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Bis(allyl)gallium Cation, Tris(allyl)gallium, and Tetrakis(allyl)gallate: Synthesis, Characterization, and Reactivity

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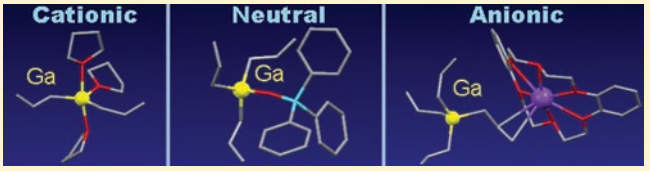
Supporting Information

ABSTRACT: A series of cationic, neutral, and anionic allylgallium complexes has been isolated and fully characterized. It includes neutral $[Ga(\eta^1\text{-}C_3H_5)_3(L)]$ (**1**, L = THF; **2**, L = $OPPh_3$), cationic $[Ga(\eta^1\text{-}C_3H_5)_2(THF)_2]^+[A]^-$ (**3**, $[A]^-$ = $[B(C_6F_5)_4]^-$; **4**, $[A]^-$ = $[B(C_6H_3Cl_2)_4]^-$), as well as anionic $[Cat]^+[Ga(\eta^1\text{-}C_3H_5)_4]^-$ (**5**, $[Cat]^+$ = K^+; **6**, $[Cat]^+$ = $[K(dibenzo\text{-}18\text{-}c\text{-}6]^+$; **7**, $[Cat]^+$ = $[PPh_4]^+$). Binding modes of the allyl ligand in solution and in the solid state have been studied comparatively. Single crystal X-ray analyses revealed a four-coordinate neutral gallium center in **2**, a five-coordinate cationic gallium center in **4** and [**4**·THF], and a four-coordinate anionic gallium center with a bridging μ_2-η^1:η^2 coordination mode of the allyl ligand in **6**. The reactivity of this series of allylgallium complexes toward benzophenone and *N*-heteroaromatics has been investigated. Counterion effects have also been studied. Reactions of **1** and **5** with isoquinoline revealed the first examples of organogallium complexes reacting under 1,2-insertion with pyridine derivatives.



INTRODUCTION

In recent years, organogallium compounds have attracted interest in homogeneous catalysis[1] and organic synthesis.[2] Organogallium reagents combine a moderate Lewis acidity with a relatively low polarity of the metal−carbon bond.[2b,d] Their reactivity significantly differs not only from organolithium, -magnesium, -copper, and -tin compounds, but in some cases also from homologous organoaluminum and -indium reagents.[2b,d,g] Due to the importance of the allyl substituent in organic synthesis, there is an ongoing effort to develop allyl transfer reagents.[3] Consequently, allylgallium species have frequently been applied in organic synthesis.[4] However, these reagents are mostly generated in situ and remain ill-defined. Only one allylgallium compound, $[Ga(\eta^1\text{-}C_3H_3(SiMe_3)_2)_3]$, has been isolated and fully characterized but has not been subjected to reactivity studies.[5]

None of the allylgallium reagents mentioned above bear formal charges at the metal center. In general, charged organogallium species have also been in the focus of research efforts since their characteristics differ notably from their neutral parent compounds.[2d,6] Cationic organogallium compounds show enhanced Lewis acidity as demonstrated by rapid polymerization of propylene oxide or cyclohexene oxide, for instance.[1a,d] Anionic tetrakis(organo)gallate moieties have been used in organic reactions and as chelating ligands in the synthesis of heterobimetallic complexes.[7] We report here the synthesis and characterization of cationic, neutral, and anionic allylgallium complexes along with their reactivity toward electrophilic substrates.

RESULTS AND DISCUSSION

Neutral Allylgallium Complexes. The THF adduct of the parent allylgallium complex, $[Ga(\eta^1\text{-}C_3H_5)_3(THF)]$ (**1**), was synthesized by salt metathesis of gallium chloride with allylpotassium in pentane/THF (5:1) (Scheme 1). Low temperatures (−78 to −30 °C) had to be applied in this reaction as well as during workup, since **1** is temperature sensitive. Degradation of **1** at ambient temperature in hydrocarbons is much faster than in donor solvents hinting at an intermolecular degradation mechanism (in C_6D_6, $t_{1/2}$ = 5 days, decomposition products detected by ^{1}H NMR after a few hours;[8] in THF-d_8, no decomposition products detected after more than 14 days). NMR spectra of **1** in toluene-d_8 at ambient temperature show fluxional behavior of the allyl ligands with the methylene groups giving rise to one broad resonance. An AX_4 pattern with one quintet and one doublet (relative intensity 1:4) is observed at 90 °C in toluene-d_8.[9] The η^1 bonding mode of the allyl ligands with its $AMNX_2$ pattern is recorded at −60 °C in toluene-d_8 or at ambient temperature in THF-d_8. Thus, donor solvents significantly slow down the allyl exchange rate in **1**. In $[Ga(\eta^1\text{-}C_3H_3(SiMe_3)_2)_3]$, the η^1 bonding mode in toluene-d_8 solution was not frozen out at temperatures as low as −75 °C.[5] When comparing **1** to the homologous allyl complexes $[E(\eta^1\text{-}C_3H_5)_3(L)]$ (E = Al, In; L = neutral ligand), the rate of allyl exchange reactions increases in the order Al < Ga < In.[10,11] This is ascribed to (i) the ionic radii of the metal centers and (ii) the shielding of the cationic charge of the metal centers by core electrons, which both increase in the same order.

The THF ligand in $[Ga(\eta^1\text{-}C_3H_5)_3(THF)]$ (**1**) could not be removed by exposing **1** to reduced pressure, but is labile in the presence of excess THF-d_8 or stoichiometric amounts of

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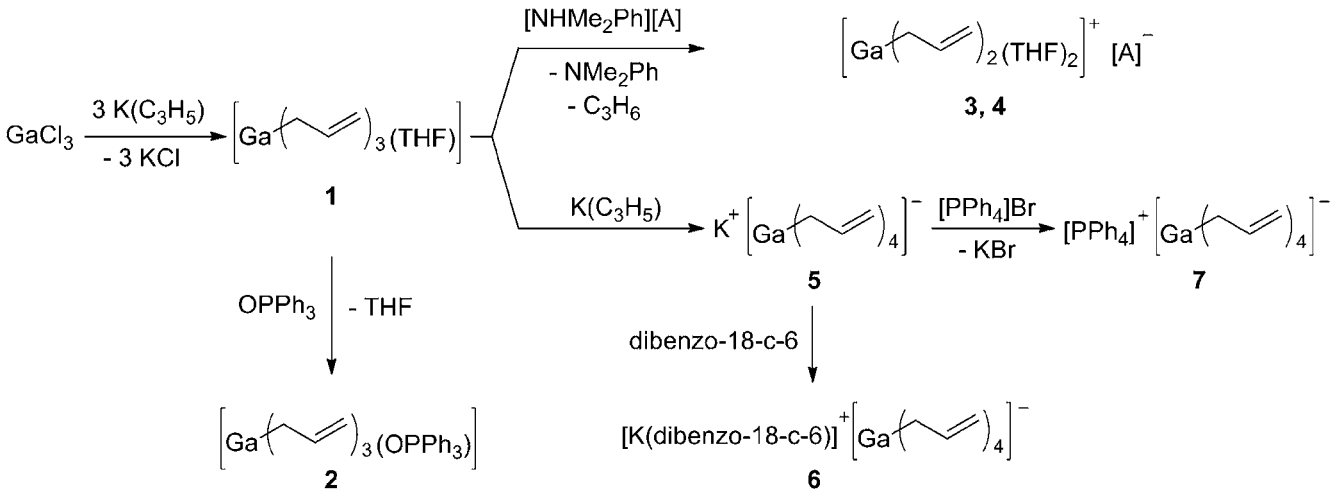
Scheme 1. Synthesis of Tris(allyl)gallium Compounds 1 and 2, Bis(allyl)gallium Cations 3 and 4, and Tetrakis(allyl)gallates 5, 6, and 7[a]



[a] **3**, $[A]^- = [B(C_6F_5)_4]^-$; **4**, $[A]^- = [B(C_6H_3Cl_2)_4]^-$.

stronger neutral donors. Reaction of **1** with 1 equiv of triphenylphosphine oxide $OPPh_3$ gave $[Ga(\eta^1\text{-}C_3H_5)_3(OPPh_3)]$ (**2**) (Scheme 1). The $OPPh_3$ ligand in **2** is also labile as shown by ^1H and ^{31}P NMR spectroscopic analysis of a THF-d_8 solution containing equimolar amounts of $OPPh_3$ and **2**. On the basis of VT ^{31}P NMR spectroscopic measurements, the exchange rate of the $OPPh_3$ ligands was estimated to be $k_C = 2 \times 10^3\ s^{-1}$ at the coalescence temperature of $T_C = 178$ K. The coalescence temperature is more than 100 K lower than for the same process of $[Al(\eta^1\text{-}C_3H_5)_3(OPPh_3)]$.[12] Thus, the M–$OPPh_3$ bond is weaker in the case of the Ga compound when compared with the Al congener.[13]

Single crystals of **2** were obtained by cooling a saturated solution in CH_2Cl_2/pentane to −30 °C. Compound **2** crystallized in the monoclinic space group $P2_1/c$ with $Z = 4$. The gallium center is found in a distorted tetrahedral coordination geometry (C–Ga–C/O, 97.6(4)–120.0(4)°) (Figure 1). The allyl ligands adopt an η^1 bonding mode with one long and one short C–C bond in each allyl group. The same bonding mode has been reported for $[Ga(\eta^1\text{-}C_3H_3(SiMe_3)_2)_3]$.[5] A mean Ga–C bond length of 1.995 Å is found in **2**, which ranges between the corresponding values for $[Ga(\eta^1\text{-}C_3H_3(SiMe_3)_2)_3]$ and $[Ga(t\text{Bu})_2R(OPPh_3)]$ (R = aryl).[5,14] The Ga1–O1–P1 angle in **2** (159.21(14)°) deviates from 180°, suggesting that the $OPPh_3$ ligand is a pure σ donor. In contrast, $[GaCl_3(OPPh_3)]$ shows a linear Ga–O–P unit.[15]

Cationic Allylgallium Complexes. Cationic allylgallium complexes $[Ga(\eta^1\text{-}C_3H_5)_2(THF)_2]^+[A]^-$ (**3**, $[A]^- = [B(C_6F_5)_4]^-$; **4**, $[A]^- = [B(C_6H_3Cl_2)_4]^-$) were obtained by treating **1** with dimethylanilinium borates (Scheme 1). The allyl ligands in **3** and **4** exhibit an η^1 binding mode in THF-d_8 solutions at ambient temperature. The THF ligands are labile as shown by ^1H NMR spectroscopy. Cooling a solution of **4** in CH_2Cl_2/pentane (1:2) to −30 °C gave colorless, block-shaped single crystals. Compound **4** crystallized in the triclinic space group $P\bar{1}$ with $Z = 2$. The gallium center in **4** experiences weak contacts with a Cl atom of the counterion (Figure 2a). Thus, a coordination number of five and a distorted trigonal bipyramidal coordination geometry were assigned (O1–Ga1–Cl7, 167.84(9)°; Σ(C–Ga–$O^{equatorial}$), 348.9(2)°), although four-coordinate gallium cations are most

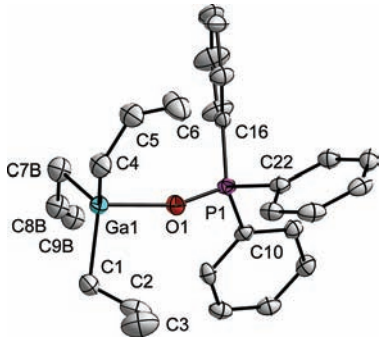


Figure 1. Molecular structure of $[Ga(\eta^1\text{-}C_3H_5)_3(OPPh_3)]$ (**2**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Atoms C7, C8, and C9 are shown with only one split position. Selected bond lengths [Å] and angles [deg]: Ga1–C1, 2.001(3); Ga1–C4, 1.981(3); Ga1–O1, 1.980(2); C1–C2, 1.495(5); C2–C3, 1.250(5); C4–C5, 1.451(5); C5–C6, 1.328(5); O1–P1, 1.490(2); C1–Ga1–C4, 113.78(15); C1–Ga1–O1, 97.96(11); C4–Ga1–O1, 103.90(12); C1–C2–C3, 130.0(5); C4–C5–C6, 127.4(4); Ga1–O1–P1, 159.21(14).

common.[6a,b] The Ga1–Cl7 distance of 3.5113(16) Å is longer than Ga–Cl bonds in other cationic gallium species (ca. 2.2 Å) and only 3% below the sum of the van der Waals radii of Ga and Cl.[16] Consequently, the Ga–O^{axial} bond (2.001(3) Å) is only slightly longer than the Ga–$O^{equatorial}$ bond (1.973(3) Å). The allyl ligands show an η^1 bonding mode with one short and one long C–C bond within each allyl group. The mean Ga–C bond length in **4** (1.966(4) Å) is significantly shorter than the corresponding values in neutral $[Ga(\eta^1\text{-}C_3H_5)_3(OPPh_3)]$ (**6**) or $[Ga(\eta^1\text{-}C_3H_3(SiMe_3)_2)_3]$.[5] This is ascribed to the increased Lewis acidity of cationic **4**. The weak Ga–Cl contact in **4** hinted at the tendency of the gallium center in the $[Ga(\eta^1\text{-}C_3H_5)_2(THF)_2]^+$ complex cation to increase its coordination number from four to five. To provide further evidence for this, **4** was crystallized from a saturated solution in THF/pentane at −30 °C to give colorless blocks of [**4**·THF] as shown by single crystal X-ray analysis (Figure 2b). [**4**·THF] crystallized in the orthorhombic space group $P2_12_12_1$ with two crystallographically independent formula units ($Z = 8$) that exhibit highly similar structural parameters.

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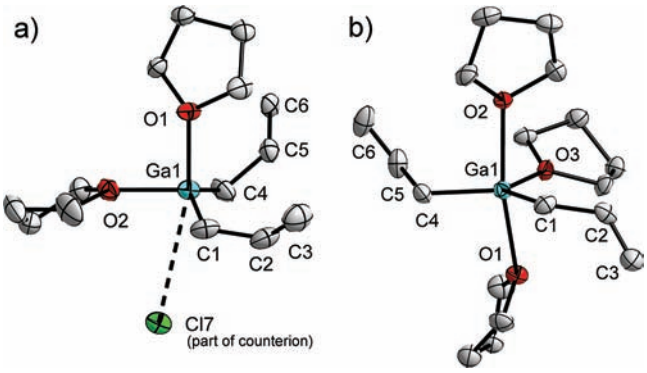

Figure 2. Molecular structures of the cationic parts of (a) $[Ga(\eta^1\text{-}C_3H_5)_2(THF)_2]^+[B(C_6H_3Cl_2)_4]^-$ (**4**) and (b) $[Ga(\eta^1\text{-}C_3H_5)_2(THF)_3]^+[B(C_6H_3Cl_2)_4]^-$ ([**4**·THF]). A Cl atom which is part of the counterion and shows weak contacts to the Ga center is shown for **4** (a). For [**4**·THF], only one of the two crystallographically independent cations is shown. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: (a) Ga1−C1, 1.962(4); Ga1−C4, 1.969(4); Ga1−O1, 2.001(3); Ga1−O2, 1.973(3); Ga1−Cl7, 3.5113(16); C1−C2, 1.479(6); C2−C3, 1.311(6); C4−C5, 1.483(6); C5−C6, 1.302(6); O1−Ga1−O2, 92.09(12); O1−Ga1−C1, 102.36(16); O1−Ga1−C4, 105.77(16); O2−Ga1−C1, 107.49(17); O2−Ga1−C4, 108.57(16); C1−Ga1−C4, 132.7(2); O1−Ga1−Cl7, 167.84(9); C1−C2−C3, 126.7(5); C4−C5−C6, 126.5(4). (b) Ga1−C1, 1.968(4); Ga1−C4, 1.966(4); Ga1−O1, 2.235(2); Ga1−O2, 2.186(2); Ga1−O3, 1.987(2); C1−C2, 1.479(5); C2−C3, 1.300(5); C4−C5, 1.491(5); C5−C6, 1.312(5); O1−Ga1−O2, 162.51(9); O1−Ga1−O3, 80.82(9); O3−Ga1−C1, 116.91(13); O3−Ga1−C4, 113.95(13); C1−Ga1−C4, 129.13(15); C1−C2−C3, 126.9(4); C4−C5−C6, 125.8(4).

The gallium center in [**4**·THF] shows a coordination number of five, which is highly unusual for cationic gallium complexes.[6a,b] This is the first example of a five-coordinate, cationic organogallium compound without chelating ligands and any direct interactions with the counterion.[6a,b,17,18] The coordination polyhedron found in the cationic part of [**4**·THF] is a trigonal bipyramid. As the THF ligands are weaker σ donors than the η^1 bound allyl moieties, they occupy the axial positions interacting with the same orbital of the central atom (O1−Ga1−O2, 162.51(9)°).[19] Consequently, the third THF ligand and the two allyl moieties are located in equatorial positions (Σ(C−Ga−O^{equatorial}), 360.0(2)°). Ga−C bond lengths are highly similar and average to 1.968(4) Å, which is equal within limits of error to the corresponding value found in **4**. The Ga−O^{equatorial} bond length (1.987(2) Å) is much shorter than the Ga−O^{axial} bond lengths (2.186(2) Å and 2.235(2) Å), since the two axial ligands experience a thermodynamic *trans* effect. Ga−O bond lengths in comparable compounds range between the corresponding values observed in [**4**·THF].[17]

Anionic Allylgallium Complexes. The potassium tetrakis(allyl)gallate $K^+[Ga(\eta^1\text{-}C_3H_5)_4]^-$ (**5**) was obtained by reacting neutral **1** with 1 equiv of allylpotassium (Scheme 1). Addition of 1 equiv of dibenzo-18-*c*-8 gave $[K(\text{dibenzo-18-}c\text{-}6)]^+[Ga(\eta^1\text{-}C_3H_5)_4]^-$ (**6**). Substitution of the potassium ion was achieved by treating **5** with $[PPh_4]^+Br^-$ to give $[PPh_4]^+[Ga(\eta^1\text{-}C_3H_5)_4]^-$ (**7**) (Scheme 1). ^{1}H NMR spectroscopic analysis of **5**, **6**, and **7** in THF-d_8 solutions at ambient temperature indicate an η^1 binding mode of the allyl ligands.[20] Single crystals of **6** were obtained by cooling a saturated CH_2Cl_2/pentane (3:1) solution to −30 °C. Compound **6** crystallized in the monoclinic space group $P2_1/c$ with two crystallographically independent formula units in the asymmetric unit (Z = 8) with highly similar structural parameters. The gallium center in **6** adopts a slightly distorted tetrahedral coordination geometry (C−Ga−C, 103.79(14)−113.93(13)°) (Figure 3). Three of the allyl ligands

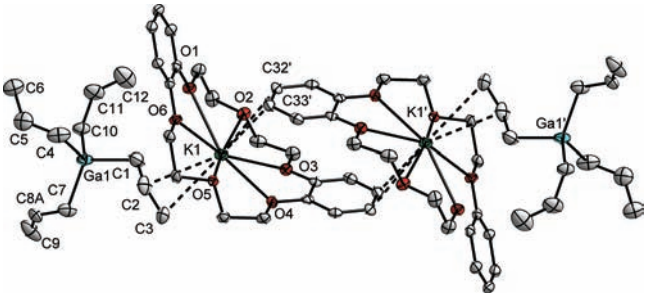

Figure 3. Dimeric arrangement of $[K(\text{dibenzo-18-}c\text{-}6)]^+[Ga(\eta^1\text{-}C_3H_5)_4]^-$ (**6**) in the solid state. One of two crystallographically independent dimers is shown. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Atom C8 is shown with only one split position. Selected bond lengths [Å] and angles [deg]: Ga1−C1, 2.025(3); Ga1−C4, 2.052(3); Ga1−C7, 2.013(3); Ga1−C10, 2.023(3); K1−C2, 3.278(3); K1−C3, 3.355(3); K1−C32′, 3.343(3); K1−C33′, 3.293(3); K1−(O1−O6), 2.766(2)−2.813(2); C1−Ga1−C4, 103.8(1); C1−Ga1−C7, 110.5(1); C1−Ga1−C10, 107.6(1); C4−Ga1−C7, 110.2(1); C4−Ga1−C10, 110.3(1); C7−Ga1−C10, 113.9(1); center(C2−C3)−K1−center(C32′−C33′), 165.30(8); C1−C2−C3, 128.5(4); C4−C5−C6, 128.2(4); C7−C8A−C9, 131.0(7); C10−C11−C12, 128.3(4).

coordinate to the gallium center in an η^1 fashion. One allyl ligand adopts a bridging μ_2-η^1:η^2 coordination mode; i.e., it shows a σ type interaction with the gallium ion and its double bond of localized type binds to the potassium ion. This is the first structurally authenticated example of a μ_2-η^1:η^2 coordination mode in group 13 allyl complexes,[21,22] suggesting the importance of counterion effects. In contrast to other tetrakis(organo)gallates,[7b−f] the organic ligands in **6** do not interact via the same carbon atom with two different metal centers. All Ga−C bond lengths are similar and average to 2.029(3) Å, which is longer than corresponding mean values in neutral **2** and cationic **4** or [**4**·THF], but compares well to corresponding mean values in other tetrakis(organo)gallates.[23] The potassium ion in **6** shows a hexagonal bipyramidal coordination geometry with the equatorial positions being occupied by oxygen atoms of the crown ether ligand. The C═C double bond of an allyl ligand is found in one of the axial positions. The second axial position is occupied by an aromatic C−C bond which is part of the crown ether ligand (center(C2−C3)−K1−center(C32′−C33′), 165.30(2)°). This leads to a C_i symmetrical dimeric arrangement of two formula units of **6** in the solid state. K−C distances range from 3.278(3) to 3.355(3) Å, which compare well to literature values.[24]

Reactivity of Allylgallium Species toward Benzophenone. The reactivity of cationic, neutral, and anionic allylgallium species toward benzophenone in THF solution at ambient temperature was investigated (Scheme 2). A stoichiometry of 1 equiv of benzophenone per allyl substituent was used. Neutral $[Ga(\eta^1\text{-}C_3H_5)_3(THF)]$ (**1**) gave the expected insertion product **8** within a reaction time of $t \leq 10$ min in full conversion. For cationic **3**, insertion of only 1 equiv of benzophenone was observed within $t \leq 10$ min. The resulting cationic alkoxy species **9** subsequently initiated polymerization of THF.[25] The same was observed for cationic **4**. Tetrakis(allyl)gallate **5** also inserted

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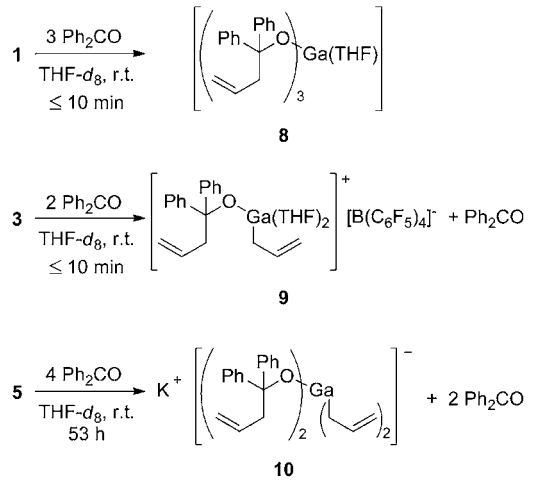
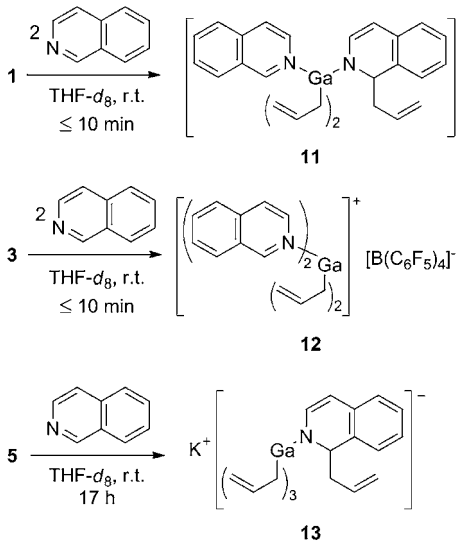
Scheme 2. Reactivity of Tris(allyl)gallium 1, Bis(allyl)gallium Cation 3, and Tetrakis(allyl)gallate 5 towards Benzophenone



benzophenone. This reaction was substantially slower than those of the cationic and neutral allylgallium species, probably due to negligible Lewis acidity of **5**.[26] Moreover, no full conversion was observed, but the reaction essentially stopped after insertion of 2 equiv of benzophenone to give the alkylalkoxy gallate **10** after a reaction time of 53 h. Reaction of $[PPh_4]^+[Ga(\eta^1\text{-}C_3H_5)_4]^-$ (**7**) with 4 equiv of benzophenone proceeded with a similar initial rate, but selective insertion of 75% of the substrate was observed. Thus, in reactions of tetrakis(allyl)gallates **5** and **7** with benzophenone, insertion of the first equivalent of ketone proceeds without a significant counterion effect. The reactivity of the resulting alkoxygallates, however, is counterion dependent (for time conversion plot of reactions of **5** and **7** with benzophenone, see Supporting Information). Overall, neutral **1** was most efficient in the allylation of benzophenone and proved superior compared to in situ generated allylgallium species reported in the literature.[27] Gallates **5** and **7** reacted much more slowly, but still with 100% selectivity.

Reactivity of Allylgallium Species toward *N*-Heteroaromatics. Lewis base adducts of tris(allyl)boron have been reported to react with pyridine under 1,2 insertion.[28] Recently, this type of insertion chemistry has been extended to Lewis base adducts of tris(allyl)aluminum.[12] In contrast to the lighter group 13 homologues, none of the allylgallium species **1**, **3**, and **5** reacted with pyridine or quinoline under insertion. Instead, substitution of the THF ligands for *N*-heteroaromatics was observed for **1** and **3**, as shown by ^{1}H and ^{13}C NMR spectroscopy. Pronounced differences between cationic, neutral, and anionic allylgallium species in their reactivity toward *N*-heteroaromatics became apparent, when isoquinoline was chosen as a substrate: whereas substitution of the THF ligands was observed for cationic **3**, 1,2-insertion pathways were found to occur with neutral **1** and anionic **5** (Scheme 3). Under optimized reaction conditions, **1** reacted with 2 equiv of isoquinoline within $t \leq 10$ min to give the 1-allylated insertion product **11** with a selectivity of 92%.[29] The insertion reaction between tetrakis(allyl)gallate **5** and 1 equiv of isoquinoline to give **13** was substantially slower (17 h until full conversion), but no side products were detected.[29b] The connectivity in the anionic part of **13** was proved by single crystal X-ray analysis of a derivative of this insertion product (compound **14**, see Supporting Information). Whereas adduct formation of organogallium complexes with pyridine and its derivatives is

Scheme 3. Reactivity of Tris(allyl)gallium 1, Bis(allyl)gallium Cation 3, and Tetrakis(allyl)gallate 5 towards Isoquinoline



well documented,[30] **1** and **5** are the first examples of organogallium species to exhibit insertion reactivity patterns toward *N*-heteroaromatics. The fact that allylgallium species show a decreased reactivity toward pyridine compared to the boron and aluminum homologues could be ascribed to the higher Lewis acidity of the latter compounds.

■ CONCLUSIONS

The THF adduct of previously elusive tris(allyl)gallium, $[Ga(\eta^1\text{-}C_3H_5)_3(THF)]$ (**1**), was isolated as a liquid; crystalline $[Ga(\eta^1\text{-}C_3H_5)_3(OPPh_3)]$ (**2**) could be fully characterized. Protonolysis of one allyl ligand of **1** gave the cationic allylgallium species $[Ga(\eta^1\text{-}C_3H_5)_2(THF)_2]^+[A]^-$ (**3**, A = $[B(C_6F_5)_4]^-$; **4**, A = $[B(C_6H_3Cl_2)_4]^-$). In the solid state, **4** and [**4**·THF] show a five-coordinate gallium center in a trigonal bipyramidal coordination geometry. Potassium gallate $K^+[Ga(\eta^1\text{-}C_3H_5)_4]^-$ (**5**) was synthesized from allylpotassium and **1**. The adduct $[K(dibenzo\text{-}18\text{-}c\text{-}6)]^+[Ga(\eta^1\text{-}C_3H_5)_4]^-$ (**6**) was fully characterized and shows a bridging $\mu_2\text{-}\eta^1\text{:}\eta^2$ coordination mode of one allyl ligand in the solid state, which is unprecedented for group 13 compounds. In all allylgallium compounds of this work, the allyl ligands show σ type interactions with the gallium center in the solid state and in solution. The reactivity of a series of cationic, neutral, and anionic allylgallium complexes (**1**, **3**, **5**) toward benzophenone and *N*-heteroaromatics was investigated. Neutral **1** was an effective allylation reagent for benzophenone and proved superior compared to in situ generated allylgallium reagents previously reported. Neutral **1** and anionic **5** reacted with isoquinoline under 1,2-insertion.

■ EXPERIMENTAL SECTION

General Remarks. All operations were carried out under argon using standard Schlenk-line and glovebox techniques. Starting materials were purchased from Sigma Aldrich or Boulder Scientific and purified following standard laboratory procedures. Starting materials which were not commercially available were synthesized according to the literature. $[NHMe_2Ph][B(C_6H_3Cl_2)_4]$ was synthesized in analogy to protocols established for $[NHMe_2Ph][BPh_4]$. Nondeuterated solvents were purified using an MB SPS-800 solvent

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purification system. Benzene-d_6 and THF-d_8 were distilled from sodium benzophenone ketyl. Py-d_5 was distilled from calcium hydride. NMR spectra were recorded at ambient temperature using a Varian Mercury-200 or a Bruker Avance II 400 MHz spectrometer. The chemical shifts of ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and are reported relative to the chemical shift of tetramethylsilane. The resonances in ^{1}H and ^{13}C NMR spectra were assigned on the basis of two-dimensional NMR experiments (COSY, HMQC, HMBC) when necessary. The resonances recorded in ^{11}B, ^{19}F, and ^{31}P NMR measurements are reported relative to external standards, an ethereal solution of $BF_3{\cdot}Et_2O$, $CFCl_3$, and phosphoric acid (85%), respectively. The metal content of organogallium compounds was determined by titration.[31] Elemental analyses were performed by the microanalytical laboratory of the Institute of Organic Chemistry at the RWTH Aachen University.

[Ga(η^1-C_3H_5)$_3$(THF)] (1). At −78 °C, THF (2.0 mL) was added dropwise to a suspension of $GaCl_3$ (732 mg, 4.16 mmol) in pentane (10 mL). Neat allylpotassium (1.00 g, 12.47 mmol) was added portionwise. The reaction mixture was kept at −78 °C for 3 h. After warming to −30 °C, the reaction mixture was filtered, and the residue was washed with pentane/THF (5:1) (2 × 12 mL). All volatiles were removed from the colorless filtrate under reduced pressure at −30 °C to give a slightly yellow oil, which was dried in vacuo at the same temperature for 2.5 h. Yield: 929 mg (3.51 mmol), 84%.

^{1}H NMR (400.1 MHz, C_6D_6): δ = 1.08−1.12 (m, 4H, β-THF), 1.0−5.0 (br s, 12H, CH_2CHCH_2), 3.31−3.35 (m, 4H, α-THF), 6.26 (quint, $^3J_{HH}$ = 11.0 Hz, 3H, CH_2CHCH_2) ppm. ^{1}H NMR (400.1 MHz, Tol-d_8, −60 °C): δ = 0.95−0.98 (m, 4H, β-THF), 1.68 (d, $^3J_{HH}$ = 8.5 Hz, 6H, CH_2−CH=CH_2), 3.16−3.99 (m, 4H, α-THF), 4.93 (br dd, $^2J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 10.0 Hz, 3H, CH_2−CH=C$H^{cis}H^{trans}$), 4.93 (ddt, $^2J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 16.8 Hz, $^4J_{HH}$ = 1.3 Hz, 3H, CH_2−CH=C$H^{cis}H^{trans}$), 6.30 (ddt, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.8 Hz, 3H, CH_2−CH=CH_2) ppm. ^{1}H NMR (400.1 MHz, Tol-d_8, 24 °C): δ = 1.17−1.20 (m, 4H, β-THF), 1.0−5.0 (br s, 12H, CH_2CHCH_2), 3.35−3.39 (m, 4H, α-THF), 6.18 (quint, $^3J_{HH}$ = 11.0 Hz, 3H, CH_2CHCH_2) ppm. ^{1}H NMR (400.1 MHz, Tol-d_8, 90 °C): δ = 1.36−1.39 (m, 4H, β-THF), 3.16 (br d, $^3J_{HH}$ = 11.0 Hz, 12H, CH_2CHCH_2), 3.47−3.50 (m, 4H, α-THF), 6.13 (quint, $^3J_{HH}$ = 11.0 Hz, 3H, CH_2CHCH_2) ppm. Up to 19% of the starting material had undergone thermal decomposition while heating the sample from ambient temperature to 90 °C over a period of 40 min according to ^{1}H NMR spectra. ^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.43 (br d, $^3J_{HH}$ = 8.8 Hz, 6H, CH_2−CH=CH_2), 1.76−1.79 (m, 4H, β-THF), 3.60−3.63 (m, 4H, α-THF), 4.48 (br d, $^3J_{HH}$ = 9.3 Hz, 3H, CH_2−CH=C$H^{cis}H^{trans}$), 4.63 (br d, $^3J_{HH}$ = 16.6 Hz, 3H, CH_2−CH=C$H^{cis}H^{trans}$), 5.94−6.05 (m, 3H, CH_2−CH=CH_2) ppm. ^{1}H NMR (400.1 MHz, Py-h_5/Py-d_5(1:1)): δ = 1.60−1.64 (m, 4H, β-THF), 1.77 (ddd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.0 Hz, $^4J_{HH}$ = 1.3 Hz, 6H, CH_2−CH=CH_2), 3.64−3.67 (m, 4H, α-THF), 4.69 (ddt, $^2J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 1.0 Hz, 3H, CH_2−CH=C$H^{cis}H^{trans}$), 4.82 (ddt, $^2J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 16.8 Hz, $^4J_{HH}$ = 1.25 Hz, 3H, CH_2−CH=C$H^{cis}H^{trans}$), 6.28 (m, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.8 Hz, 3H, CH_2−CH=CH_2) ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 25.60 (s, β-THF), 70.54 (s, α-THF), 141.15 (s, CH_2CHCH_2) ppm. A signal for the methylene carbon atoms could not be detected, not even with more than 20 000 scans. ^{13}C NMR (50.3 MHz, THF-d_8): δ = 21.29 (s, CH_2−CH=CH_2), 26.54 (s, β-THF), 68.39 (s, α-THF), 107.32 (s, CH_2−CH=CH_2), 141.39 (s, CH_2−CH=CH_2) ppm. Anal. Calcd for $C_{13}H_{23}GaO$ (265.04 g/mol): Ga, 26.31. Found: Ga, 27.02. A test for halides was negative.

[Ga(η^1-C_3H_5)$_3$(OPPh$_3$)] (2). $OPPh_3$ (100 mg, 0.36 mmol) was added to a solution of **1** (95 mg, 0.36 mmol) in THF (0.8 mL) to give a colorless solution. All volatiles were removed under reduced pressure to give a colorless solid which was washed with pentane (2 × 1.5 mL) and dried in vacuo. Yield: 112 mg (0.24 mmol) 67%.

^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.34 (br d, $^3J_{HH}$ = 8.5 Hz, 6H, CH_2−CH=CH_2), 4.37 (br dd, $^2J_{HH}$ = 2.2 Hz, $^3J_{HH}$ = 9.8 Hz, 3H, CH_2−CH=C$H^{cis}H^{trans}$), 4.51 (dm, $^3J_{HH}$ = 16.8 Hz, 3H, CH_2−CH=C$H^{cis}H^{trans}$), 5.89−6.00 (m, 3H, CH_2−CH=CH_2), 7.48−7.53 (m, 6H, *m*-Ph), 7.58−7.63 (m, 3H, *p*-Ph), 7.67−7.73 (m, 6H, *o*-Ph) ppm. ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 1.28 (br s, 6H, CH_2−CH=CH_2), 4.35 (br s, 3H, CH_2−CH=C$H^{cis}H^{trans}$), 4.45 (br d, $^3J_{HH}$ = 14.8 Hz, 3H, CH_2−CH=C$H^{cis}H^{trans}$), 5.90−6.01 (m, 3H, CH_2−CH=CH_2), 7.50−7.54 (m, 6H, *m*-Ph), 7.63−7.68 (m, 9H, *p*-Ph, *o*-Ph) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 22.37 (s, CH_2−CH=CH_2), 106.37 (s, CH_2−CH=CH_2), 129.66 (d, $^3J_{CP}$ = 13.9 Hz, *m*-Ph), 132.45 (d, $^1J_{CP}$ = 102.3 Hz, *ipso*-Ph), 133.32 (d, $^2J_{CP}$ = 9.5 Hz, *o*-Ph), 133.47 (d, $^4J_{CP}$ = 3.5 Hz, *p*-Ph), 142.29 (s, CH_2−CH=CH_2) ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 22.63 (br s, CH_2−CH=CH_2), 105.66 (br s, CH_2−CH=CH_2), 129.39 (d, $^3J_{CP}$ = 12.1 Hz, *m*-Ph), 132.96 (d, $^2J_{CP}$ = 10.4 Hz, *o*-Ph), 133.62 (d, $^4J_{CP}$ = 2.6 Hz, *p*-Ph), 142.69 (s, CH_2−CH=CH_2) ppm. A resonance due to the *ispo*-carbon atom was not detected. ^{31}P NMR (162.0 Hz, THF-d_8): δ = 30.60 (s) ppm. ^{31}P NMR (162.0 Hz, CD_2Cl_2): δ = 35.69 (s) ppm. Anal. Calcd for $C_{27}H_{30}GaOP$ (471.22 g/mol): Ga, 14.80. Found: Ga, 15.20.

[Ga(η^1-C_3H_5)$_2$(THF)$_2$]$^+$[B(C_6F_5)$_4$]$^-$ (3). A solution of [$NHMe_2Ph$]-[B(C_6F_5)$_4$] (58 mg, 0.072 mmol) in THF (600 μL) was added to a solution of **1** (20 mg, 0.076 mmol) in THF (400 μL) to give a colorless solution. After 10 min pentane (15 mL) was added, upon which a colorless oil precipitated. The supernatant was decanted and the residue washed with pentane (5 × 2 mL) to give a colorless solid, which was dried in vacuo for 1.5 h. Yield: 67 mg (0.069 mmol), 96%.

^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.76−1.79 (m, 8H, β-THF), 1.91 (ddd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.5 Hz, $^4J_{HH}$ = 1.0 Hz, 4H, CH_2−CH=CH_2), 3.60−3.63 (m, 8H, α-THF), 4.86 (ddt, $^2J_{HH}$ = 1.8 Hz, $^3J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, CH_2−CH=C$H^{cis}H^{trans}$), 5.00 (ddt, $^2J_{HH}$ = 1.8 Hz, $^3J_{HH}$ = 16.8 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, CH_2−CH=C$H^{cis}H^{trans}$), 5.99 (ddt, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.8 Hz, 2H, CH_2−CH=CH_2) ppm. ^{1}H NMR (400.1 MHz, Py-h_5/Py-d_5(1:1)): δ = 1.60−1.63 (m, 8H, β-THF), 2.26 (d, $^3J_{HH}$ = 8.5 Hz, 4H, CH_2−CH=CH_2), 3.67−3.64 (m, 8H, α-THF), 4.83 (ddt, $^2J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, CH_2−CH=C$H^{cis}H^{trans}$), 5.03 (ddt, $^2J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 16.8 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, CH_2−CH=C$H^{cis}H^{trans}$), 6.03 (ddt, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.8 Hz, 2H, CH_2−CH=CH_2) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 20.57 (s, CH_2−CH=CH_2), 26.53 (s, β-THF), 68.39 (s, α-THF), 114.00 (s, CH_2−CH=CH_2), 125.53 (br s, *ipso*-C_6F_5), 135.59 (s, CH_2−CH=CH_2), 137.26 (dm, $^1J_{CF}$ = 241.9 Hz, *m*-C_6F_5), 139.29 (dm, $^1J_{CF}$ = 246.2 Hz, *p*-C_6F_5), 149.34 (dm, $^1J_{CF}$ = 241.9 Hz, *o*-C_6F_5) ppm. ^{11}B NMR (128.4 MHz, THF-d_8): δ = −18.45 (s) ppm. ^{19}F NMR (188.1 MHz, THF-d_8): δ = −129.09 to −129.35 (m, *m*-C_6F_5), −161.47 (t, $^3J_{FF}$ = 20.3 Hz, *p*-C_6F_5), −164.98 (t, $^3J_{FF}$ = 18.7 Hz, *o*-C_6F_5) ppm. Anal. Calcd for $C_{38}H_{26}BF_{20}GaO_2$ (975.11 g/mol): Ga, 7.15. Found: Ga, 6.86.

[Ga(η^1-C_3H_5)(THF)$_2$]$^+$[B($C_6H_3Cl_2$)$_4$]$^-$ (4). [$NHMe_2Ph$][B-($C_6H_3Cl_2$)$_4$] (50 mg, 0.070 mmol) was added to a solution of **1** (20 mg, 0.075 mmol) in THF (1 mL) to give a pale yellow solution. After 10 min pentane (9 mL) was added, upon which a colorless oil precipitated, which turned into a colorless solid after 30 min. The supernatant was decanted. The white solid washed with pentane (3 × 2 mL) and dried in vacuo for 2 h. Yield: 61 mg (0.068 mmol), 97%.

^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.75−1.79 (m, 8H, β-THF), 1.89 (ddd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.1 Hz, $^4J_{HH}$ = 1.1 Hz, 4H, CH_2−CH=CH_2), 3.60−3.64 (m, 8H, α-THF), 4.86 (ddt, $^2J_{HH}$ = 1.9 Hz, $^3J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, CH_2−CH=C$H^{cis}H^{trans}$), 4.99 (ddt, $^2J_{HH}$ = 1.9 Hz, $^3J_{HH}$ = 16.9 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, CH_2−CH=C$H^{cis}H^{trans}$), 5.98 (ddt, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.9 Hz, 2H, CH_2−CH=CH_2) 6.97 (t, $^4J_{HH}$ = 2.0 Hz, 4H, *p*-($C_6H_3Cl_2$)), 7.02−7.04 (m, 8H, *o*-($C_6H_3Cl_2$)) ppm. ^{1}H NMR (400.1 MHz, Py-d_5): δ = 1.61−1.65 (m, 8H, β-THF), 2.24 (ddd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 0.9 Hz, $^4J_{HH}$ = 1.3 Hz, 4H, CH_2−CH=CH_2), 3.65−3.69 (m, 8H, α-THF), 4.85 (ddt, $^2J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, CH_2−CH=C$H^{cis}H^{trans}$), 4.97 (ddt, $^2J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 16.8 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, CH_2−CH=C$H^{cis}H^{trans}$), 6.12 (ddt, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.8 Hz, 2H, CH_2−CH=CH_2) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 20.62 (s, CH_2−CH=CH_2), 26.53 (s, β-THF), 68.39 (s, α-THF), 114.05 (s, CH_2−CH=CH_2), 123.93 (s, *p*-($C_6H_3Cl_2$)), 133.92 (q, $^3J_{BC}$ = 4.3 Hz, *m*-($C_6H_3Cl_2$)), 134.23 (q, $^2J_{BC}$ = 1.7 Hz, *o*-($C_6H_3Cl_2$)), 135.59 (s, CH_2−CH=CH_2), 165.25

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(q, $^1J_{BC}$ = 49.7 Hz, *ipso*-($C_6H_3Cl_2$)) ppm. ^{11}B NMR (128.4 MHz, THF-d_8): δ = −6.91 (s) ppm. Anal. Calcd for $C_{38}H_{38}BCl_8GaO_2$ (890.87 g/mol): C, 51.23; H, 4.30. Found: C, 50.08; H, 3.80.

$K^+[Ga(\eta^1\text{-}C_3H_5)_4]^-$ (5). A solution of allylpotassium (20 mg, 0.25 mmol) in THF (600 μL) was added to a solution of **1** (66 mg, 0.25 mmol) in THF (400 μL). The yellow reaction mixture turned colorless after a few minutes. Upon addition of pentane (15 mL) a colorless oil precipitated. The supernatant was decanted and the residue washed with pentane (4 × 2 mL) to give a colorless solid, which was dried in vacuo for 2 h. Yield: 67 mg (0.25 mmol), quantitative.

^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.08 (br d, $^3J_{HH}$ = 8.5 Hz, 8H, CH_2–CH=CH_2), 4.73 (br dd, $^2J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 10.0 Hz, 4H, CH_2–CH=C$H^{cis}H^{trans}$), 5.03 (br dd, $^2J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 16.8 Hz, 4H, CH_2–CH=CH$^{cis}H^{trans}$), 6.90 (ddt, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.8 Hz, 4H, CH_2–CH=CH_2) ppm. ^{1}H NMR (400.1 MHz, Py-h_5/Py-d_5(1:1)): δ = 2.05 (br s, 8H, CH_2–CH=CH_2), 4.01 (br dd, $^2J_{HH}$ = 3.5 Hz, $^3J_{HH}$ = 10.0 Hz, 4H, CH_2–CH=C$H^{cis}H^{trans}$), 4.24 (ddm, $^2J_{HH}$ = 3.5 Hz, $^3J_{HH}$ = 16.8 Hz, 4H, CH_2–CH=CH$^{cis}H^{trans}$), 6.06 (ddt, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.8 Hz, 4H, CH_2–CH=CH_2) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 22.68 (br s, CH_2–CH=CH_2), 99.26 (s, CH_2–CH=CH_2), 148.22 (s, CH_2–CH=CH_2) ppm. Anal. Calcd for $C_{12}H_{20}GaK$ (273.11 g/mol): Ga, 25.53. Found: Ga, 25.15.

$[K(dibenzo\text{-}18\text{-}c\text{-}6)]^+[Ga(\eta^1\text{-}C_3H_5)_4]^-$ (6). Dibenzo-18-crown-6 (52 mg, 0.14 mmol) was added to a solution of **5** (39 mg, 0.14 mmol) in THF (1.5 mL). The reaction mixture was filtered. All volatiles were removed from the filtrate under reduced pressure to give a pale yellow oil. Upon addition of pentane (2 mL) a colorless solid precipitated. The supernatant was decanted and the residue washed with pentane (4 × 2 mL) to give a colorless solid which was dried in vacuo. Yield: 86 mg, 0.14 mmol, quantitative.

^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.10 (br s, 8H, $CH_2^{a,b}$–CH=CH_2), 3.98–4.00 (m, 8H, O(CH_2CH_2)O), 4.02 (br s, 4H, CH_2–CHC=$H^{cis}H^{trans}$), 4.22 (br s, 4H, CH_2–CH=CH$^{cis}H^{trans}$), 4.24–4.26 (m, 8H, O(CH_2CH_2)O), 6.02–6.13 (m, 4H, CH_2–CH=CH_2), 6.93–6.97 (m, 4H, $Ph^{3,6}$), 7.01–7.05 (m, 4H, $Ph^{4,5}$) ppm. ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 1.10 (br d, $^3J_{HH}$ = 8.1 Hz, 8H, $CH_2^{a,b}$–CH=CH_2), 4.00–4.02 (m, 8H, O(CH_2CH_2)O), 4.07 (br d, $^3J_{HH}$ = 9.2 Hz, 4H, CH_2–CHC=$H^{cis}H^{trans}$), 4.18–4.20 (m, 8H, O(CH_2CH_2)O), 4.25 (br d, $^3J_{HH}$ = 17.1 Hz, 4H, CH_2–CH=CH$^{cis}H^{trans}$), 5.96–6.07 (m, 4H, CH_2–CH=CH_2), 6.90–6.95 (m, 4H, $Ph^{3,6}$), 6.99–7.03 (m, 4H, $Ph^{4,5}$) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 21.74 (br s, CH_2–CH=CH_2), 68.49 (s, O(CH_2CH_2)O), 70.52 (s, O(CH_2-CH_2)O), 99.29 (br s, CH_2–CH=CH_2), 112.58 (s, $Ph^{3,6}$), 122.46 (s, $Ph^{4,5}$), 148.26 (s, CH_2–CH=CH_2, $Ph^{1,2}$ (overlapped)) ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 22.01 (br s, CH_2–CH=CH_2), 67.43 (s, O(CH_2CH_2)O), 69.88 (s, O(CH_2CH_2)O), 99.78 (s, CH_2–CH=CH_2), 112.00 (s, $Ph^{3,6}$), 122.43 (s, $Ph^{4,5}$), 146.95 (s, $Ph^{1,2}$), 147.59 (s, CH_2–CH=CH_2) ppm. Anal. Calcd for $C_{32}H_{44}GaKO_6$ (537.42 g/mol): Ga, 11.01. Found: Ga, 10.59.

$[PPh_4]^+[Ga(\eta^1\text{-}C_3H_5)_4]^-$ (7). THF (2.0 mL) was added to a mixture of **5** (99 mg, 0.36 mmol) and $[PPh_4]^+Br^-$ (152 mg, 0.36 mmol) to give a suspension which was stirred at ambient temperature for 2 h. The reaction mixture was filtered, and all volatiles were removed from the orange filtrate under reduced pressure. The residue was washed with pentane (3 × 2 mL) to yield an off-white solid, which was dried in vacuo for 3 h. Yield: 169 mg, 0.29 mmol, 81%.

^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.07 (br s, 8H, CH_2–CH=CH_2), 3.97 (br dd, $^2J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 9.5 Hz, 4H, CH_2–CH=C$H^{cis}H^{trans}$), 4.21 (br d, $^3J_{HH}$ = 16.8 Hz, 4H, CH_2–CH=CH$^{cis}H^{trans}$), 5.98–6.09 (m, 4H, CH_2–CH=CH_2), 7.74–7.82 (m, 16H, *o*-, *m*-Ph), 7.93–7.97 (m, 4H, *p*-Ph) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 22.53 (br s, CH_2–CH=CH_2), 99.26 (s, CH_2–CH=CH_2), 119.30 (d, $^1J_{CP}$ = 90.2 Hz, *ipso*-Ph), 131.55 (d, $^3J_{CP}$ = 13.0 Hz, *m*-Ph), 135.84 (d, $^2J_{CP}$ = 10.4 Hz, *m*-Ph), 136.56 (d, $^4J_{CP}$ = 3.5 Hz, *p*-Ph), 148.28 (s, CH_2–CH=CH_2) ppm. ^{31}P NMR (162.0 MHz, THF-d_8): δ = 21.20 (s) ppm. Anal. Calcd for $C_{36}H_{40}GaP$ (573.40 g/mol): Ga, 12.16. Found: Ga, 12.40.

Reactivity toward Benzophenone. A solution of benzophenone (for **1**, 31 mg, 170 μmol; for **3**, 10 mg, 55 μmol; for **5**, 29 mg, 160 μmol) in THF-d_8 (300 μL) was added to a solution of the gallium compound (**1**, 15 mg, 57 μmol; **3**, 27 mg, 28 μmol; **5**, 11 mg, 40 μmol) in THF-d_8 (300 μL). In each case a colorless solution was obtained.

Compound 1. Full conversion of **1** to insertion product **8** was observed after ≤10 min.

$[Ga(OC(C_3H_5)Ph_2)_3(THF)]$ (8). ^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.75–1.78 (m, 4H, β-THF), 3.26 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_2–CH=CH_2), 3.60–3.63 (m, 4H, α-THF), 4.77 (dm, $^3J_{HH}$ = 10.3 Hz, 3H, CH_2–CH=C$H^{cis}H^{trans}$), 4.87 (dm, $^3J_{HH}$ = 17.3 Hz, 3H, CH_2–CH=CH$^{cis}H^{trans}$), 5.63 (ddt, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 17.3 Hz, 3H, CH_2–CH=CH_2) 7.08–7.12 (m, 6H, *p*-Ph), 7.16–7.20 (m, 12H, *m*-Ph), 7.36–7.39 (m, 12H, *o*-Ph) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 26.53 (s, β-THF), 48.66 (s, CH_2–CH=CH_2), 68.39 (s, α-THF), 81.54 (s, C–CH_2–CH=CH_2), 116.50 (s, CH_2–CH=CH_2), 126.81 (s, *p*-Ph), 128.22 (s, *m*-Ph), 128.76 (s, *o*-Ph), 137.48 (s, CH_2–CH=CH_2) 151.23 (s, *ipso*-Ph) ppm.

Compound 3. Insertion of 1 equiv of benzophenone was detected after ≤10 min to give **9**. The second equivalent of benzophenone did not react within 45 min, after which beginning polymerization of THF was observed.

$[Ga(\eta^1\text{-}C_3H_5)(OC(C_3H_5)Ph_2)(THF)_2]^+[B(C_6F_5)_4]^-$ (9). ^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.51 (dm, $^3J_{HH}$ = 8.3 Hz, 2H, Ga–CH_2–CH=CH_2), 1.76–1.79 (m, 8H, β-THF), 3.14 (br d, $^3J_{HH}$ = 7.0 Hz, 2H, C–CH_2–CH=CH_2), 3.60–3.63 (m, 8H, α-THF), 4.83 (ddt, $^2J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ga–CH_2–CH=C$H^{cis}H^{trans}$), 4.89 (ddt, $^2J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 16.8 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, Ga–CH_2–CH=CH$^{cis}H^{trans}$), 5.10 (dm, $^3J_{HH}$ = 10.2 Hz, 1H, C–CH_2–CH=C$H^{cis}H^{trans}$), 5.14 (dm, $^3J_{HH}$ = 17.2 Hz, 1H, C–CH_2–CH=CH$^{cis}H^{trans}$), 5.52 (ddt, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.8 Hz, 1H, Ga–CH_2–CH=CH_2), 5.78 (ddt, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 17.2 Hz, 1H, C–CH_2–CH=CH_2), 7.22–7.27 (m, 2H, *p*-Ph), 7.30–7.35 (m, 4H, *m*-Ph), 7.40–7.43 (m, 4H, *o*-Ph) ppm. Noncoordinate benzophenone was also detected. Reaction of **3** with 1 equiv of benzophenone under the conditions described above gives the same spectrum without the resonances of noncoordinate benzophenone. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 19.13 (s, Ga–CH_2–CH=CH_2), 26.49 (s, β-THF), 49.17 (s, C–CH_2–CH=CH_2), 68.38 (s, α-THF), 81.09 (s, C–CH_2–CH=CH_2), 115.83 (s, Ga–CH_2–CH=CH_2), 119.42 (s, C–CH_2–CH=CH_2), 125.47 (br s, *ipso*-C_6F_5), 127.39 (s, *o*-Ph), 128.22 (s, *p*-Ph), 129.41 (s, *m*-Ph), 136.23 (s, Ga–CH_2–CH=CH_2), 137.25 (dm, $^1J_{CF}$ = 244.5 Hz, *m*-C_6F_5), 138.91 (s, C–CH_2–CH=CH_2), 139.55 (dm, $^1J_{CF}$ = 245.4 Hz, *p*-C_6F_5), 149.30 (dm, $^1J_{CF}$ = 241.0 Hz, *o*-C_6F_5), 150.14 (s, *ipso*-Ph) ppm. Unreacted benzophenone and small amounts of byproducts (presumably due to polymerization of THF) were also detected. ^{11}B NMR (128.4 MHz, THF-d_8): δ = −18.44 (s) ppm.

When the reaction was carried out in pyridine-d_5 at ambient temperature, no insertion product was detected by ^{1}H NMR analysis after a reaction time of more than 1 day. Insertion of 1 equiv of benzophenone was observed after a reaction time of 6 days at 60 °C.

$[Ga(\eta^1\text{-}C_3H_5)(OC(C_3H_5)Ph_2)(Py\text{-}d_5)_n]^+[B(C_6F_5)_4]^-$. ^{1}H NMR (400.1 MHz, Py-d_5): δ = 1.97 (dt, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, Ga–CH_2–CH=CH_2), 3.32 (br d, $^3J_{HH}$ = 6.8 Hz, 2H, C–CH_2–CH=CH_2), 4.87 (ddt, $^2J_{HH}$ = 1.8 Hz, $^3J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ga–CH_2–CH=C$H^{cis}H^{trans}$), 4.97 (ddt, $^2J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, C–CH_2–CH=C$H^{cis}H^{trans}$), 4.99 (dm, $^3J_{HH}$ = 17.1 Hz, 1H, Ga–CH_2–CH=CH$^{cis}H^{trans}$) 5.03 (dm, $^3J_{HH}$ = 17.1 Hz, 1H, C–CH_2–CH=CH$^{cis}H^{trans}$), 5.84 (ddt, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 17.1 Hz, 1H, Ga–CH_2–CH=CH_2), 5.90 (ddt, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 17.1 Hz, 1H, C–CH_2–CH=CH_2), 7.26–7.33 (m, 6H, *o*-, *p*-Ph), 7.55–7.59 (m, 4H, *m*-Ph) ppm. Noncoordinate THF (2 equiv) and 1 equiv of unreacted benzophenone were also detected. ^{13}C NMR (100.6 MHz, Py-d_5): δ = 17.77 (s, Ga–CH_2–CH=CH_2), 48.82 (s, C–CH_2–CH=CH_2), 80.91 (s, C–CH_2–CH=CH_2), 114.77 (s, Ga–CH_2–CH=CH_2), 118.85 (s, C–CH_2–CH=CH_2), 125.71 (br s, *ipso*-C_6F_5), 127.58 (s, *o*-Ph),

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127.86 (s, *p*-Ph), 129.13 (s, *m*-Ph), 134.94 (s, Ga−CH_2−CH=CH_2), 139.31 (dm, $^1J_{CF}$ = 251.4 Hz, *m*-C_6F_5), 138.57 (s, C−CH_2−CH=CH_2), 137.44 (dm, $^1J_{CF}$ = 248.8 Hz, *p*-C_6F_5), 149.49 (dm, $^1J_{CF}$ = 241.0 Hz, *o*-C_6F_5), 150.69 (s, *ipso*-Ph) ppm. Noncoordinate THF and unreacted benzophenone were also detected.

Compound 5. After 53 h 2 equiv of benzophenone had been consumed. The remaining 2 equiv of benzophenone did not undergo insertion within a total reaction time of more than 9 days.

$K^+[Ga(\eta^1\text{-}C_3H_5)_2(OC(C_3H_5)Ph_2)_2]^-$ (10). ^{1}H NMR (400.1 MHz, THF-d_8): δ = 0.88 (dm, $^3J_{HH}$ = 8.5 Hz, 4H, Ga−CH_2−CH=CH_2), 3.13 (dt, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.3 Hz, 4H, C−CH_2−CH=CH_2), 4.31 (br dd, $^2J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 10.0 Hz, 2H, Ga−CH_2−CH=$CH^{cis}H^{trans}$), 4.42 (ddt, $^2J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 16.9 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, Ga−CH_2−CH=$CH^{cis}H^{trans}$), 4.83 (br dd, $^2J_{HH}$ = 2.5 Hz, $^3J_{HH}$ = 10.3 Hz, 2H, C−CH_2−CH=$CH^{cis}H^{trans}$), 4.97 (ddt, $^2J_{HH}$ = 2.5 Hz, $^3J_{HH}$ = 17.3 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, C−CH_2−CH=$CH^{cis}H^{trans}$), 5.75 (ddt, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 17.3 Hz, 2H, C−CH_2−CH=CH_2), 5.75 (ddt, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.9 Hz, 2H, Ga−CH_2−CH=CH_2), 7.08−7.12 (m, 4H, *p*-Ph), 7.18−7.23 (m, 8H, *m*-Ph), 7.44−7.47 (m, 8H, *o*-Ph) ppm. Unreacted benzophenone was also detected. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 25.69 (s, Ga−CH_2−CH=CH_2), 49.81 (s, C−CH_2−CH=CH_2), 80.50 (s, C−CH_2−CH=CH_2), 105.40 (s, Ga−CH_2−CH=CH_2), 116.45 (s, C−CH_2−CH=CH_2), 126.48 (s, *p*-Ph), 128.29 (s, *m*-Ph), 128.62 129.41 (s, *m*-Ph), 138.94 (s, C−CH_2−CH=CH_2), 144.42 (s, Ga−CH_2−CH=CH_2), 152.71 (s, *ipso*-Ph) ppm. Unreacted benzophenone was also detected.

Reactivity toward Isoquinoline. A solution of isoquinoline (for **1**, 19 mg, 0.15 mmol; for **3**, 5 mg, 0.039 mmol; for **5**, 10 mg, 0.077 mmol) in THF-d_8 (300 μL) was added to a solution of the allylgallium compound (**1**, 20 mg, 0.075 mmol; **3**, 19 mg, 0.019 mmol; **5**, 21 mg, 0.077 mmol) in THF (300 μL) to give an orange (in the case of **1**) or colorless solution (in the case of **3** and **5**). The reaction was finished after reaction times of $t \leq 10$ min (in the case of **1** and **3**) and t = 17 h (in the case of **5**), respectively.

$[Ga(\eta^1\text{-}C_3H_5)_2(NC_9H_7(C_3H_5))(NC_9H_7)]$ (11). ^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.73 (dm, $^3J_{HH}$ = 8.5 Hz, 4H, Ga−CH_2−CH=CH_2), (ddm, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 7.4 Hz, 2H, C−CH_2−CH=CH_2), 4.46 (t, $^3J_{HH}$ = 6.8 Hz, 2H, H^1-($NC_9H_7(C_3H_5)$)), 4.51 (ddt, $^2J_{HH}$ = 2.5 Hz, $^3J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, Ga−CH_2−CH=$CH^{cis}H^{trans}$), 4.68 (ddt, $^2J_{HH}$ = 2.5 Hz, $^3J_{HH}$ = 16.8 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, Ga−CH_2−CH=$CH^{cis}H^{trans}$), 4.88 (ddt, $^2J_{HH}$ = 2.5 Hz, $^3J_{HH}$ = 17.1 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, C−CH_2−CH=$CH^{cis}H^{trans}$), 4.91 (br dd, $^2J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 10.0 Hz, 1H, C−CH_2−CH=$CH^{cis}H^{trans}$), 5.35 (d, $^3J_{HH}$ = 6.7 Hz, 1H, H^4-($NC_9H_7(C_3H_5)$)), 5.76 (ddt, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 17.1 Hz, 1H, C−CH_2−CH=CH_2), 6.04 (ddt, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.8 Hz, 2H, Ga−CH_2−CH=CH_2), 6.55 (d, $^3J_{HH}$ = 6.7 Hz, 1H, H^3-($NC_9H_7(C_3H_5)$)), 6.80 (dd, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, H^5-($NC_9H_7(C_3H_5)$)), 6.84 (br d, $^3J_{HH}$ = 7.4 Hz, 1H, H^8), 6.87 (ddd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H^7-($NC_9H_7(C_3H_5)$)), 7.05 (ddd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H^6-($NC_9H_7(C_3H_5)$)) 7.67 (ddd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H^7-(NC_9H_7)), 7.82 (ddd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H^6-(NC_9H_7)), 7.85 (br d, $^3J_{HH}$ = 8.3 Hz, 1H, H^8-(NC_9H_7)), 7.87 (br d, $^3J_{HH}$ = 6.0 Hz, 1H, H^4-(NC_9H_7)), 7.94 (br d, $^3J_{HH}$ = 8.0 Hz, 1H, H^5-(NC_9H_7)), 8.31 (d, $^3J_{HH}$ = 6.0 Hz, 1H, H^3-(NC_9H_7)), 9.05 (s, 1H, H^1-(NC_9H_7)) ppm. Noncoordinate THF (1 equiv) was also detected. A second set of signals (relative intensity: ca. 8%) was detected which was ascribed to ligand scrambling. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 19.37 (s, Ga−CH_2−CH=CH_2), 41.07 (s, C−CH_2−CH=CH_2), 60.89 (s, C^1-($NC_9H_7(C_3H_5)$)), 98.11 (s, C^4-($NC_9H_7(C_3H_5)$)), 108.91 (s, Ga−CH_2−CH=CH_2), 116.52 (s, C−CH_2−CH=CH_2), 122.20 (s, C^8-($NC_9H_7(C_3H_5)$)), 123.14 (s, C^4-(NC_9H_7)), 123.65 (s, C^7-($NC_9H_7(C_3H_5)$)), 126.80 (s, C^5-($NC_9H_7(C_3H_5)$)), 127.60 (s, C^6-($NC_9H_7(C_3H_5)$)), 129.49 (s, C^7-(NC_9H_7)), 129.53 (s, C^{8a}-(NC_9H_7)), 129.59 (s, C^8-($NC_9H_7(C_3H_5)$)), 129.83 (s, C^{8a}-($NC_9H_7(C_3H_5)$)), 133.55 (s, C^6-(NC_9H_7)), 136.03 (s, C^{4a}-($NC_9H_7(C_3H_5)$)), 137.61 (s, C−CH_2−CH=CH_2), 138.47 (s, C^{4a}-(NC_9H_7)), 140.55 (s, Ga−CH_2−CH=CH_2), 141.19 (s, C^3-(NC_9H_7)), 141.94 (s, C^3-($NC_9H_7(C_3H_5)$)), 153.26 (s, C^1-(NC_9H_7)) ppm.

$[Ga(\eta^1\text{-}C_3H_5)_2(NC_9H_7)_2]^+[B(C_6F_5)_4]^-$ (12). ^{1}H NMR (400.1 MHz, THF-d_8): δ = 2.25 (dt, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.0 Hz, $^4J_{HH}$ = 1.5 Hz, 4H, CH_2−CH=CH_2), 4.74 (ddt, $^2J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, CH_2−CH=$CH^{cis}H^{trans}$), 4.92 (ddt, $^2J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 16.8 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, CH_2−CH=$CH^{cis}H^{trans}$), 6.09 (ddt, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.8 Hz, 2H, CH_2−CH=CH_2), 7.92 (ddd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, H^7), 8.09 (ddd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, H^6), 8.15 (br d, $^3J_{HH}$ = 8.3 Hz, 2H, H^5), 8.23 (br d, $^3J_{HH}$ = 6.4 Hz, 2H, H^4), 8.31 (br d, $^3J_{HH}$ = 8.3 Hz, 2H, H^8), 8.41 (br d, $^3J_{HH}$ = 6.4 Hz, 2H, H^3), 9.46 (s, 2H, H^1) ppm. Noncoordinate THF (2 equiv) was also detected. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 18.83 (s, Ga−CH_2−CH=CH_2), 112.52 (s, Ga−CH_2−CH=CH_2), 125.40 (br s, *ipso*-C_6F_5), 125.78 (s, C^4), 128.09 (s, C^5), 129.75 (s, C^{8a}), 130.43 (s, C^8), 131.44 (s, C^7), 136.47 (s, C^6), 137.18 (s, Ga−CH_2−CH=CH_2), 137.32 (dm, $^1J_{CF}$ = 243.6 Hz, *m*-C_6F_5), 138.82 (s, C^{4a}), 138.97 (s, C^3), 139.29 (dm, $^1J_{CF}$ = 245.4 Hz, *p*-C_6F_5), 149.34 (dm, $^1J_{CF}$ = 241.9 Hz, *o*-C_6F_5), 153.85 (s, C^1) ppm. Noncoordinate THF was also detected. ^{11}B NMR (128.4 MHz, THF-d_8): δ = −16.59 (s) ppm. ^{19}F NMR (188.1 MHz, THF-d_8): δ = −129.15 (br s, *m*-C_6F_5), −161.35 (t, $^3J_{FF}$ = 20.5 Hz, *p*-C_6F_5), −164.85 (t, $^3J_{FF}$ = 18.7 Hz, *o*-C_6F_5) ppm.

$K^+[Ga(\eta^1\text{-}C_3H_5)_3(NC_9H_7(C_3H_5))]^-$ (13). ^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.26 (dm, $^3J_{HH}$ = 8.8 Hz, 6H, Ga−CH_2−CH=CH_2), 1.98 (dddt, $^2J_{HH}$ = 12.8 Hz, $^3J_{HH}$ = 4.3 Hz, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, C−CH^aH^b−CH=CH_2), 2.59 (dddt, $^2J_{HH}$ = 12.8 Hz, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 9.1 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, C−CH^aH^b−CH=CH_2), 4.19 (ddt, $^2J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 9.9 Hz, $^4J_{HH}$ = 0.8 Hz, 3H, Ga−CH_2−CH=$CH^{cis}H^{trans}$), 4.31 (dd, $^3J_{HH}$ = 4.3 Hz, $^3J_{HH}$ = 9.1 Hz, 1H, H^1), 4.42 (ddt, $^2J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 16.8 Hz, $^4J_{HH}$ = 1.2 Hz, 3H, Ga−CH_2−CH=$CH^{cis}H^{trans}$), 4.72 (ddt, $^2J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 10.2 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, C−CH_2−CH=$CH^{cis}H^{trans}$), 4.74 (d, $^3J_{HH}$ = 6.3 Hz, 1H, H^4), 4.75 (ddt, $^2J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 17.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, C−CH_2−CH=$CH^{cis}H^{trans}$), 5.64 (dddd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 17.0 Hz, 1H, C−CH_2−CH=CH_2), 6.08 (ddt, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 9.9 Hz, $^3J_{HH}$ = 16.8 Hz, 3H, Ga−CH_2−CH=CH_2), 6.47 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H^5), 6.51 (d, $^3J_{HH}$ = 6.3 Hz, 1H, H^3), 6.52 (ddd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H^7), 6.58 (dd, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H^8), 6.74 (ddd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H^6) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 22.24 (s, Ga−CH_2−CH=CH_2), 40.43 (s, C−CH_2−CH=CH_2), 62.25 (s, C^1), 90.16 (s, C^4), 102.44 (s, Ga−CH_2−CH=CH_2), 114.69 (s, C−CH_2−CH=CH_2), 119.71 (s, C^5), 119.81 (s, C^7), 126.09 (s, C^6), 127.04 (s, C^8), 127.92 (s, C^{8a}), 138.47 (s, C^{4a}), 139.22 (s, C−CH_2−CH=CH_2), 146.16 (s, Ga−CH_2−CH=CH_2), 146.38 (s, C) ppm.

Reactivity toward Quinoline. A solution of quinoline (10 mg, 0.077 mmol) in THF-d_8 (300 μL) was added to a solution of the allylgallium compound (**1**, 21 mg, 0.079 mmol; **3**, 38 mg, 0.039 mmol) in THF (300 μL) to give an orange (in the case of **1**) or colorless solution (in the case of **3**), respectively.

$[Ga(\eta^1\text{-}C_3H_5)_3(NC_9H_7)]$. ^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.51 (d, $^3J_{HH}$ = 8.5 Hz, 6H, CH_2−CH=CH_2), 4.43 (br dd, $^2J_{HH}$ = 2.3 Hz, $^3J_{HH}$ = 10.0 Hz, 3H, CH_2−CH=$CH^{cis}H^{trans}$), 4.58 (br d,$^3J_{HH}$ = 16.8 Hz, 3H, CH_2−CH=$CH^{cis}H^{trans}$), 5.94−6.05 (m, 3H, CH_2−CH=CH_2), 7.50 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 4.4 Hz, 1H, H^3), 7.59 (ddd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H^6), 7.76 (ddd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H^7), 7.92 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H^5), 8.18 (br d, $^3J_{HH}$ = 8.6 Hz, 1H, H^8), 8.34 (br d, $^3J_{HH}$ = 8.5 Hz, 1H, H^4), 8.87 (dd, $^3J_{HH}$ = 4.4 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, H^2) ppm. Noncoordinate THF (1 equiv) was also detected. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 21.69 (s, CH_2−CH=CH_2), 107.12 (s, CH_2−CH=CH_2), 122.13 (s, C^3), 127.79 (s, C^6), 129.16 (s, C^5), 129.48 (s, C^8), 129.84 (s, C^{4a}), 130.78 (s, C^7), 138.38 (s, C^4), 141.64 (s, CH_2−CH=CH_2), 148.42 (s, C^{8a}), 151.53 (s, C^2) ppm. Noncoordinate THF was also detected.

$[Ga(\eta^1\text{-}C_3H_5)_2(NC_9H_7)_2]^+[B(C_6F_5)_4]^-$. ^{1}H NMR (400.1 MHz, THF-d_8): δ = 2.19 (br d, $^3J_{HH}$ = 7.3 Hz, CH_2−CH=CH_2), 4.72 (br d,

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$^3J_{HH}$ = 9.0 Hz, 2H, CH_2−CH=C*H*^{cis}H^{trans}), 4.86 (br d, $^3J_{HH}$ = 16.8 Hz, 2H, CH_2−CH=CH^{cis}*H*^{trans}), 5.93−6.05 (m, 2H, CH_2−C*H*=CH_2), 7.80 (br s, 2H, H^8), 7.81 (br s, 2H, H^4), 7.91−7.95 (br m, 2H, H^6), 8.11 (br d, $^3J_{HH}$ = 8.8 Hz, 2H, H^5), 8.17−8.21 (br m, 2H, H^7), 8.78−8.85 (br m, 2H, H^3), 8.96−8.98 (s, 2H, H^2) ppm. Noncoordinate THF (2 equiv) was also detected. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 21.82 (s, Ga−*C*H_2−CH=CH_2), 113.08 (s, Ga−CH_2−CH=CH_2), 122.96 (s, C^4), 124.88 (br s, *ipso*-C_6F_5), 125.59 (s, C^{4a}), 125.83 (br s, C^5), 129.66 (br s, C^8), 130.72 (s, C^7), 133.70 (br s, C^6), 136.69 (s, Ga−CH_2−*C*H=CH_2), 137.26 (dm, $^1J_{CF}$ = 244.5 Hz, *m*-C_6F_5), 139.29 (dm, $^1J_{CF}$ = 244.5 Hz, *p*-C_6F_5), 143.76 (br s, C^3), 145.50 (br s, C^{8a}), 149.35 (dm, $^1J_{CF}$ = 244.5 Hz, *o*-C_6F_5), 152.15 (s, C^2) ppm. Noncoordinate THF was also detected. ^{11}B NMR (128.4 MHz, THF-d_8): δ = −18.44 (s) ppm. ^{19}F NMR (188.1 MHz, THF-d_8): δ = −129.16 (br s, *m*-C_6F_5), −161.29 (t, $^3J_{FF}$ = 20.3 Hz, *p*-C_6F_5), −164.80 (t, $^3J_{FF}$ = 18.3 Hz, *o*-C_6F_5) ppm.

Single Crystal X-ray Analysis. X-ray diffraction data were collected on a Bruker CCD area-detector diffractometer with Mo Kα radiation (graphite monochromator, λ = 0.710 73 Å) using ω scans. The SMART program package was used for the data collection and unit cell determination, processing of the raw frame data was performed using SAINT, and absorption corrections were applied with SADABS[32a] (**4**, **14**) or MULABS[32b] (**2**, [**4**·THF], **6**). The structures were solved by direct methods and refined against F^2 using all reflections with the SHELXL-97 software as implemented in the program system WinGX.[33] The non-hydrogen atoms were refined anisotropically; only the carbon atoms in disordered fragments were refined with isotropic displacement parameters. All hydrogen atoms were included in calculated positions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full crystallographic data, in CIF format, for compounds **2**, **4**, [**4**·THF], **6**, and **14**; time conversion plots for reactions of **5** and **7** with benzophenone; and synthesis and characterization of **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) In THF solutions of compounds **5** and **6**, interactions of the allyl ligands of the $[Ga(C_3H_5)_4]^-$ moieties with the potassium counterions cannot be excluded.
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