₃₆Ga₂N₂O: C, 52.23; H, 7.89; N, 6.09. Found: C, 52.09; H, 7.88; N, 6.05. ¹H NMR (toluene-*d*₈, 400 MHz): -0.40 (s, 6H, GaCH₃), 0.02 (s, 9H, GaCH₃), 1.49 (m, 2H, CH₂), 1.88 (s, 6H, CH₃), 2.02 (s, 3H, CH₃), 2.63 (m, 2H, NCH₂), 2.79 (m, 2H, NCH₂), 3.28 (br t, ${}^{3}J(H,H) = 5.9$ Hz, 2H, NCH₂), 3.76 (t, ${}^{3}J(H,H) =$

5.9 Hz, 2H, OCH₂), 6.58 (s, 2H, CH_{Ar}), $^{13}C{^{1}H}$ NMR (toluene- $d_{8^{\prime}}$, 100 MHz): -6.7, -3.2, (GaMe₃), 17.4, 20.8, 29.1, 43.4, 49.5, 50.6, 60.2, 129.7, 133.9, 135.7, 139.1, 199.3 (carbene).

Reaction of $Me_2Ga(O,O')(SIMes)$ with Me_3Ga . To a stirred solution of $Me_2Ga(O,O')(SIMes)$ ((HO,O') = (S)-methyl lactate) (302.1 mg, 0.59 mmol) in toluene (10 mL) was added 1 mL of a toluene solution of Me_3Ga (68.2 mg, 0.59 mmol) dropwise at room temperature. Then the reaction mixture was stirred for 10 min and the solvent and volatile residues were removed under vacuum to give a white crystalline solid. The product was dissolved and crystallized from toluene/hexane to give colorless crystals of $Me_3Ga(SIMes)$ (205 mg, 82%). ¹H NMR (toluene- d_8 , 400 MHz): -0.74 (s, 9H, GaCH₃), 2.09 (s, 6H, CH₃), 2.20 (s, 12H, CH₃), 3.09 (s, 4H, CH₂), 6.74 (s, 4H, CH_{Ar}) ¹³C{¹H} NMR (toluene- d_8 , 100 MHz): -5.8 (GaMe₃), 17.9, 21.0, 50.9, 128.5, 129.6, 135.6, 136.0, 138.3, 206.1 (carbene).

Synthesis of 3. A stirred solution of [HL³]Cl (546.4 mg, 1.65 mmol) in CH₂Cl₂ (10 mL) was cooled to -50 °C, and 1 mL of a CH₂Cl₂ solution of Me₃Ga (190.0 mg, 1.65 mmol) was added. After addition, the cooling bath was removed and the reaction mixture was warmed. Before the reaction mixture reached room temperature, the evolution of gas and formation of a white precipitate was observed. Then the reaction mixture was stirred for 1 h and the solvent and volatile residues were removed under vacuum to give a white crystalline solid of [(Me₂Ga(HL³))Cl] in essentially quantitative yield. ¹H NMR (CD₂Cl₂, 200 MHz): -0.40 (s, 6H, GaCH₃), 2.27 (s, 6H, CH₃), 2.31 (s, 3H, CH₃), 4.00 (s, 4H, CH₂), 4.65 (s, 2H, CH₂), 6.58-6.72 (m, 2H, CH_{Ar}), 6.99 (s, 2H, CH_{Ar}), 7.08-7.21 (m, 2H, CH_{Ar}), 8.73 (s, 1H, CH). Next, [(Me₂Ga(HL³))Cl)] (500.0 mg, 1.16 mmol) and KH (46.5 mg, 1.16 mmol) were placed in a Schlenk vessel and toluene (20 mL) was added at room temperature. After subsequent addition of around 5 mol % of KO^tBu the evolution of gas was observed and the reaction mixture was stirred for 2 h until gas evolution essentially ceased. The solution was filtered through a 0.45 μ m hydrophobic syringe filter, and the solvent and volatile residues were then removed under vacuum to give a yellow oil. The obtained oil was subsequently dissolved in 3 mL of toluene, and the slow addition of 20 mL of n-hexane resulted in the formation of a white crystalline solid, which was washed twice with 10 mL of *n*-hexane and dried under vacuum to give 3 in 46% yield (210 mg). Anal. Calcd for 3, C21H27GaN2O: C, 64.15; H, 6.92; N, 7.12. Found: C, 64.15; H, 7.05; N, 7.14. ¹H NMR (toluene-d₈, 400 MHz): -0.34 (s, 6H, GaCH₃), 1.80 (s, 6H, CH₃), 1.98 (s, 3H, CH₃), 2.78 (m, 2H, CH₂), 3.00 (m, 2H, CH₂), 4.22 (br, 2H, CH₂), 6.56 (s, 2H, CH_{Ar}), 6.67 (td, ${}^{3}J(H,H) = 7.3, 1.5 \text{ Hz}, 1H, CH_{Ar}), 6.91 (dd, {}^{3}J(H,H) = 7.3, 2.0 \text{ Hz},$ 1H, CH_{Ar}), 7.14 (dd, ${}^{3}J(H,H) = 8.3$, 1.5 Hz, 1H, CH_{Ar}), 7.21 (m, 1H, CH_{Ar}), ¹³C{¹H} NMR (toluene-d₈, 100 MHz): -7.2 (GaMe₃), 17.4, 20.8, 49.8, 50.0, 50.1, 115.3, 122.8, 126.0, 129.5, 130.7, 134.4, 135.9, 138.7, 166.0, 198.4 (carbene).

Second Approach. [H₂L³]Cl (724.0 mg, 2.19 mmol) and KH (88.0 mg, 2.19 mmol) were placed in a Schlenk vessel, toluene (20 mL) was added at room temperature, and evolution of gas was observed. The reaction mixture was stirred for 2 h until gas evolution essentially ceased and the yellow solution was filtered through a 0.45 μ m hydrophobic syringe filter, and the solvent and volatile residues were then removed under vacuum to give the yellow crystalline solid $\lceil HL^3 \rceil$ in 60% yield (391 mg). ¹H NMR (toluene-*d*₈, 400 MHz): 2.15 (s, 3H, CH₃), 2.32 (s, 6H, CH₃), 2.91 (m, 2H, CH₂), 3.07 (m, 2H, CH₂), 3.83 (s, 2H, CH₂), 5.90 (br, 1H, CH), 6.73–6.79 (m, 4H, CH_{Ar}), 6.87 (br d, 1H, CH_{Ar}), 6.98–7.10 (m, 2H, CH_{Ar}). To a stirred solution of [HL³] (612.0 mg, 2.08 mmol) in toluene (20 mL) was added Me₃Ga (239.0 mg, 2.08 mmol) at -50 °C to give a white precipitate. The reaction mixture was warmed and slowly heated, and gas evolution was observed at around 50 °C. Then, the reaction mixture was stirred at 80 °C for 3.5 h, at which point evolution of gas essentially ceased. Next the solvent and volatile residues were removed under vacuum to give a yellow oil. Crystallization from a toluene/n-hexane solution followed by washing of the yellow oily precipitate with cold toluene (cooled to around -70 °C) and n-hexane gave colorless crystals of 3 in 15% yield (125 mg). ¹H ¹³C NMR was the same as that reported above for 3.

Synthesis of 4. A stirred solution of $[H_2L^4]Cl$ (1.04 g, 2.79 mmol) in CH₂Cl₂ (15 mL) was cooled to -70 °C, and 1 mL of a CH₂Cl₂ solution of Me₃Ga (320.0 mg, 2.79 mmol) was added. After addition, the cooling bath was removed and the reaction mixture was warmed. Before the reaction mixture reached room temperature, the evolution of gas and formation of a white precipitate was observed. Then the reaction mixture was stirred for 1 h and the solvent and volatile residues were removed under vacuum to give $[(Me_2Ga(HL^4))Cl)]$ as a white crystalline solid in essentially quantitative yield. $^1\!\mathrm{H}$ NMR $(CD_2Cl_2, 400 \text{ MHz}): -0.42 \text{ (s, 6H, GaCH_3), 1.25 1.26 (d, {}^3J(H,H) =$ 6.7 Hz, 12H, CH₃), 2.85 (sept, ${}^{3}J(H,H) = 6.7$ Hz, 2H, CH), 4.05 (m, 4H, CH₂), 4.68 (s, 2H, CH₂), 6.63 (td, ${}^{3}J(H,H) = 7.4$, 1.2 Hz, 1H, CH_{Ar}), 6.71 (dd, ${}^{3}J(H,H) = 8.2$, 1.2 Hz, 1H, CH_{Ar}), 7.12 (dd, ${}^{3}J(H,H)$ = 7.4, 2.0 Hz, 1H, CH_{Ar}), 7.18 (m, 1H, CH_{Ar}), 7.27 (d, ³J(H,H) = 7.8 Hz, 2H, CH_{Ar}), 7.46 (t, ${}^{3}J(H,H) = 7.8$ Hz, 1H, CH_{Ar}), 8.85 (s, 1H, CH). Next, $[(Me_2Ga(HL^4))Cl)]$ (1.037 g, 2.20 mmol) and KH (88.1 mg, 2.20 mmol) were placed in a Schlenk vessel, and toluene (30 mL) was added at room temperature. After subsequent addition of around 5 mol % of KO'Bu the evolution of gas was observed and the reaction mixture was stirred for 2 h until gas evolution essentially ceased. The solution was filtered through a 0.45 μ m hydrophobic syringe filter, and the solvent and volatile residues were then removed under vacuum to give a pale yellow crystalline solid. The obtained solid was subsequently dissolved in 3 mL of toluene, and the slow addition of 15 mL of *n*-hexane resulted in the formation of a white crystalline solid, which was washed twice with 10 mL of *n*-hexane and dried under vacuum to give 4 in 47% yield (450 mg). Anal. Calcd for 4, C₂₄H₃₃GaN₂O: C, 66.23; H, 7.64; N, 6.44. Found: C, 66.36; H, 7.64; N, 6.26. ¹H NMR (toluene-*d*₈, 400 MHz): -0.35 (s, 6H, GaCH₃), 0.92, 1.10 (d, ${}^{3}J(H,H) = 6.7$ Hz, 12H, CH₃), 2.56 (sept, ${}^{3}J(H,H) = 6.7$ Hz, 2H, CH), 3.00 (m, 4H, CH₂), 4.30 (br, 2H, CH₂), 6.62 (td, ${}^{3}J(H,H) = 7.4, 1.2$ Hz, 1H, CH_{Ar}), 6.82 (dd, ${}^{3}J(H,H) = 7.4, 2.0$ Hz, 1H, CH_{Ar}), 6.84 (d, ${}^{3}J$ (H,H) = 7.8 Hz, 2H, CH_{Ar}), 7.06 (t, ${}^{3}J$ (H,H) = 7.8 Hz, 1H, CH_{Ar}), 7.12 (m, 1H, CH_{Ar}), 7.20 (m, 1H, CH_{Ar}) ${}^{13}C{}^{1}H$ NMR (toluene-d₈, 100 MHz): -5.8 (GaMe₃), 23.7, 24.9, 28.5, 49.0, 50.1, 53.3, 114.6, 122.9, 124.1, 124.4, 129.6, 130.0, 130.7, 134.3, 146.5, 165.9, 198.2 (carbene)

Second Approach. [H₂L⁴]Cl (464.0 mg, 1.24 mmol) and KH (50.0 mg, 1.25 mmol) were placed in a Schlenk vessel, and toluene (20 mL) was added at room temperature. After subsequent addition of a catalytic amount of KO^tBu (<5%) the evolution of gas was observed and the reaction mixture was stirred for 1.5 h until gas evolution essentially ceased. The solution was filtered through a 0.45 μm hydrophobic syringe filter, and the solvent and volatile residues were then removed under vacuum to give a yellow oily solid of [HL⁴] in 65% yield (272 mg). ¹H NMR (toluene-d₈, 400 MHz): 1.21, 1.31 (d, ${}^{3}J(H,H) = 6.7$ Hz, 12H, CHCH₃), 2.92 (t, ${}^{3}J(H,H) = 6.7$ Hz, 2H, CH_2), 3.20 (t, ${}^{3}J(H,H) = 6.7$ Hz, 2H, CH_2), 3.66 (sept, ${}^{3}J(H,H) = 6.7$ Hz, 2H, CHCH₃), 3.79 (s, 2H, CH₂), 5.75 (s, 1H, CH), 6.77 (m, 2H, CH_{Ar}), 6.77 (m, 2H, CH_{Ar}), 6.88 (d, ${}^{3}J(H,H) = 6.7$ Hz, 1H, CH_{Ar}), 6.97-7.12 (m, CH_{Ar}) 7.20 (m, 1H, CH_{Ar}). To the stirred solution of [HL⁴] (250.0 mg, 0.75 mmol) in toluene (10 mL) was added Me₃Ga (86 mg, 0.75 mmol) at -70 °C. The reaction mixture was warmed, but no gas evolution was observed until room temperature. Heating to around 90 °C resulted in only a slight evolution of gas, which ceased after 0.5 h. Next the solvent and volatile residues were removed under vacuum to give a yellow oily solid. ¹H NMR of the reaction mixture was complex (see the Supporting Information), indicating the presence of unreacted CH of [HL4].

Synthesis of 5. A stirred solution of $[H_2L^5]Cl$ (640 mg, 1.78 mmol) in CH₂Cl₂ (15 mL) was cooled to -70 °C, and 1 mL of a CH₂Cl₂ solution of Me₃Ga (205.0 mg, 1.79 mmol) was added. After addition, the cooling bath was removed and the reaction mixture was warmed. Before the reaction mixture reached room temperature, the evolution of gas and formation of a white precipitate was observed. Then the reaction mixture was stirred for 1 h and the solvent and volatile residues were removed under vacuum to give $[(Me_2Ga(HL^5))Cl]$ as a white crystalline solid in essentially quantitative yield. ¹H NMR (CD₂Cl₂, 400 MHz): -0.21 (s, 6H, GaCH₃), 1.31 (d, ³*J*(H,H) = 6.7 Hz, 12H, CH₃), 3.01 (br sept, ³*J*(H,H) = 6.7 Hz, 2H, CH), 4.20 (m, 2H, CH₂), 4.65 (m, 2H, CH₂), 6.78 (br t, ${}^{3}J(H,H) = 7.4$, 1H, CH_{Ar}), 6.94 (br d, ${}^{3}J(H,H) = 8.2$, 1H, CH_{Ar}), 7.04 (br d, ${}^{3}J(H,H) = 8.2$ Hz, 1H, CH_{Ar}), 7.13 (br d, ³*J*(H,H) = 7.4 Hz, 1H, CH_{Ar}), 7.32 (d, ³*J*(H,H) = 7.8 Hz, 2H, CH_{Ar}), 7.51 (t, ${}^{3}J(H,H)$ = 7.8 Hz, 1H, CH_{Ar}), 10.15 (br, 1H, CH). Next, [(Me₂Ga(HL⁵))Cl] (502.9 mg, 1.10 mmol) and KH (44.1 mg, 1.10 mmol) were placed in a Schlenk vessel and toluene (20 mL) was added at room temperature. After subsequent addition of around 5 mol % of KO^tBu the evolution of gas was observed and the reaction mixture was stirred for 6 h until gas evolution essentially ceased. The solution was filtered through a 0.45 μ m hydrophobic syringe filter, and the solvent and volatile residues were then removed under vacuum to give a pale yellow oily solid. The obtained product was purified by washing with a toluene/n-hexane (1/1) mixture cooled to around 0 °C, and subsequent crystallization from toluene/n-hexane solution gave 5 in 39% yield (180 mg). Anal. Calcd for 5, C23H31GaN2O: C, 65.58; H, 7.42; N, 6.65. Found: C, 65.64; H, 7.44; N, 6.54. ¹H NMR (toluene-d₈, 400 MHz): -0.39 (s, 6H, GaCH₃), 1.00, 1.20 (d, ³J(H,H) = 6.7 Hz, 12H, CH₃), 2.85 (sept, ${}^{3}J(H,H) = 6.7$ Hz, 2H, CH), 3.16 (m, 4H, CH₂), 6.53 (td, ${}^{3}J(H,H) =$ 8.2, 1.6 Hz, 1H, CH_{Ar}), 6.66 (dd, ${}^{3}J(H,H) = 7.4$, 1.6 Hz, 1H, CH_{Ar}), 6.95 (d, ${}^{3}J(H,H) = 7.8$ Hz, 2H, CH_{Ar}), 7.05 (td, ${}^{3}J(H,H) = 7.4$, 1.6 Hz, 1H, CH_{Ar}), 7.10 (t, ${}^{3}J(H,H) = 7.8$ Hz, 1H, CH_{Ar}), 7.29 (dd, ${}^{3}J(H,H) =$ 8.2, 1.6 Hz, 1H, CH_{Ar}) ${}^{13}C{}^{1}H$ NMR (toluene- d_{8} , 100 MHz): -8.1 (GaMe2), 23.4, 25.9, 28.4, 49.0, 51.4, 114.9, 117.7, 123.1, 124.5, 126.6, 130.1, 134.1, 147.0, 158.0, 193.9 (carbene).

Synthesis of **6**. To a stirred solution of 4 (213.0 mg, 0.49 mmol) in toluene (6 mL) was added 1 mL of a toluene solution of Me₃Ga (56.0 mg, 0.49 mmol) dropwise at room temperature. Then the reaction mixture was stirred for 10 min and the solvent and volatile residues were removed under vacuum to give a white crystalline solid in essentially quantitative yield. Anal. Calcd for **6**, $C_{27}H_{42}Ga_2N_2O$: C, 58.95; H, 7.70; N, 5.09. Found: C, 59.97; H, 7.60; N, 5.06. ¹H NMR (toluene- d_8 , 400 MHz): -0.33 (br, 6H, GaCH₃), 0.01 (s, 9H, GaCH₃), 0.84 (d, ³J(H,H) = 6.7 Hz, 6H, CH₃), 0.96 (br d, 6H, CH₃), 2.32 (br, 2H, CH), 2.80–2.97 (m, 4H, CH₂), 3.5–4.9 (br, 2H, CH₂), 6.69–6.76 (m, 2H, CH_{Ar}), 6.82 (d, ³J(H,H) = 7.8 Hz, 2H, CH_{Ar}), 7.01 (t, ³J(H,H) = 7.8 Hz, 1H, CH_{Ar}), 7.07 (br d, 2H, CH_{Ar}), $1^3C\{^1H\}$ NMR (toluene- d_8 , 100 MHz): -5.5 (br), -1.9 (GaMe₃), 23.2, 25.5, 28.4, 49.0, 50.4, 53.3, 120.0, 124.4, 125.6, 128.3, 128.5, 129.8, 129.9, 130.3, 133.7, 146.4, 159.3, 200.5 (carbene).

Crystallographic Studies. Single crystals of 1-6 and Me₃Ga-(SIMes) suitable for X-ray diffraction studies were selected under a polarizing microscope, mounted in inert oil, and transferred to the cold gas stream of the diffractometer. Diffraction data were measured at 100(2) K with graphite-monochromated Mo K α radiation on an Oxford Diffraction ĸ-CCD Gemini A Ultra diffractometer. Cell refinement and data collection as well as data reduction and analysis were performed with the CRYSALIS^{PRO} software.³⁷ Absorption effects were corrected analytically from the crystal shape. The structures were solved by direct methods using the SHELXS-97 structure solution program and refined by full-matrix least squares against F^2 with SHELXL-2013³⁸ and OLEX2.³⁹ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added to the structure model at geometrically idealized coordinates and refined as riding atoms. The unit cell of 6 contains a toluene molecule which is disordered about a center of inversion, with the center of gravity of the six-membered ring displaced slightly from the inversion center. The atoms of one entire toluene molecule were defined with the site occupation factors equal to 0.5. The atoms of the six-membered ring of the toluene molecule were constrained to an ideal hexagon, while neighboring atoms within each orientation of the disordered toluene molecule were restrained to have similar atomic displacement parameters.

Crystal data for 1: $C_{16}H_{25}N_2OGa$, $M_r = 331.10$, monoclinic, space group $P2_1/c$, a = 14.55464(18) Å, b = 7.87134(9) Å, c = 14.22468(16) Å, $\beta = 97.6310(11)^\circ$, V = 1615.21(3) Å³, Z = 4, μ (Mo K α) = 1.702 mm⁻¹, $D_{calc} = 1.362$ g cm⁻³, 95341 reflections measured, 4436 unique reflections ($R_{int} = 0.0455$), F(000) = 696.0, R1 = 0.0194 ($I > 2\sigma(I)$), wR2 = 0.0525 [(all data).

Crystal data for 2: C₂₀H₃₆Ga₂N₂O, *M*_r = 459.95, monoclinic, space group *P*2₁/*c*, *a* = 9.11334(7) Å, *b* = 15.19257(11) Å, *c* = 16.52020(12)

Å, $\beta = 91.9516(7)^{\circ}$, V = 2285.98(3) Å³, Z = 4, μ (Mo K α) = 2.366 mm⁻¹, $D_{calc} = 1.336$ g cm⁻³, 141485 reflections measured, 6358 unique ($R_{int} = 0.0285$), F(000) = 960.0, R1 = 0.0176 ($I > 2\sigma(I)$), wR2 = 0.0483 (all data).

Crystal data for **3**: $C_{21}H_{27}GaN_2O$, $M_r = 393.16$, triclinic, space group $P\overline{1}$, a = 7.9057(4) Å, b = 8.0823(3) Å, c = 17.5181(5) Å, $\alpha = 89.256(3)^{\circ}$, $\beta = 82.908(3)^{\circ}$, $\gamma = 61.207(4)^{\circ}$, V = 972.05(8) Å³, Z = 2, μ (Mo K α) = 1.426 mm⁻¹, $D_{calc} = 1.343$ g cm⁻³, 39584 reflections measured, 5189 unique reflections ($R_{int} = 0.0352$), F(000) = 412.0, R1 = 0.0210 ($I > 2\sigma(I)$), wR2 = 0.0559 (all data).

Crystal data for 4: $C_{24}H_{33}GaN_2O$, $M_r = 435.24$, monoclinic, space group $P2_1/c$, a = 13.3098(3) Å, b = 12.43120(19) Å, c = 14.6027(3) Å, $\beta = 111.684(2)^\circ$, V = 2245.13(8) Å³, Z = 4, μ (Mo K α) = 1.241 mm⁻¹, $D_{calc} = 1.288$ g cm⁻³, 39832 reflections measured, 6233 unique reflections ($R_{int} = 0.0445$), F(000) = 920.0, R1 = 0.0272 ($I > 2\sigma(I)$), wR2 = 0.0673 (all data).

Crystal data for 5: C₂₃H₃₁GaN₂O, M_r = 421.22, monoclinic, space group P2₁/*c*, *a* = 12.2017(8) Å, *b* = 13.8740(9) Å, *c* = 13.9308(9) Å, β = 113.816(2)°, *V* = 2157.5(2) Å³, *Z* = 4, μ(Mo Kα) = 1.290 mm⁻¹, D_{calc} = 1.297 g cm⁻³, 37459 reflections measured, 5662 unique reflections (R_{int} = 0.0249), *F*(000) = 888.0, R1 = 0.0251 (*I* > 2 σ (*I*)), wR2 = 0.0646 (all data).

Crystal data for **6**: $4(C_{27}H_{42}Ga_2N_2O)\cdot C_7H_8$, $M_r = 2292.39$, triclinic, space group $P\overline{1}$, a = 10.64328(19) Å, b = 17.3159(3) Å, c = 17.6567(3) Å, $\alpha = 98.6975(16)^\circ$, $\beta = 103.4380(16)^\circ$, $\gamma = 106.7528(17)^\circ$, V = 2946.31(10) Å³, Z = 1, μ (Mo K α) = 1.850 mm⁻¹, $D_{calc} = 1.292$ g cm⁻³, 178277 reflections measured, 12415 unique reflections ($R_{int} = 0.0681$), F(000) = 1202.0, R1 = 0.0304 ($I > 2\sigma(I)$), wR2 = 0.0841 (all data).

Crystal data for $Me_3Ga(SIMes)$: $C_{24}H_{35}GaN_2$, $M_r = 421.26$, orthorhombic, space group $Pca2_1$, a = 17.6087(4) Å, b = 16.5494(4) Å, c = 15.9289(3) Å, V = 4641.88(17) Å³, Z = 8, μ (Mo K α) = 0.7107 mm⁻¹, $D_{calc} = 1.206$ g cm⁻³, 62740 reflections measured, 12156 unique reflections ($R_{int} = 0.0397$), F(000) = 1792.0, R1 = 0.0269 ($I > 2\sigma(I)$), wR2 = 0.0647 (all data).

ASSOCIATED CONTENT

S Supporting Information

CIF files of 1-6 and Me₃Ga(SIMes), synthetic details of NHC salts, NMR FTIR data, and calculations of bond valence vectors for gallium centers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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