

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

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Reaction of 5 and 7 with Benzophenone. A time conversion plot of reactions of $\text{K}^+[\text{Ga}(\eta^1\text{-C}_3\text{H}_5)_4]^-$ (**5**) and $[\text{PPh}_4]^+[\text{Ga}(\eta^1\text{-C}_3\text{H}_5)_4]^-$ (**7**) with four equivalents of benzophenone is shown in Figure S1. Species resulting from side reactions including further conversion of the substrate (presumably reaction of the alkoxy ligand with benzophenone) are observed after reaction times of more than 9 d (216 h) in both cases. In the case of **7**, the counter ion remained intact as shown by ^1H and ^{31}P NMR spectroscopy.

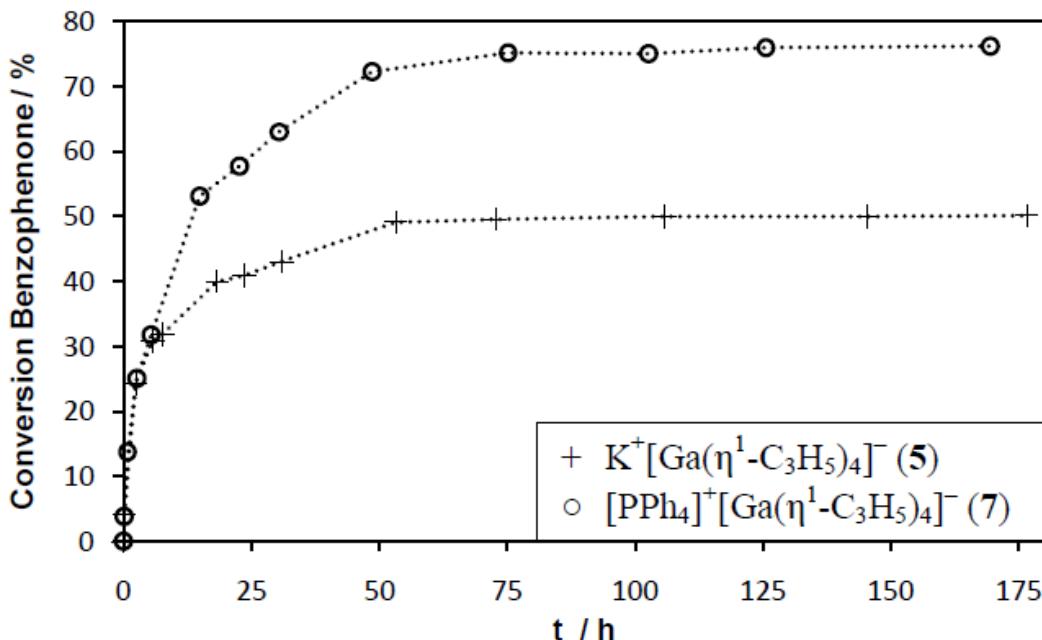


Figure S1. Time conversion plot of reactions of $\text{K}^+[\text{Ga}(\eta^1\text{-C}_3\text{H}_5)_4]^-$ (**5**) and $[\text{PPh}_4]^+[\text{Ga}(\eta^1\text{-C}_3\text{H}_5)_4]^-$ (**7**) with four equivalents of benzophenone.

$[\text{PPh}_4]^+[\text{Ga}(\eta^1\text{-C}_3\text{H}_5)(\text{OC}(\text{C}_3\text{H}_5)\text{Ph}_2)_3]^-$. ^1H NMR (400.1 MHz, THF- d_8): δ = 0.36 (br d, $^3J_{\text{HH}}$ = 8.5 Hz, 2H, Ga- $\text{CH}_2\text{-CH=CH}_2$), 3.31 (dt, $^3J_{\text{HH}}$ = 6.8 Hz, $^4J_{\text{HH}}$ = 1.3 Hz, 2H, C- $\text{CH}_2\text{-CH=CH}_2$), 4.11 (ddt, $^2J_{\text{HH}}$ = 3.5 Hz, $^3J_{\text{HH}}$ = 10.0 Hz, $^4J_{\text{HH}}$ = 1.0 Hz, 1H, Ga- $\text{CH}_2\text{-CH=CH}^{\text{cis}}\text{H}^{\text{trans}}$), 4.14 (ddt, $^2J_{\text{HH}}$ = 3.5 Hz, $^3J_{\text{HH}}$ = 16.6 Hz, $^4J_{\text{HH}}$ = 1.4 Hz, 1H, Ga- $\text{CH}_2\text{-CH=CH}^{\text{cis}}\text{H}^{\text{trans}}$), 4.57 (br dt, $^2J_{\text{HH}}$ = 3.0 Hz, $^3J_{\text{HH}}$ = 10.3 Hz, 3H, C- $\text{CH}_2\text{-CH=CH}^{\text{cis}}\text{H}^{\text{trans}}$), 4.67 (br dt, $^2J_{\text{HH}}$ = 3.0 Hz, $^3J_{\text{HH}}$ = 17.3 Hz, 3H, C- $\text{CH}_2\text{-CH=CH}^{\text{cis}}\text{H}^{\text{trans}}$), 5.50 (ddt, $^3J_{\text{HH}}$ = 8.5 Hz, $^3J_{\text{HH}}$ = 10.0 Hz, $^3J_{\text{HH}}$ = 16.6 Hz, 1H, Ga- $\text{CH}_2\text{-CH=CH}_2$), 6.30 (ddt, $^3J_{\text{HH}}$ = 6.8 Hz, $^3J_{\text{HH}}$ = 10.3 Hz, $^3J_{\text{HH}}$ = 17.3 Hz, 3H, C- $\text{CH}_2\text{-CH=CH}_2$), 6.85-6.89 (m, 6H, *p*-Ph), 6.99-7.03 (m, 12H, *m*-Ph), 7.52-7.55 (m, 12H, *o*-Ph), 7.67-7.74 (m, 16H, *o*-, *m*-PPh₄), 7.85-7.90 (m, 4H, *p*-PPh₄) ppm. Unreacted benzophenone was also detected. ^{31}P NMR (80.9 MHz, THF- d_8): δ = 24.67 (s) ppm.

Synthesis and Characterization of $[\text{K}_3\text{Cl}(\text{dibenzo-18-c-6})_3]^{2+}([\text{Ga}(\eta^1\text{-C}_3\text{H}_5)_3(\text{NC}_9\text{H}_7(\text{C}_3\text{H}_5))]^-)_2$ (14). Crystallization of **13** from CH₂Cl₂/pentane (2:1) in the presence of (dibenzo-18-c-6) at -30 °C gave KCl adduct $[\text{K}_3\text{Cl}(\text{dibenzo-18-c-6})_3]^{2+}([\text{Ga}(\eta^1\text{-C}_3\text{H}_5)_3(\text{NC}_9\text{H}_7(\text{C}_3\text{H}_5))]^-)_2$ (**14**) in moderate yield, presumably as a result of **13** reacting with CH₂Cl₂ (Figure S2). ^1H and ^{13}C NMR spectroscopic data on the gallate moiety in **13** and **14** do not differ significantly. **14** crystallized in the triclinic space group $P\bar{1}$ with $Z = 2$. Samples of **14** subjected to single crystal X-ray analysis gave high R values ($R^{int} = 0.1731$; R^1 [$I > 2\sigma(I)$] = 0.1119; wR^2 [$I > 2\sigma(I)$] = 0.2803; R^1 (all refln.) = 0.2260; wR^2 (all refln.) = 0.3921). Therefore, bond lengths and angles are not discussed, but connectivities are definite. Two chemically equivalent $[\text{Ga}(\eta^1\text{-C}_3\text{H}_5)_3(\text{NC}_9\text{H}_7(\text{C}_3\text{H}_5))]^-$ moieties are in the asymmetric unit of **14**; only one of them is shown (Figure S2 a)). The gallate moieties show no direct interactions with the counterions. The gallium centers in **14** are four coordinate like those in the only other tris(organo)amidogallate that has been analyzed by means of single crystal X-ray analysis

($[\text{GaEt}_3(\text{carbazoyl})]^-$).¹ The allyl ligands coordinate to the metal center in an η^1 fashion, which is in good agreement with ^1H and ^{13}C NMR spectroscopic data.

In the dicationic part of **14**, $[\text{K}_3\text{Cl}(\text{dibenzo-18-c-6})_3]^{2+}$, the chlorine atom is coordinated by three potassium ions (Figure S2 b)). This coordination mode is relatively rare for alkali chloride moieties and has previously been reported for dicationic $[\text{Li}_3(\text{THF})_9\text{Cl}]^{2+}$.² The potassium ions are each coordinated by a (dibenzo-18-c-6) ligand and by Cl1. In addition, two of the potassium ions show weak interactions with the arene functionalities of adjacent dibenzo-18-c-6 ligands (not shown in Figure S2).

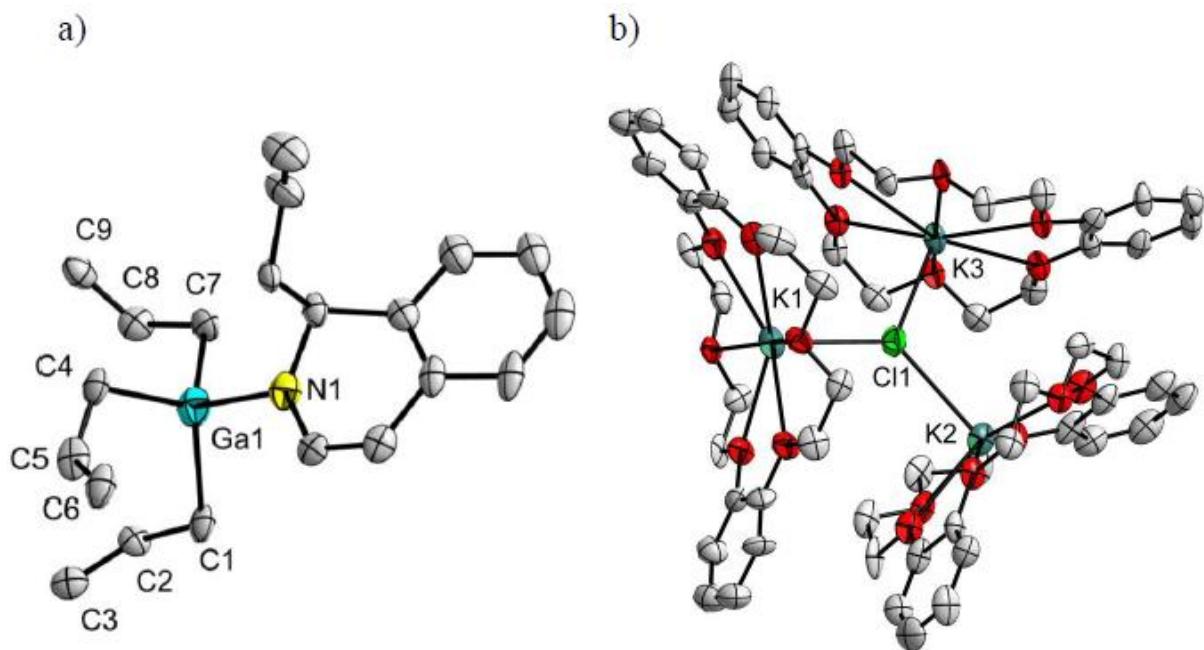


Figure S2. Molecular structure of one anionic unit (a) and the dicationic part (b) of $[\text{K}_3\text{Cl}(\text{dibenzo-18-c-6})_3]^{2+}([\text{Ga}(\eta^1\text{-C}_3\text{H}_5)_3(\text{NC}_9\text{H}_7(\text{C}_3\text{H}_5))]^-)_2$ (**14**). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

[K₃Cl(dibenzo-18-c-6)₃]²⁺([Ga(η¹-C₃H₅)₃(NC₉H₇(C₃H₅))]⁻)₂ (14). A solution of isoquinoline (25 mg, 0.19 mmol) in THF (0.5 mL) was added to a solution of **5** (53 mg, 0.19 mmol) in THF (0.5 mL). After 17 h all volatiles were removed under reduced pressure to give a yellow

oil, which was dissolved in CH_2Cl_2 (0.4 mL). Neat (dibenzo-18-c-6) (70 mg, 0.19 mmol) was added. Addition of pentane (0.2 mL) led to precipitation of small amounts of a colorless solid, which was filtered off. Storing the filtrate at -30°C gave colorless single crystalline **14** after 1 d. Yield: 50 mg, 0.025 mmol, 39%.

^1H NMR (400.1 MHz, THF- d_8): δ = 1.28 (dm, $^3J_{\text{HH}} = 8.8$ Hz, 12H, Ga- $\text{CH}_2\text{-CH=CH}_2$), 2.01 (dddt, $^2J_{\text{HH}} = 12.8$ Hz, $^3J_{\text{HH}} = 4.4$ Hz, $^3J_{\text{HH}} = 8.3$ Hz, $^4J_{\text{HH}} = 1.1$ Hz, 2H, C- $\text{CH}^{\text{a}}\text{H}^{\text{b}}\text{-CH=CH}_2$), 2.62 (dddt, $^2J_{\text{HH}} = 12.8$ Hz, $^3J_{\text{HH}} = 6.8$ Hz, $^3J_{\text{HH}} = 9.4$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 2H, C- $\text{CH}^{\text{a}}\text{H}^{\text{b}}\text{-CH=CH}_2$), 3.94-3.96 (m, 24H, O(CH_2CH_2)O), 4.13-4.15 (m, 24H, O(CH_2CH_2)O) 4.20 (ddt, $^2J_{\text{HH}} = 3.3$ Hz, $^3J_{\text{HH}} = 10.0$ Hz, $^4J_{\text{HH}} = 0.8$ Hz, 6H, Ga- $\text{CH}_2\text{-CH=CH}^{\text{cis}}\text{H}^{\text{trans}}$), 4.35 (dd, $^3J_{\text{HH}} = 4.4$ Hz, $^3J_{\text{HH}} = 9.4$ Hz, 2H, H¹), 4.44 (ddt, $^2J_{\text{HH}} = 3.3$ Hz, $^3J_{\text{HH}} = 16.8$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 6H, Ga- $\text{CH}_2\text{-CH=CH}^{\text{cis}}\text{H}^{\text{trans}}$), 4.72 (ddt, $^2J_{\text{HH}} = 2.8$ Hz, $^3J_{\text{HH}} = 10.3$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 2H, C- $\text{CH}_2\text{-CH=CH}^{\text{cis}}\text{H}^{\text{trans}}$), 4.75 (ddt, $^2J_{\text{HH}} = 2.8$ Hz, $^3J_{\text{HH}} = 17.0$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, 2H, C- $\text{CH}_2\text{-CH=CH}^{\text{cis}}\text{H}^{\text{trans}}$), 4.76 (dd, $^3J_{\text{HH}} = 6.4$ Hz, $^4J_{\text{HH}} = 0.6$ Hz, 2H, H⁴), 5.65 (dddt, $^3J_{\text{HH}} = 6.8$ Hz, $^3J_{\text{HH}} = 8.3$ Hz, $^3J_{\text{HH}} = 10.3$ Hz, $^3J_{\text{HH}} = 17.0$ Hz, 2H, C- $\text{CH}_2\text{-CH=CH}_2$), 6.10 (ddt, $^3J_{\text{HH}} = 8.8$ Hz, $^3J_{\text{HH}} = 10.0$ Hz, $^3J_{\text{HH}} = 16.8$ Hz, 6H, Ga- $\text{CH}_2\text{-CH=CH}_2$), 6.47 (dd, $^3J_{\text{HH}} = 7.7$ Hz, $^4J_{\text{HH}} = 1.1$ Hz, 2H, H⁵), 6.52 (ddt, $^3J_{\text{HH}} = 7.3$ Hz, $^3J_{\text{HH}} = 7.3$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, 2H, H⁷), 6.55 (d, $^3J_{\text{HH}} = 6.5$ Hz, 2H, H³), 6.58 (dd, $^3J_{\text{HH}} = 7.3$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, 2H, H⁸), 6.73 (ddt, $^3J_{\text{HH}} = 7.3$ Hz, $^3J_{\text{HH}} = 7.3$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, 2H, H⁶), 6.89-6.96 (m, 24H, Ph) ppm. ^{13}C NMR (100.6 MHz, THF- d_8): δ = 22.33 (s, Ga- $\text{CH}_2\text{-CH=CH}_2$), 40.52 (s, C- $\text{CH}_2\text{-CH=CH}_2$), 61.34 (s, C¹), 68.85 (s, O(CH_2CH_2)O), 70.53 (s, O(CH_2CH_2)O), 90.03 (s, C⁴), 102.52 (s, Ga- $\text{CH}_2\text{-CH=CH}_2$), 113.03 (s, Ph^{3,6}), 114.52 (s, C- $\text{CH}_2\text{-CH=CH}_2$), 119.68 (s, C⁵), 119.72 (s, C⁷), 122.30 (s, Ph^{4,5}), 126.08 (s, C⁶), 127.08 (s, C⁸), 128.08 (s, C^{8a}), 138.75 (s, C^{4a}), 139.28 (s, C- $\text{CH}_2\text{-CH=CH}_2$), 146.16 (s, Ga- $\text{CH}_2\text{-CH=CH}_2$), 146.60 (s, C³) 148.75 (s, Ph^{1,2}) ppm. A test for halides was positive. Anal. calcd. for $\text{C}_{104}\text{H}_{130}\text{ClGa}_2\text{K}_3\text{N}_2\text{O}_{18}$ (1988.34 g/mol): Ga, 7.01; found: Ga, 6.52.

References

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- 2 Rosa, P.; Mézailles, N.; Ricard, L.; Mathey, F.; Le Floch, P., *Angew. Chem.* **2000**, *112*, 1893-1896; *Angew. Chem. Int. Ed.* **2000**, *39*, 1823-1826.