

Syntheses and Structures of a Stable Gallole Free of Lewis Base Coordination and Its Dianion[†]

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Abstract: A stable Lewis base-free gallole bearing a bulky Mes* group (= 2,4,6-*t*-Bu)₃C₆H₂) was synthesized by the treatment of Mes*GaCl₂ with a 3,6-dilithio-3,5-octadiene derivative. Reduction of the gallole with lithium metal afforded the corresponding gallole dianion species as a lithium salt. Structures of the gallole and the lithium salt of the gallole dianion have been elucidated by using X-ray crystallographic analysis, NMR spectroscopies, and density functional theory (DFT) calculations.

Keywords: heteroles of heavier group 13 elements; gallole; gallole dianions; X-ray crystallographic analysis

Introduction

Heteroles of group 13 elements have attracted much attention in the fields of not only fundamental organometallic chemistry but also functional materials, because they are expected to exhibit unique optical and electronic properties owing to the possible interactions between the π/π^* orbitals of the butadiene moieties and the vacant p orbitals on the group 13 elements. Especially, stable borole derivatives bearing various substituents on the butadiene moieties and the boron atoms have been synthesized, and their properties and reactivities have been investigated extensively.^[1] In contrast, studies on the syntheses and properties of heavier element analogues of boroles have remained limited so far,^[2,3,4,5] despite the fact that gallole **I**, the first example of an isolable gallole free of Lewis base coordination (*i.e.*, the gallium center is not coordinated by Lewis bases), was synthesized two decades ago (Figure 1).^[6] In particular, there had been no report on the electron acceptability of the heavier group 13 heteroles. Recently, we have reported the synthesis and properties of the first stable alumole **1a**.^[7,8] Reduction of alumole **1a** with lithium afforded the lithium salt of the corresponding alumole dianion **2a**, suggesting the electron acceptability of heteroles of heavier group 13 elements. These results invoke the question on electron-accepting ability of other group 13 heteroles, such as galloles. Herein, we report the synthesis and reduction of stable gallole **1b**.

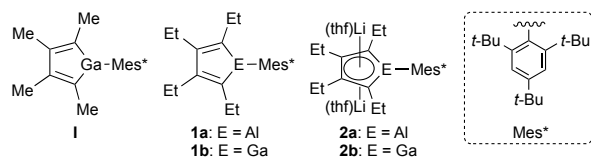


Figure 1. Examples of stable alumoles and galloles. Mes* = 2,4,6-(*t*-Bu)₃C₆H₂.

Experimental

General remarks

All the manipulations were conducted under an inert atmosphere of dry argon by using standard

Schlenk techniques and glove boxes. Solvents were purified by the Ultimate Solvent System, Glass Contour Company^[9] and by bulb-to-bulb distillation from a potassium mirror. NMR spectra were measured on a Bruker Avance III 600US Plus spectrometer. Chemical shifts (δ) are reported in parts per million and are referenced against solvent signals (^1H , ^{13}C) or an external standard (^7Li : LiBr in D_2O). Mass spectra were recorded on a Bruker micrOTOF mass spectrometer equipped with an AMR DART-SVP ion source using He as an ionization gas. UV/vis spectra were recorded on a SHIMADZU UV-1700 UV-vis-NIR spectrometer. Melting points were determined on a Yanaco micro melting point apparatus and uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. $\text{Mes}^*\text{GaCl}_2$ ^[10] and 3,6-dilithio-3,5-octadiene derivative **3**^[11] were prepared according to literatures.

Synthesis of gallole **1b**

To a toluene solution (5 mL) of 3,6-dilithio-3,5-octadiene **3** (0.25 g, 0.84 mmol) was added $\text{Mes}^*\text{GaCl}_2$ (0.33 g, 0.84 mmol) at room temperature. The solution was stirred for 6 h. After removal of the solvent under reduced pressure, the residue was dissolved in hexane and filtered. The filtrate was concentrated and stored at $-35\text{ }^\circ\text{C}$ to afford **1b** as colorless crystals (0.17 g, 0.35 mmol, 42%). mp $109\text{--}110\text{ }^\circ\text{C}$. ^1H NMR (600 MHz, C_6D_6): δ 1.11 (t, $J = 7.4\text{ Hz}$, 6H, $\alpha\text{-CH}_2\text{CH}_3$), 1.11 (t, $J = 7.5\text{ Hz}$, 6H, $\beta\text{-CH}_2\text{CH}_3$), 1.30 (s, 9H, $p\text{-C}(\text{CH}_3)_3$), 1.47 (s, 18H, $o\text{-C}(\text{CH}_3)_3$), 2.42 (q, $J = 7.5\text{ Hz}$, 4H, $\beta\text{-CH}_2\text{CH}_3$), 2.52 (q, $J = 7.4\text{ Hz}$, 4H, $\alpha\text{-CH}_2\text{CH}_3$), 7.52 (s, 2H, $m\text{-ArH}$); ^{13}C NMR (151 MHz, C_6D_6): δ 15.31 ($\beta\text{-CH}_2\text{CH}_3$), 17.33 ($\alpha\text{-CH}_2\text{CH}_3$), 21.73 ($\beta\text{-CH}_2\text{CH}_3$), 25.16 ($\alpha\text{-CH}_2\text{CH}_3$), 31.57 ($p\text{-C}(\text{CH}_3)_3$), 31.79 ($o\text{-C}(\text{CH}_3)_3$), 34.90 ($p\text{-C}(\text{CH}_3)_3$), 38.12 ($o\text{-C}(\text{CH}_3)_3$), 121.66 ($m\text{-ArC}$), 134.40 ($ipso\text{-ArC}$), 142.49 (Ga-C=C), 150.02 ($p\text{-ArC}$), 153.68 (Ga-C=C), 156.39 ($o\text{-ArC}$); UV/vis (hexane): λ_{max} 333 nm (ϵ 1.4×10^3); HRMS (ESI-DART TOF, positive-mode) m/z calcd for $\text{C}_{30}\text{H}_{50}^{69}\text{Ga}^+$ ($[\text{M}+\text{H}]^+$): 479.3163, found: 479.3155. Because of extremely high air- and moisture-sensitivity, satisfactory results of the elemental analyses could not be obtained.

Synthesis of lithium salt of gallole dianion **2b**

To a THF solution (1.5 mL) of gallole **1b** (0.061 g, 0.094 mmol) was added lithium (0.078 g, 1.1 mmol) at room temperature, and the mixture was stirred for 12 h. Excess lithium was removed by filtration, and the filtrate was concentrated and stored at $-35\text{ }^{\circ}\text{C}$ to afford **2b** as orange crystals (0.046 g, 0.072 mmol, 56%). mp $149\text{ }^{\circ}\text{C}$ (dec.). ^1H NMR (600 MHz, C_6D_6): δ 1.17–1.19 (m, 8H, $\text{O}-\text{CH}_2\text{CH}_2$), 1.33 (t, $J = 7.4\text{ Hz}$, 6H, $\beta\text{-CH}_2\text{CH}_3$), 1.42 (t, $J = 7.4\text{ Hz}$, 6H, $\alpha\text{-CH}_2\text{CH}_3$), 1.52 (s, 9H, $p\text{-C}(\text{CH}_3)_3$), 2.06 (s, 18H, $o\text{-C}(\text{CH}_3)_3$), 2.88 (q, $J = 7.4\text{ Hz}$, 4H, $\beta\text{-CH}_2\text{CH}_3$), 2.99 (q, $J = 7.4\text{ Hz}$, 4H, $\alpha\text{-CH}_2\text{CH}_3$), 3.27–3.30 (m, 8H, $\text{O}-\text{CH}_2\text{CH}_2$), 7.82 (s, 2H, $m\text{-ArH}$); ^{13}C NMR (151 MHz, C_6D_6): δ 19.89 ($\beta\text{-CH}_2\text{CH}_3$), 21.53 ($\beta\text{-CH}_2\text{CH}_3$), 21.73 ($\alpha\text{-CH}_2\text{CH}_3$), 25.30 ($\text{O}-\text{CH}_2\text{CH}_2$), 27.05 ($\alpha\text{-CH}_2\text{CH}_3$), 32.01 ($p\text{-C}(\text{CH}_3)_3$), 34.32 ($o\text{-C}(\text{CH}_3)_3$), 35.18 ($p\text{-C}(\text{CH}_3)_3$), 38.81 ($o\text{-C}(\text{CH}_3)_3$), 68.62 ($\text{O}-\text{CH}_2\text{CH}_2$), 110.59 ($\text{Ga}-\text{C}=\text{C}$), 110.61 ($\text{Ga}-\text{C}=\text{C}$), 119.85 ($m\text{-ArC}$), 145.23 ($ipso\text{-ArC}$), 147.09 ($p\text{-ArC}$), 157.39 ($o\text{-ArC}$); ^7Li NMR (117 MHz, C_6D_6): δ -6.75 ; UV/vis (THF): λ_{max} 372 (ϵ 9.3×10^2), 308 nm (ϵ 1.7×10^3). HRMS (ESI-DART TOF, positive-mode) m/z calcd for $\text{C}_{30}\text{H}_{50}^{69}\text{Ga}^+$ ($[\text{M}-2\text{Li}-2\text{THF}+\text{H}]^+$): 479.3163, found: 479.3123. Elemental analysis calcd (%): C, 71.46; H, 10.72; found: C, 70.29; H, 10.11. Because of extremely high air- and moisture-sensitivity of **2b**, satisfactory analytical data could not be obtained.

X-Ray crystallographic analysis

Single crystals of **1b** and **2b** suitable for the X-ray crystallographic analyses were obtained by the cooling of their saturated solutions in hexane or THF, respectively, to $-35\text{ }^{\circ}\text{C}$. The reflection data of **1b** and **2b** were collected at $-170\text{ }^{\circ}\text{C}$ on a Rigaku Mercury CCD diffractometer by using a graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71070\text{ \AA}$) and were integrated, scaled, and averaged by using the HKL-2000 program package.^[12] Semi-empirical absorption correction was applied using the program of MULABS.^[13] The structures were solved by a direct method (SIR2004^[14]) and refined by full-matrix least square method on F^2 for all reflections (SHELXL-97^[15]). All hydrogen atoms were

placed using AFIX instructions, while all other atoms were refined anisotropically. CCDC-974707 (**1b**) and 974708 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **1b**: triclinic, space group $P-1$ (#2), $a = 11.3257(2)$, $b = 14.0405(2)$, $c = 19.1576(4)$ Å, $\alpha = 70.7847(8)$, $\beta = 89.1931(13)$, $\gamma = 79.8546(12)^\circ$, $V = 2828.55(9)$ Å³, $Z = 4$, $\mu = 0.986$ mm⁻¹, $1.56^\circ < \theta < 25.50^\circ$, Reflections collected 24967, Independent reflections 10462, $R_{\text{int}} = 0.0361$, Completeness to θ_{max} 99.5%, 601 parameters refined, R_1 ($I > 2\sigma(I)$) = 0.0383, wR_2 (all data) = 0.1109, GOF = 1.035, largest diff. peak and hole 1.022 and -0.680 e Å⁻³.

Crystal data for **2b**: tetragonal, space group $P4_32_12$ (#96), $a = b = 10.4517(1)$, $c = 34.1107(5)$ Å, $V = 3726.19(7)$ Å³, $Z = 4$, $\mu = 0.767$ mm⁻¹, $2.04^\circ < \theta < 25.49^\circ$, Reflections collected 39038, Independent reflections 3468, $R_{\text{int}} = 0.0426$, Completeness to θ_{max} 100.0%, 218 parameters refined, R_1 ($I > 2\sigma(I)$) = 0.0215, wR_2 (all data) = 0.0597, GOF = 1.064, largest diff. peak and hole 0.236 and -0.322 e Å⁻³.

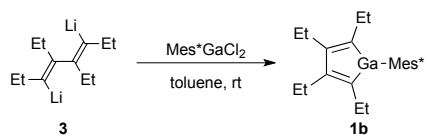
Density functional theory (DFT) calculations

For geometry optimization and frequency calculations of **1b** and **2b**, the B3PW91 density functional with the 6-31G(d) basis set was employed. The 6-311+G(2df) basis set and the B3PW91 density functional were used for the time-dependent (TD)-DFT and GIAO calculations. *Gaussian 09* (Revision C.01)^[16] program package was used for the calculations. Cartesian coordinates of the optimized structures of **1b** and **2b** are included in the Supporting Information.

Results and Discussion

Gallol **1b** was synthesized according to the synthetic protocol of alumole **1a** (Scheme 1).^[7] Reaction of Mes*GaCl₂,^[10] which was prepared from Mes*Li and GaCl₃ in Et₂O/hexane, with 3,6-dilithio-3,5-octadiene derivative **3**^[11] in toluene at room temperature afforded **1b** almost quantitatively. After

recrystallization from hexane at $-35\text{ }^{\circ}\text{C}$, gallole **1b** was isolated as a colorless, highly air- and moisture-sensitive solid (isolated yield: 42%).



Scheme 1. Synthesis of gallole **1b**.

Although the crystal structure of stable gallole **I** was reported previously,^[6] relatively large standard errors in the structural parameters of **I** make it difficult to precisely analyze the structure of the gallole ring (*e.g.*, selected bond lengths (Å) for **I**: Ga–C 1.888(21)–1.953(22), C_α–C_β 1.312(37), 1.317(37), C_β–C_γ 1.542(37)). Therefore, in this work molecular structure of gallole **1b** was established by the X-ray crystallographic analysis. In the unit cell, two crystallographically independent molecules of **1b** were found, while their structural parameters were almost identical to each other (Figure 2). The Ga–C bond lengths in **1b** are comparable to those observed in the previously reported triorganogallium compounds (*e.g.*, GaMes₃: Ga–C 1.968(4) Å^[17]). The gallole ring is completely planar, as shown by the sum of the internal bond angles (540°). The bond-length alternation was observed in the butadiene moiety of the gallole ring. These structural features of **1b** are closely related to those of alumole **1a**. The structural parameters for **1b** have been well reproduced by the DFT calculations at the B3PW91/6-31G(d) level of theory.

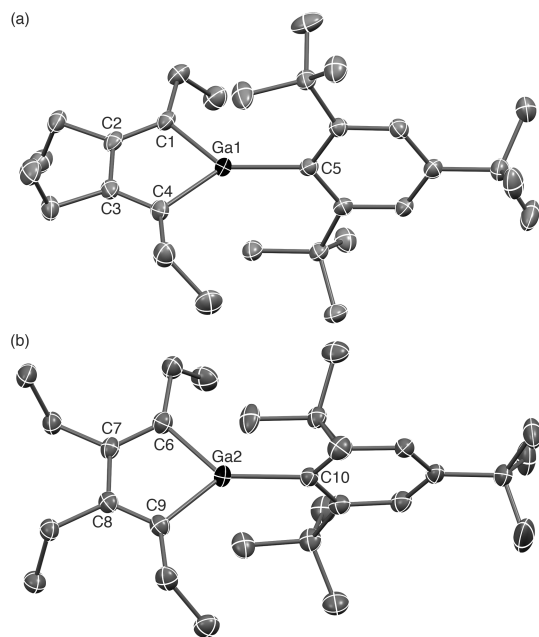


Figure 2. Molecular structure of gallole **1b**. (a) Molecule **A**. (b) Molecule **B**. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Molecule **A**: Ga1–C1 1.976(2), Ga1–C4 1.969(2), Ga1–C5 1.966(2), C1–C2 1.342(3), C2–C3 1.526(3), C3–C4 1.344(3); Molecule **B**: Ga2–C6 1.974(2), Ga2–C9 1.974(2), Ga2–C10 1.969(2), C6–C7 1.347(3), C7–C8 1.523(3), C8–C9 1.346(3).

UV-vis spectrum of gallole **1b** in hexane exhibited the longest absorption maximum at $\lambda_{\text{max}} = 333$ nm, which is bathochromically shifted compared to that of alumole **1a** ($\lambda_{\text{max}} = 318$ nm in hexane).^[7] TD-DFT calculations on **1a** and **1b** (B3PW91/6-311+G(2df)) suggested that these absorptions correspond to their HOMO–LUMO excitations (**1a**: $\lambda_{\text{calcd}} = 334$ nm, $f = 0.0526$; **1b**: $\lambda_{\text{calcd}} = 346$ nm, $f = 0.0372$), indicating that the HOMO–LUMO energy gap of **1b** should slightly decrease compared to that of **1a**. The DFT calculations revealed that the lowering of the LUMO energy level of **1b** compared to that of **1a** leads to the decrease of the HOMO–LUMO energy gap (Figure 3). The HOMOs of **1a** and **1b** are dominantly composed of the $\pi(\text{diene})$ orbitals, while the LUMOs should be formed by the overlap of the vacant p orbitals of the central group 13 elements and the $\pi^*(\text{diene})$ orbitals.

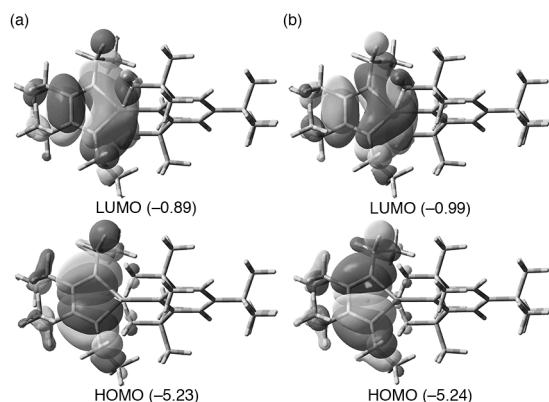
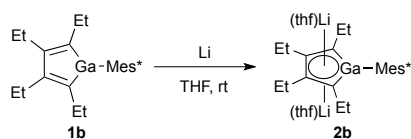


Figure 3. Frontier molecular orbitals of (a) **1a** and (b) **1b**. Energies are shown in eV.

As in the case of reduction of alumole **1a**, treatment of gallole **1b** with excess amount of lithium metal in THF at room temperature afforded the lithium salt of gallole dianion **2b** as orange-colored crystals in 56% yield (Scheme 2). Compound **2b** is extremely air- and moisture-sensitive and readily decompose to form a mixture containing Mes*H and (3*E*,5*E*)-4,5-diethyl-3,5-octadiene upon exposure to air even in the solid state.



Scheme 2. Synthesis of lithium salt of gallole dianion **2b**.

Molecular structure of **2b** was determined by X-ray crystallographic analysis (Figure 4). In the crystalline state, compound **2b** adopts a C_2 symmetric structure with a two-fold axis passing through the Ga1 atom and the midpoint of the C2–C2* bond. Each of the two lithium cations is coordinated by a THF molecule and the gallole ring in an η^5 -fashion. The distances between the Li1 atom and the gallole ring atoms (Li1–Ga1 2.554(3), Li1–C1 2.278(3), Li1–C1* 2.297(3), Li1–C2 2.098(3), Li1–C2* 2.113(3) Å) are comparable to those in **2a** (Li–Al 2.578(3) Å, Li–C 2.090(3)–2.299(3) Å).^[7] The gallole

ring is completely planar, as shown by the sum of the internal bond angles (540°), and the C–C bond lengths are almost equalized. The Ga1–C1 bond (1.9430(14) Å) is slightly shortened compared to the Ga1–C1 and Ga1–C4 bonds of **1b** (1.969(2)–1.976(2) Å), while the Ga1–C3 bond length (2.0063(19) Å) is elongated compared to the Ga–C(Mes*) bond in **1b** (1.966(2), 1.969(2) Å). Such Ga–C(Mes*) bond elongation in **2b** may be partly due to the steric repulsion between the Mes* group and the [Li(thf)] moieties.

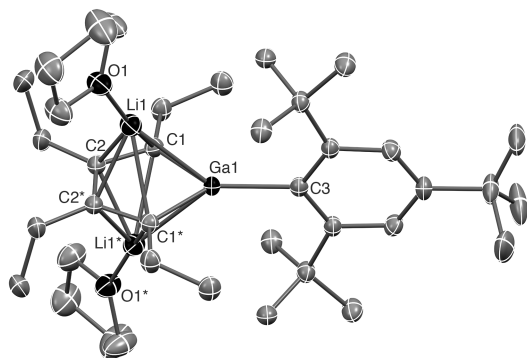


Figure 4. Molecular structure of the lithium salt of gallole dianion **2b**. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ga1–C1 1.9430(14), Ga1–C3 2.0063(19), C1–C2 1.451(2), C2–C2* 1.434(3), Li1–Ga1 2.554(3), Li1–C1 2.278(3), Li1–C1* 2.297(3), Li1–C2 2.098(3), Li1–C2* 2.113(3), Li1–O1 1.909(3).

Selected NMR spectral data of heteroles **1** and dianions **2** are summarized in Figure 5. The ^{13}C NMR spectrum of **2b** in C_6D_6 showed two signals corresponding to the gallole ring carbons at $\delta = 110.55$ (C_α) and 110.57 (C_β) ppm, which are substantially upper-field shifted compared to those of **1b** ($\delta(\text{C}_\alpha) = 142.4$ ppm, $\delta(\text{C}_\beta) = 153.6$ ppm). Reduction of **1a** ($\delta(\text{C}_\alpha) = 144.0$ ppm, $\delta(\text{C}_\beta) = 156.4$ ppm) with lithium also resulted in remarkable upper field shifts of the alumole ring carbon signals ($\delta(\text{C}_\alpha) = 102.6$ ppm, $\delta(\text{C}_\beta) = 112.5$ ppm). These spectral features indicate that the carbon atoms in the heterole rings of **2a** and **2b** have much higher electron densities compared to those in the neutral compounds **1a** and **1b**, respectively. The ^7Li NMR chemical shifts of **2a** ($\delta = -6.0$ ppm) and **2b** ($\delta = -6.8$ ppm) are in good

agreement with the calculated values by using the gauge-independent atomic orbital (GIAO) methods on the optimized structures of **2a** and **2b**, respectively, suggesting that the contact ion pair structures observed in the crystalline state are retained in solution. The small positive NICS values (**1a**: +2.78, **1b**: +3.35) suggest that the heterole rings of **1a** and **1b** are non-aromatic rather than anti-aromatic.^[18] Meanwhile, **2a** and **2b** exhibit highly negative NICS values at the heterole ring centers (**2a**: -15.01, **2b**: -15.45) due to substantial diamagnetic ring currents, which would be interpreted in terms of the spherical aromaticity in the *closo*-7-vertex ELi_2C_4 cluster structures (E = Al, Ga).^[19]

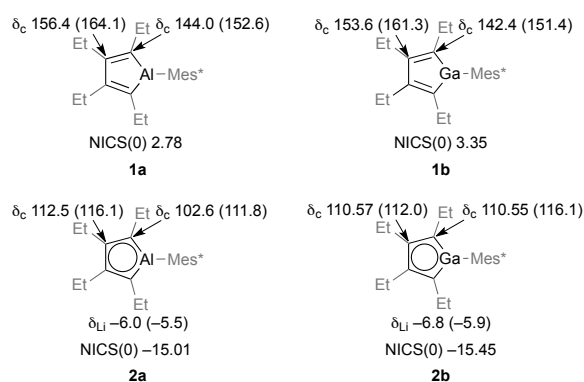


Figure 5. ^{13}C and 7Li NMR spectral data of the heteroles and the dianions (in C_6D_6). Chemical shifts are reported in ppm. Numbers in the parentheses are GIAO-calculated chemical shifts at the B3PW91/6-311+G(2df) level of theory. Nucleus-independent chemical shift (NICS) was calculated at the center of the heterole ring.

Conclusions

Stable gallole **1b** was synthesized and structurally characterized. Reduction of gallole **1b** with lithium afforded the corresponding gallole dianion as the lithium salt **2b**, suggesting that gallole derivatives are promising candidates for electron-accepting materials. The crystal structures and the NMR spectroscopic data of **1b** and **2b** are closely related to those of the aluminum analogues **1a** and **2a**, respectively. In these group 13 heterole dianionic species, the carbon atoms in the heterole rings should

possess remarkably high electron densities.

Acknowledgements

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Graphical Table of Contents

Title: Syntheses and Structures of a Stable Gallole Free of Lewis Base Coordination and Its Dianion

Authors: Tomohiro Agou, Tatsuya Wasano, Takahiro Sasamori, and Norihiro Tokitoh*

Short abstract: A stable Lewis base-free gallole was synthesized. Reduction of a stable gallole with lithium metal afforded the corresponding gallole dianion as the lithium salt, indicating the electron acceptability of the gallole. Structure of the lithium salt of the gallole dianion has been investigated.

