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Communications to the Editor

Synthesis and Characterization of the First Example of a Gallocenium Cation

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The past decade has witnessed an upsurge of interest in the chemistry of main group metallocenes.[1] Apart from the fact that much less is known about s- and p-block metallocenes than their d- and f-block counterparts, interest in the main group metallocenes has been stimulated by structure and bonding considerations,[1] their utility as reagents and chemical vapor deposition sources,[2] and the possibility that cationic species might serve as useful catalysts for, e.g., alkene polymerization.[3] In the context of group 13 metallocenes, we are aware of only two structurally authenticated cations, namely the decamethylborocenium cation ($\mathbf{1}^+$)[4,5] and the decamethylaluminocenium cation ($\mathbf{2}^+$).[6] Cation $\mathbf{1}^+$ features an unprecedented "tightly squeezed" η^5/η^1 structure, while $\mathbf{2}^+$ possesses a ferrocene-like structure. Herein, we report for the first time (i) various synthetic approaches to the decamethylgallocenium cation ($\mathbf{3}^+$), (ii) the unique structure of $\mathbf{3}^+$ as determined by X-ray crystallography, and (iii) insights gained from DFT calculations on the parent gallocenium cation, $[Cp_2Ga]^+$.

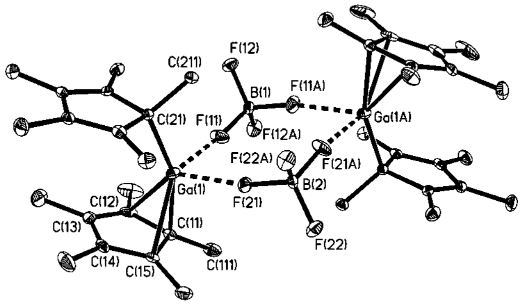

Figure 1. Molecular structure of $[(\eta^1\text{-}C_5Me_5)(\eta^3\text{-}C_5Me_5)Ga][BF_4]$ ([**3**][BF_4]) showing the atom numbering scheme. Important parameters: Ga(1)−C(11) 2.011(5) Å, Ga(1)−C(12) 2.359(5) Å, Ga(1)−C(15) 2.360(5) Å, Ga(1)−C(21) 1.974(5) Å, Ga(1)−F(21) 2.176(3) Å, Ga(1)−F(11) 2.184(3) Å, B(1)−F(11) 1.422(6) Å, B(1)−F(12) 1.358(6) Å, B(2)−F(21) 1.422(6) Å, B(2)−F(22) 1.361(5) Å, C(11)−C(12) 1.471(8) Å, C(12)−C(13) 1.409(9) Å, C(11)−C(15) 1.458(7) Å, C(13)−C(14) 1.416(9) Å, C(14)−C(15) 1.391(8) Å, C(21)−C(22) 1.515(7) Å, C(21)−C(25) 1.496(7) Å, C(22)−C(23) 1.355(8) Å, C(23)−C(24) 1.473(8) Å, C(24)−C(25) 1.357(8) Å, C(21)−Ga(1)−C(11) 157.6(2)°, C(21)−Ga(1)−F(21) 100.2(2)°, C(11)−Ga(1)−F(21) 98.0(2)°, C(21)−Ga(1)−F(11) 100.1(2)°, C(11)−Ga(1)−F(11) 95.7(2)°, F(21)−Ga(1)−F(11) 80.2(2)°, C(21)−Ga(1)−C(12) 123.7(2)°, C(11)−Ga(1)−C(12) 38.3(2)°, F(21)−Ga(1)−C(12) 135.8(2)°, F(11)−Ga(1)−C(12) 95.1(2)°, C(21)−Ga(1)−C(15) 128.5(2)°, C(11)−Ga(1)−C(15) 37.9(2)°, F(21)−Ga(1)−C(15) 91.0(2)°, F(11)−Ga(1)−C(15) 131.3(2)°, C(12)−Ga(1)−C(15) 59.4(2)°, F(12)−B(1)−F(12)#1 114.1(7)°, F(12)−B(1)−F(11) 109.5(2)°, F(12)#1−B(1)−F(11) 108.4(2)°, F(12)−B(1)−F(11)#1 108.4(2)°, F(12)#1−B(1)−F(11)#1 109.5(2)°, F(11)−B(1)−F(11)#1 106.8(6)°, B(1)−F(11)−Ga(1) 169.1(3)°, F(22)#1−B(2)−F(22) 114.4(6)°, F(22)#1−B(2)−F(21)#1 108.4(2)°, F(22)−B(2)−F(21)#1 109.5(2)°, F(22)#1−B(2)−F(21) 109.5(2)°, F(22)−B(2)−F(21) 108.4(2)°, F(21)#1−B(2)−F(21) 106.3(6)°, B(2)−F(21)−Ga(1) 167.2(2)°.

Of the various synthetic methods employed, the most successful one for the isolation of crystalline material was the protonolysis of Cp*$_3$Ga with HBF_4 in CH_2Cl_2 solution, which resulted in a 56% yield of pale yellow crystalline [**3**][BF_4].[7] The HRMS data for [**3**][BF_4][7] were in satisfactory accord with the calculated *m*/*e* values for both $\mathbf{3}^+$ and the BF_4^- anion, and the presence of the latter in CD_2Cl_2 solution was established on the basis of ^{11}B and ^{19}F NMR spectroscopy.[7] The ^1H and ^{13}C NMR spectra for $\mathbf{3}^+$ exhibited only singlet resonances for the CH_3 groups and ring carbon atoms down to −70 °C.[7] However, given the possibility of fluxional behavior, an X-ray crystal structure was desirable.[9] The solid-state structure of [**3**][BF_4] comprises pairs of decamethylgallocenium cations that are connected by two bridging BF_4^- anions such that the symmetry of each dimeric unit is C_2 (Figure 1). In contrast to the decamethylborocenium cation, the Cp* rings of $\mathbf{3}^+$ are almost parallel (1.8° angle between the normals to the least-squares planes). One ring is attached to

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[1] For recent reviews, see: (a) Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969. (b) Shapiro, P. J. *Coord. Chem. Rev.* **1999**, *189*, 1.

[2] See, for example: Wojtczak, W. A.; Fleig, P. F.; Hampden-Smith, M. J. *Adv. Organomet. Chem.* **1996**, *40*, 215.

[3] (a) Bochmann, M.; Dawson, D. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2226. (b) Shapiro, P. J.; Burns, C. T. *Abstracts of Papers*, 218th ACS National Meeting, New Orleans, LA, August 22−26, 1999; American Chemical Society: Washington, DC, 1999; INOR 329.

[4] Voigt, A.; Filipponi, S.; Macdonald, C. L. B.; Gorden, J. D.; Cowley, A. H. *Chem. Commun.* **2000**, 911.

[5] The salt [**1**][BCl_4] was prepared first by Jutzi et al.; however, the X-ray crystal structure was not determined. See: Jutzi, P.; Seufert, A. *J. Organomet. Chem.* **1978**, *161*, C5.

[6] (a) Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1655. (b) Üffing, C.; Ecker, A.; Baum, E.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1354. (c) Dohmeier, C.; Baum, E.; Ecker, A.; Koppe, R.; Schnöckel, H. *Organometallics* **1996**, *15*, 4702.

[7] For the preparation of [**3**][BF_4], a solution of HBF_4 (54% solution in Et_2O, 1.1 mmol) in CH_2Cl_2 (20 mL) was added to a stirred pale yellow solution of Cp*$_3$Ga[8] (0.377 g, 0.79 mmol) in CH_2Cl_2 (20 mL) at room temperature. After the dark yellow reaction mixture was stirred for 48 h, the volatiles were removed under reduced pressure, and the resulting pale yellow powder was recrystallized from CH_2Cl_2 to give pale yellow plates of [**3**][BF_4] (0.19 g, 56%). Mp 170−171 °C. HRMS (CI, CH_4): calcd for $C_{20}H_{30}Ga$, 339.1603; found, 339.1597; calcd for BF_4, 87.0029; found 87.0029. ^1H NMR (300 MHz, CD_2Cl_2): δ 1.80 (s, C_5Me_5). ^{13}C NMR (75.48 MHz, CD_2Cl_2): δ 11.9 (s, C_5-$(CH_3)_5$), 120.4 (s, η^5-$C_5(CH_3)_5$). ^{11}B NMR (96.28 MHz, CD_2Cl_2): δ 0.8 (s, sharp). ^{19}F NMR (282 MHz, CD_2Cl_2): δ −104.2. For the preparation of **4**, a solution of $B(C_6F_5)_3$ (0.325 g, 0.92 mmol) in Et_2O (20 mL) was added to a stirred pale yellow solution of Cp*$_2$GaMe (0.468 g, 0.91 mmol) in Et_2O (20 mL) at room temperature. After the pale yellow reaction mixture was stirred for 48 h, the solution was concentrated to a volume of 5 mL and cooled to −20 °C to afford a crop of colorless needles of **4** (0.4 g, 78%). Mp 145 °C dec. CI HRMS: calcd for $C_{26}H_{31}F_5Ga$, 507.1602; found, 507.1627. ^1H NMR (300 MHz, C_6D_6): δ 1.73 (s, C_5Me_5). ^{13}C NMR (75.48 MHz, C_6D_6): δ 14.3 (s, $C_5(CH_3)_5$), 121.0 (s, η^5-$C_5(CH_3)_5$). ^{19}F NMR (282 MHz, C_6D_6): δ −92.5 (s, 2F, *o*-Ar−F), −110.8 (s, 1F, *p*-Ar−F), −123.7 (s, 2F, *m*-Ar−F).

[8] Schumann, H.; Nickel, S.; Wiemann, R. *J. Organomet. Chem.* **1994**, *468*, 43.

[9] Crystal data for [**3**][BF_4]: $C_{20}H_{30}BF_4Ga$, orthorhombic, *Pbcn*, a = 11.972(2), b = 16.481(3), and c = 20.449(4) Å, V = 4.034.7(14) Å^3, Z = 8, D_{calcd} = 1.406 g cm^{-3}, μ(Mo Kα) = 1.40 mm^{-1}. Crystal data for **4**: $C_{26}H_{30}F_5$-Ga, monoclinic, $P2_{1/n}$, a = 9.7661(2), b = 16.3514(4), and c = 15.2095(4) Å, β = 95.384(1)°, V = 2418.1(1) Å^3, Z = 4, D_{calcd} = 1.393 g cm^{-3}. Suitable single crystals of [**3**][BF_4] and **4** were covered with perfluorinated polyether oil and mounted on a Nonius-Kappa CCD diffractometer at 133 K. Totals of 4539 and 5518 unique reflections were collected in the ranges 6.32° < 2θ < 54.94° and 4.92° < 2θ < 54.96° for [**3**][BF4] and **4**, respectively, using Mo Kα radiation (λ = 0.71073 Å). Both structures were solved by direct methods and refined by full-matrix least squares on F^2 using the Siemens SHELX PLUS 5.0 (PC) software package.[10] Final R values: **3** [BF_4], R_1 = 0.0478, wR_2 = 0.0836; **4**, R_1 = 0.0396, wR_2 = 0.0721. In the case of **4**, the η^2-bonded Cp* ring was modeled in two positions; only the major contributor is shown in Figure 2.

[10] Sheldrick, G. M., SHELXTL PC Version 5.0, Siemens Analytical X-ray Instruments, Inc., 1994.

10.1021/ja002888x CCC: $19.00

gallium in an η^1 fashion, as indicated by the localized bonding (average $C_\alpha-C_\beta = 1.348(4)$ Å; $C_\beta-C_\beta = 1.475(4)$ Å) and by the protrusion of the ipso methyl carbon (C(211)) above the least-squares plane of the C_5 ring (Ga(1)−C(21)−C(211) = 109.5(2)°). Furthermore, the Ga−C bond length of 1.974(5) Å is similar to that reported[8] for (η^1-C_5Me_5)$_3$Ga (2.038(4) Å). The other ring is bonded in an η^3 fashion, as evidenced by the fact that three of the Ga−C distances (2.001(3) Å to C(11), 2.352(3) Å to C(12), and 2.353(3) Å to C(15)) are considerably shorter than the other two (2.735(3) Å to C(13) and 2.741(3) Å to C(14). The bonding in the η^3 ring is much more delocalized (average $C_\alpha-C_\beta = 1.381(4)$ Å; $C_\beta-C_\beta = 1.415(4)$ Å); however, the ipso methyl carbon atom (C(111)) lies 0.43 Å out of the least-squares plane of the C_5 ring. The interactions between the decamethylgallocenium cations and BF_4^- anions are manifested by the Ga···F contacts (Ga(1)−F(11) = 2.186(2); Ga(1)−F(21) = 2.174(2) Å) and disparities in the B−F bond distances (e.g., B(1)−F(12) = 1.358(3); B(1)−F(11) = 1.419(3) Å).

The structure of $\mathbf{3}^+$ is clearly different from those of the cognate boron and aluminum cations. We have already explained the structure of $\mathbf{1}^+$ on the basis of repulsions between the π clouds of the Cp* rings.[4] Our expectation was that such repulsions would be negligible in the case of $\mathbf{3}^+$ because of the larger ionic radius of Ga^{3+} and that consequently, like $\mathbf{2}^+$, it would possess a ferrocene-like structure. We have gained some insight into this structural question by means of DFT calculations[11] on the model cations $[Cp_2Ga]^+$ and $[Cp_2Al]^+$. The global minimum for the gallocenium cation corresponds to the $[(\eta^1\text{-Cp})(\eta^5\text{-Cp})Ga]^+$ geometry with C_s symmetry. The $[(\eta^5\text{-Cp})_2Ga]^+$ structure is higher in energy by 8.81 kcal mol^{-1} (cf. $[Cp_2B]^+$, where the energy difference is 45 kcal/mol),[4] and there is only 0.09 kcal mol^{-1} difference in energy between the staggered (D_{5d}) and eclipsed (D_{5h}) conformations. It is important to note that the D_{5d} and D_{5h} structures are not minima on the potential energy surface ($N_{\text{imag}} = 2$ for each). Each pair of doubly degenerate imaginary frequencies corresponds to a ring slippage that lowers the symmetry to C_s. In contrast, the global minimum for $[Cp_2Al]^+$ is the D_{5d} $[(\eta^5\text{-Cp})_2Al]^+$ structure, and there is no stationary point corresponding to the C_s geometry. A haptotropic search across the π-bonded Cp ring reveals a very shallow potential with respect to deformation of the π-Cp−Ga bond (see the Supporting Information for full details). In summary, the unique bonding mode observed in gallocenium cation $\mathbf{3}^+$ appears to be a consequence of three factors: (i) the π-cloud repulsion effect is insignificant compared to that in the tightly bonded borocenium cation, $\mathbf{1}^+$; (ii) the ionic character of the Cp*−metal bonding in $\mathbf{3}^+$ is less than that in the aluminocenium cation $\mathbf{2}^+$ due to the lower electronegativity of aluminum; and (iii) the π-Cp*−Ga bonding has a shallow potential which allows for perturbation of the cation structure by the accompanying anions.

Since methyl abstraction by $B(C_6F_5)_3$ represents a viable route to d-block metallocene cations,[12] we investigated the reaction of $Cp^*{}_2GaMe$[13] with $B(C_6F_5)_3$ in the hope of preparing $[Cp^*{}_2Ga][MeB(C_6F_5)_3]$. The initial formation of the desired product in CH_2Cl_2 solution was evident from the identification of $[Cp^*{}_2Ga]^+$ and $[MeB(C_6F_5)_3]^-$ ions by multinuclear NMR experiments. However, upon attempted isolation of this salt, it was converted into $Cp^*{}_2GaC_6F_5$ (**4**) via a putative C_6F_5 back-transfer reaction.[14] Interestingly, if the reaction of $Cp^*{}_2GaMe$ with $B(C_6F_5)_3$ is carried out in Et_2O solution, there is no evidence for the intermediacy of $[Cp^*{}_2Ga][MeB(C_6F_5)_3]$. In view of the recent concern with the molecular structures of bis(cyclopentadienyl) compounds of aluminum,[3b,15] we decided to investigate that of **4**. The solid-state structure (Figure 2) consists of monomeric units with an unprecedented (for gallium) geometry in which the Cp* rings are η^1- and η^2-bonded to the group 13 element. As in the aluminum derivatives, (η^2-C_5R_5)$_2$AlMe (R = H,[15] Me[3b]), the faces of the cyclopentadienyl rings are located above and below the metal center. In the case of **4**, the η^2-attached Cp* ring is close to planar, and the bonding in the η^1-attached Cp* ring is somewhat less localized than that in $\mathbf{3}^+$.

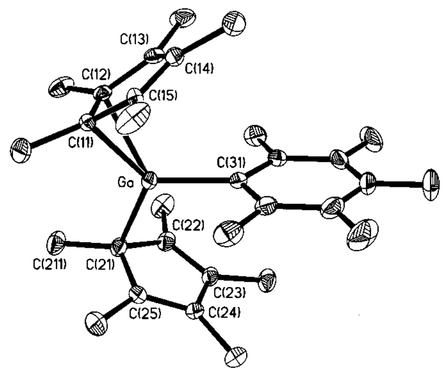

Figure 2. Molecular structure of (η^1-C_5Me_5)(η^2-C_5Me_5)Ga(C_6F_5) (**4**) showing the atom numbering scheme. Important parameters: Ga−C(11) 2.183(5) Å, Ga−C(12) 2.17(2) Å, Ga−C(31) 1.985(2) Å, Ga−C(21) 2.043(2) Å, C(11)−C(12) 1.50(2) Å, C(11)−C(15) 1.451(13) Å, C(12)−C(13) 1.406(10) Å, C(13)−C(14) 1.403(12) Å, C(14)−C(15) 1.38(2) Å, C(21)−C(25) 1.470(3) Å, C(21)−C(22) 1.473(3) Å, C(22)−C(23) 1.371(3) Å, C(23)−C(24) 1.432(4) Å, C(24)−C(25) 1.373(3) Å, C(31)−Ga−C(12) 117.6(3)°, C(21)−Ga−C(12) 119.3(3)°, C(31)−Ga−C(11) 116.7(2)°, C(21)−Ga−C(11) 123.4(2)°, C(31)−Ga−C(21) 117.14(9)°.

In summary, we have prepared $[(\eta^1\text{-}C_5Me_5)(\eta^3\text{-}C_5Me_5)Ga][BF_4]$, the first example of a structurally characterized gallocenium cation. The structure of this cation is quite different from that of the analogous boron and aluminum cations and furthermore exhibits only marginal stability, particularly with respect to back-transfer reactions.

Acknowledgment. Funding of this work by the National Science Foundation and the Robert A. Welch Foundation is gratefully acknowledged.

Supporting Information Available: X-ray experimental details with positional parameters and full bond distances and angles for [**3**][BF_4] and **4** and a summary of theoretical results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. All DFT calculations were performed using the Gaussian 94 (Revision B2) suite of programs. All-electron basis sets were used for C, H (6-31 G(d)), and the group 13 elements (6-31+G(d)).

[12] See, for example: Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345.

[13] Prepared by treatment of $MeGaCl_2$ with 2 equiv of Cp*Li. Details will be published in a forthcoming full paper.

[14] For a discussion of C_6F_5 transfer reactions, see, e.g.: Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1997**, *16*, 2798.

[15] Fisher, J. D.; Wei, M.-Y.; Willett, R.; Shapiro, P. J. *Organometallics* **1994**, *13*, 3324.