

Aromatic Tetralithiodigalloles with a Ga–Ga Bond: Synthesis and Structural Characterization

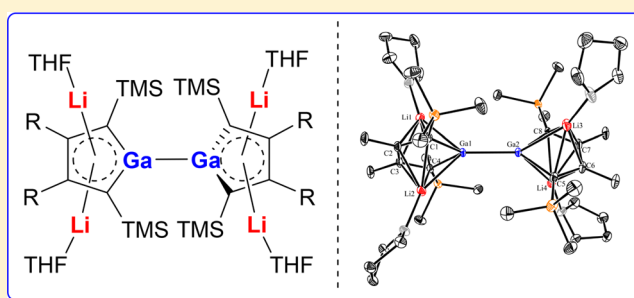
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S Supporting Information

ABSTRACT: Aromatic 1,1,2,2-tetralithiodigalloles **5** with a Ga–Ga bond were realized. Reaction of 1,4-dilithio-1,3-butadienes **6** with 0.5 equiv of GaCl₃ afforded lithium spirogallane ate complexes **7** in excellent isolated yields. Reduction of the above ate complexes **7** with an excess amount of lithium generated the 1,1,2,2-tetralithiodigalloles **5** in moderate isolated yields. The structures of compounds **5** and **7** were both determined by single-crystal X-ray structural analysis. The 1,1,2,2-tetralithiodigalloles **5** contained two aromatic dilithiogalloles connected by a Ga–Ga bond. The aromaticity of **5** was confirmed by both experimental measurements (X-ray structural analysis, NMR spectroscopy) and theoretical analysis (ISE, NICS).



INTRODUCTION

The chemistry of metal-containing aromatics is a fascinating topic and has attracted much attention. A large variety of metallabenzenes, metallabenzynes, dilithiometalloles, and their analogues have been synthesized and characterized in recent years.^{1,2} However, reports on galla-aromatics are very rare,³ probably due to a lack of efficient synthetic methods (Figure 1).

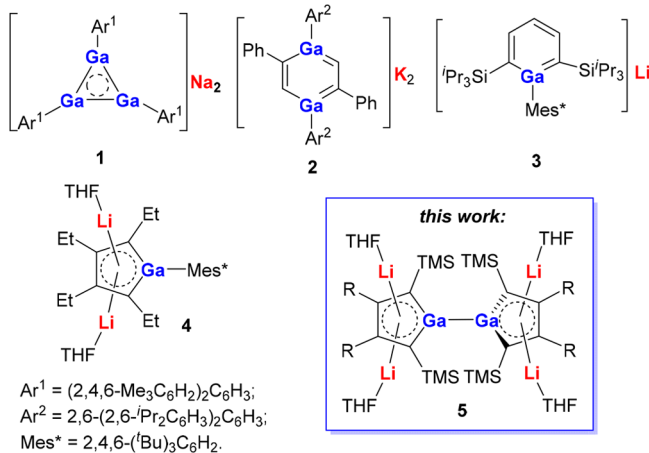


Figure 1. Examples of galla-aromatics.

In 1995, Robinson et al. reported the synthesis and characterization of the cyclogallane **1**.^{3b} In 2009, Power et al. reported the synthesis and characterization of a digallatabenzene **2**.⁴ In 2015, Yamashita et al. reported the synthesis and isolation of

the anionic gallabenzene **3**⁵ and Tokitoh et al. reported the formation and crystal structure of the aromatic dilithiogalloles **4**.⁶ For all of the above successful examples, highly hindered substituents on the Ga atom are required to stabilize the organogallium compounds. We have been interested in the synthetic applications of multiply substituted 1,4-dilithio-1,3-butadienes (dilithio reagents for short),⁷ which could behave as non-innocent ligands and formal oxidants.⁸ On the basis of this unique behavior of dilithio reagents, we have reported the synthesis and characterization of dilithionickeloles,⁹ dilithio rhodacycles,¹⁰ dicupra[10]annulenes,¹¹ and spiro metallaaromatics of Pd, Pt, and Rh,¹² which extended the concept of aromaticity. In this paper, we report the successful synthesis, isolation, and characterization of multiply substituted aromatic 1,1,2,2-tetralithiodigalloles **5** with a Ga–Ga bond.¹³ Both experimental measurements (X-ray structural analysis, NMR spectroscopy) and theoretical analysis (ISE, NICS) demonstrated the aromaticity of **5**.

RESULTS AND DISCUSSION

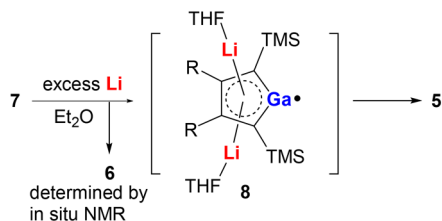
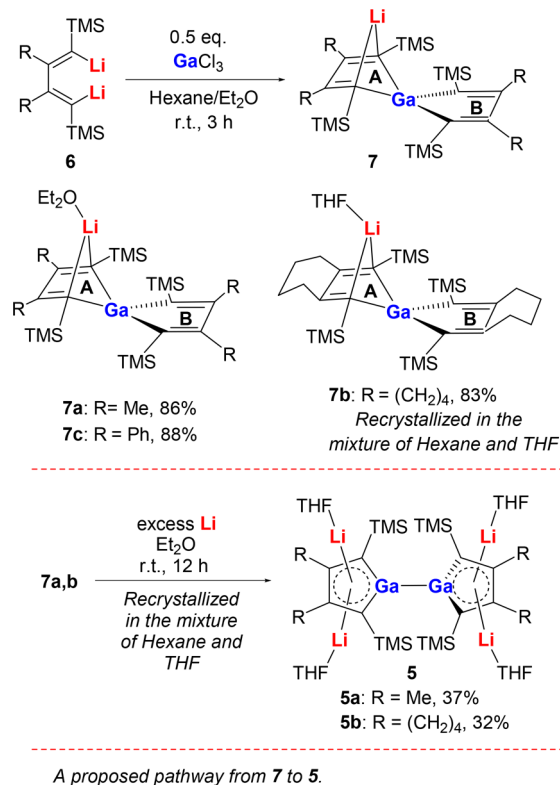
As shown in Scheme 1, on treatment of dilithio reagents **6** with 0.5 equiv of GaCl₃ in a mixture of hexane and diethyl ether (Et₂O) at room temperature for 3 h, the lithium spirogallane ate complexes **7a–c** were obtained as white solids in excellent isolated yields. Reduction of **7a,b** with an excess amount of lithium in Et₂O at room temperature for 12 h resulted in the formation of the 1,1,2,2-tetralithiodigalloles **5a,b**. No reaction

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was observed when **7c** was treated with lithium. Compounds **5** and **7** were all air sensitive but thermally stable under inert conditions. A proposed reaction pathway for the reduction process is also given in Scheme 1. Reduction of **7** with lithium

Scheme 1. Synthesis of Lithium Spirogallane Ate Complexes **7 and 1,1,2,2-Tetalithiodigalloses **5****



would afford the dilithiogallole radical **8**,¹⁴ along with the concomitant loss of the dilithio reagent **6**,^{2a,b,13e} which was detected by in situ NMR characterization. Dimerization of the dilithiogallole radical **8** would lead to **5**, forming a Ga–Ga bond.¹⁴

Single crystals of compounds **7a,c** suitable for X-ray diffraction were obtained via recrystallization from a mixture of hexane and Et₂O, while single crystals of **7b** were obtained via recrystallization from a mixture of hexane and tetrahydrofuran (THF). The molecular structures of **7a–c** were confirmed by X-ray crystallographic analysis (see the Supporting Information). All crystallized in the monoclinic *P*₂₁/*n* space group. Figure 2 shows the structure of **7a**. The structure contains two galloles that share a common tetrahedral spiro Ga atom. The Et₂O-coordinated lithium atom was located above one gallole (ring A). Both ring A and ring B exhibited clear bond alternation. Ring A is not coplanar with a 16.0° envelope angle due to the coordination effect of lithium, while ring B is nearly coplanar, which is different from the lithium salt of spirogallane with two planar gallole units as reported by Robinson et al.¹⁵ Density functional theory (DFT) calculations

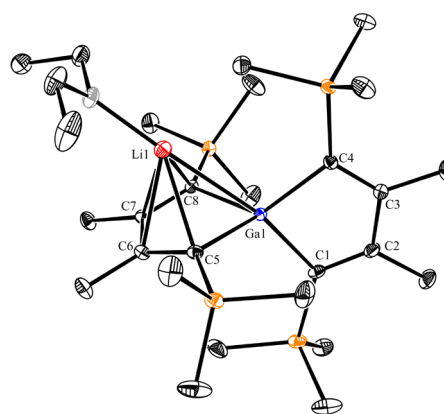


Figure 2. ORTEP drawing of **7a** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

were carried out using Gaussian 09 (see the Supporting Information).¹⁶ Structures of **7a** without coordinated Et₂O were optimized at the B3LYP level.¹⁷ The 6-31+G* basis set was used for all the elements. The optimized structures of **7a** were consistent with the X-ray structure. The HOMO mainly localizes on butadienyl parts, while the LUMO localizes both on the butadienyl parts and the Ga–C bonds (Figure S6 in the Supporting Information). The orbital structures shows no spiro conjugation between the two rings.

Single crystals of 1,1,2,2-tetalithiodigalloses **5a,b** suitable for X-ray diffraction were obtained via recrystallization from a mixture of hexane and THF at room temperature as colorless solids. They crystallized in the triclinic *P* $\bar{1}$ and *P*₂₁/*c* space groups, respectively. Here we discuss the structure of **5a** in detail as an example. In the unit cell, two crystallographically independent units of **5a** were found; the structure of one is shown in Figure 3. The structure contains two galloles

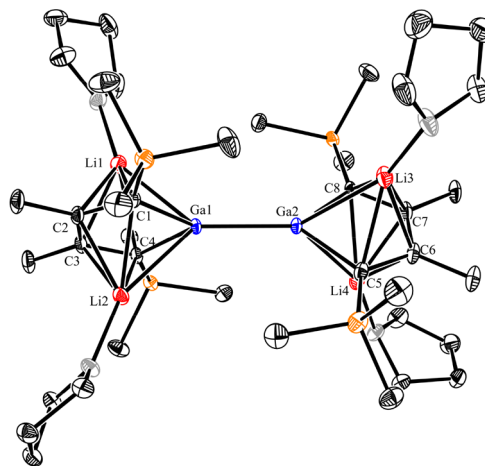


Figure 3. ORTEP drawing of **5a** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

connected by a Ga–Ga bond. Both galloles are coplanar. The four THF-coordinated Li atoms are located above and below the galloles and are bonded in an η^5 fashion. The dihedral angle between the two galloles is 74.691°. The C–C bond lengths within the galloles are remarkably averaged (1.459(4), 1.419(4), and 1.457(3) Å), implying considerable delocalization of π electrons over the ring. The Ga–C bond lengths (1.971(2), 1.970(2), 1.974(3), 1.978(2) Å) in **5a** are obviously

shorter than those in **7a** (2.0054(13), 2.0024(13), 2.0457(13), 2.0509(12) Å) but longer than those observed in the gallate dianion compounds (1.9430(14) Å).⁶ The Ga1–Ga2 bond length is 2.3705(3) Å, which falls in the range of the reported Ga–Ga distances.¹³

Multinuclear NMR measurements of **5** and **7** in *d*₈-THF were carried out. Representative data are summarized in Table 1.

Table 1. Comparison of Representative NMR Data between **5a and **7a** (ppm)^a**

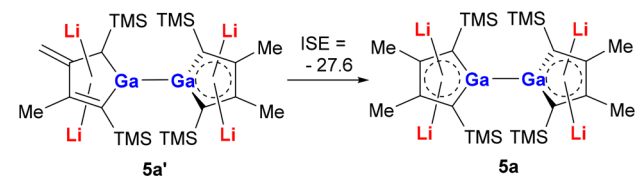
	7a	5a
¹ H NMR for Me	2.07	2.43
¹³ C NMR for Me	15.8	20.1
⁷ Li NMR	−0.96	−6.68

^aThe ¹H and ¹³C NMR data were recorded in *d*₈-THF and the ⁷Li NMR with 0.1 M LiCl in *d*₈-THF as the external standard.

In the ¹H NMR of **7a**, only one Me signal (2.07 ppm) and one TMS signal (−0.09 ppm) were found, indicating that rings A and B were identical in solution. In the ¹H NMR of **5a**, the signal attributable to Me was found at 2.43 ppm. The low-field shift of **5a** is evidently caused by the deshielding effect of the diatropic ring current. The ¹³C NMR spectra show a similar tendency. The ⁷Li NMR chemical shift attributable to **7a** was found at −0.96 ppm, which was in the range of normal organolithium compounds. However, the ⁷Li NMR signal attributable to **5a** was found at −6.68 ppm, a remarkable high-field shift obviously caused by the strong shielding effect of the diatropic ring current, clearly showing the aromaticity of **5a**.

Density functional theory (DFT) calculations were carried out. Structures of the 1,1,2,2-tetralithiodigalloses **5a** without coordinated THF and its analogues were optimized at the B3LYP level.¹⁷ The 6-31+G* basis set was used for all of the elements. As a simple and efficient tool to judge aromaticity, the nucleus-independent chemical shift (NICS) was calculated.¹⁸ The considerably negative NICS(1) value (above the center of the GaC₄ ring, −11.1 ppm) strongly suggested its aromaticity. The isomerization stabilization energy (ISE) was also calculated.¹⁹ The negative energies (−27.6 kcal/mol) of **5a** and corresponding **5a'** demonstrate that **5a** is much more stable due to aromaticity (Scheme 2).

Scheme 2. ISE Evaluations of Aromaticity of the 1,1,2,2-Tetralithiodigallose **5a and its Corresponding Spiroene (kcal/mol)**



CONCLUSIONS

In summary, we have synthesized and structurally characterized multiply substituted aromatic 1,1,2,2-tetralithiodigalloses with a Ga–Ga bond. These results extended the chemistry of gallate aromatics.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise noted, all starting materials were commercially available and were used without further

purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System. ^tBuLi was obtained from Acros. All reactions were carried out under a dry and oxygen-free nitrogen atmosphere under slight positive pressure by using Schlenk techniques or under a nitrogen atmosphere in a Mikrouna Super (1220/750) glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieve catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O₂/H₂O Combi-Analyzer to ensure that both were always below 1 ppm. The bulk purity of new compounds was established by NMR spectroscopy unless stated otherwise.

Analytical Techniques. ¹H, ¹³C, and ⁷Li NMR spectra were recorded on a Bruker ARX400 spectrometer (FT, 400 MHz for ¹H, 100 MHz for ¹³C, and 156 MHz for ⁷Li) or a Bruker AVANCE III spectrometer (FT, 500 MHz for ¹H, 126 MHz for ¹³C, and 195 MHz for ⁷Li) at 30 °C, unless otherwise noted.

X-ray diffraction studies for compound **7a–c** and **5a,b** were carried out on a SuperNova diffractometer, using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved with shelxs-97 or Olex2 and refined with the XL refinement package using least-squares minimization. Refinement was performed on *F*² anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection, and processing parameters for compounds **7a–c** and **5a,b** were summarized. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1554099 (**7a**), CCDC 1554101 (**7b**), CCDC 1554103 (**7c**), CCDC 1554104 (**5a**), and CCDC 1554105 (**5b**).

Synthesis of Compounds **7.** In a nitrogen atmosphere glovebox, 1,4-dithio-1,3-butadiene **6** (1.05 mmol) was dissolved in Et₂O (3 mL) in a 50 mL flask. Then GaCl₃ (0.5 mmol, 88 mg), which was dissolved in hexane (3 mL) first, was added at room temperature. The mixture was stirred at room temperature for 3 h. Then the solvent was removed under reduced pressure and the residue was extracted by hexane (5 mL). After filtering, the solvent was removed under reduced pressure, **7** could be obtained as white solids. Single crystals of compounds **7a,c** suitable for X-ray diffraction were obtained via recrystallization from a mixture of hexane and Et₂O, while single crystals of **7b** were obtained via recrystallization from a mixture of hexane and THF.

7a: colorless solid, isolated yield 86% (258 mg). ¹H NMR (500 MHz, *d*₈-THF): δ −0.09 (s, 36H, CH₃), 1.11 (t, *J* = 7.0 Hz, 6H, CH₂), 2.07 (s, 12H, CH₃), 3.38 (q, *J* = 7.0 Hz, 4H, CH₂). ¹³C NMR (126 MHz, *d*₈-THF): δ 2.4, 15.8, 23.9, 66.5, 157.0, 157.5. ⁷Li NMR (195 MHz, *d*₈-THF): −0.96.

7b: colorless solid, isolated yield 83% (270 mg). ¹H NMR (500 MHz, *d*₈-THF): δ −0.09 (s, CH₃, 36H), 1.59 (br, CH₂, 8H), 1.75–1.80 (m, CH₂, 4H), 2.57 (br, CH₂, 8H), 3.60–3.65 (m, CH₂, 4H). ¹³C NMR (126 MHz, *d*₈-THF): δ 2.4, 25.9, 26.5, 35.7, 68.4, 155.2, 159.8. ⁷Li NMR (195 MHz, *d*₈-THF): −0.89.

7c: colorless solid, isolated yield 88% (373 mg). ¹H NMR (400 MHz, *d*₈-THF): δ −0.22 (s, 36H, CH₃), 1.11 (t, *J* = 7.0 Hz, 6H, CH₂), 3.38 (q, *J* = 7.1 Hz, 4H, CH₂), 6.69–6.75 (m, 4H, CH), 6.80–6.86 (m, 8H, CH), 6.88–6.94 (m, 8H, CH). ¹³C NMR (100 MHz, *d*₈-THF): δ 120.28, 124.25, 129.04, 134.12, 134.64, 144.40, 193.84. ⁷Li NMR (195 MHz, *d*₈-THF): −0.91.

Synthesis of Compounds **5.** In a nitrogen atmosphere glovebox, the lithium spirogallane complex **7** (0.4 mmol) was dissolved in Et₂O (5 mL) in a 50 mL flask. Then Li (5 mmol, 35 mg) was added at room temperature. The system was continuously stirred for 12 h, and then the solvent was removed under reduced pressure and the residue was extracted with hexane (5 mL). After filtering, the solvent was removed under reduced pressure. Then hexane (4 mL) and THF (0.5 mL) were added, and after the mixture was stirred for 1 h, the solvents were removed in the glovebox naturally. After the red solids were collected and recrystallized in a mixed solvent of hexane and THF at room temperature, pure **5** could be obtained. Single crystals of **5** suitable for

X-ray analysis were grown in a mixed solvent of hexane and THF for 3 days at room temperature.

5a: dark red solid, isolated yield 37% (134 mg). ^1H NMR (500 MHz, d_8 -THF): δ 0.14 (s, CH_3 , 36H), 1.75–1.81 (m, CH_2 , 16H), 2.43 (s, CH_3 , 12H), 3.59–3.65 (m, CH_2 , 16H). ^{13}C NMR (126 MHz, d_8 -THF): δ 6.6, 20.1, 26.5, 68.4, 121.2, 121.7. ^7Li NMR (195 MHz, d_8 -THF): δ –6.68.

5b: dark red solid, isolated yield 32% (122 mg). ^1H NMR (500 MHz, d_8 -THF): δ 0.13 (s, CH_3 , 36H), 1.75–1.85 (m, CH_2 , 24H), 2.91 (br, CH_2 , 8H), 3.59–3.65 (m, CH_2 , 16H). ^{13}C NMR (126 MHz, d_8 -THF): δ 6.8, 26.5, 28.0, 33.7, 68.4, 118.9, 124.3. ^7Li NMR (195 MHz, d_8 -THF): δ –6.63.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00447.

Crystallographic data for **5a,b** and **7a–c**, NMR data, experimental details, and spectra for all new compounds, and calculation details (PDF)

Cartesian coordinates for calculated structures (XYZ)

Accession Codes

CCDC 1554099, 1554101, and 1554103–1554105 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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