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Tetrakis(trimethylsilyl)cyclobutadiene Dianion Alkaline Earth Metal Salts: New Members of the 6π-Electron Aromatics Family

Kazunori Takanashi,[a] Akira Inatomi,[a] Vladimir Ya. Lee,[a] Masaaki Nakamoto,[a] Masaaki Ichinohe,[a] and Akira Sekiguchi*[a]

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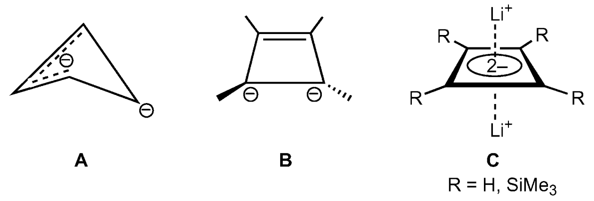
The magnesium and calcium salts of the tetrakis(trimethylsilyl)cyclobutadiene dianion, $[Mg(thf)_3]^{2+}[(Me_3Si)_4C_4]^{2-}$ (**2a**) and $[Ca(thf)_n]^{2+}[(Me_3Si)_4C_4]^{2-}$ (**2b**), were synthesized by the reduction of tetrakis(trimethylsilyl)cyclobutadiene [$(Me_3Si)_4C_4$, **1**] with metallic magnesium or calcium, respectively. X-ray analysis of **2a** showed a planar four-membered ring, featuring a diagnostic η^4-coordination to the magnesium atom and skeletal C–C bond lengths intermediate between those of typical C–C single and C=C double bonds. The structural and spectral features of the cyclobutadiene dianion magnesium salt **2a** give evidence for its appreciable aromaticity.

Introduction

The overall behavior of small doubly charged cyclic systems, such as the 6π-electron cyclobutadiene dianion, is greatly determined by the severe Coulomb repulsive interaction between the two negative charges, which might outweigh the advantage gained through cyclic π-delocalization and aromatic stabilization.[1] Such a tendency is strikingly different from the situation with the isoelectronic singly charged cyclopentadienide ion, which can benefit from the aromatic 6π-electron cyclic delocalization.[2] In sharp contrast, the delocalization in the cyclobutadiene dianion is, in effect, a destabilizing trend because of the unavoidable mixing of the two extra electrons, resulting in a strong Coulomb repulsion.[1] Another important reason, responsible for the overall destabilization of the cyclobutadiene dianion, is the fact that in the planar D_{4h} structure, four π-electrons are forced to occupy the nonbonding orbitals to form a pair of doubly degenerate HOMOs, thus giving rise to strongly repulsive 1,3-antibonding interactions. Such unfavorable trends result in appreciable electron localization and, consequently, in a significant departure of the cyclobutadiene dianion ring from D_{4h} planarity. Accordingly, the early calculations by Schaad et al. reported the structure of the $[C_4H_4]^{2-}$ dianion as a puckered four-membered ring with one localized and one allylic-type delocalized negative charge and possessing a small degree of cyclic 6π-electron delocalization (Scheme 1, **A**).[3]



Scheme 1. Cyclobutadiene dianion structures.

More elaborate calculations by van Zandwijk et al. showed that the above conformation was actually a saddle point on the potential energy surface, whereas the true minimum structure of the cyclobutadiene dianion has a C=C double bond and the two negative charges located on the two adjacent carbon atoms, thus giving a trapezoid shape to the four-membered ring (Scheme 1, **B**).[4] However, Schleyer and co-workers demonstrated that the introduction of positive lithium ions greatly counteracts the unfavorable Coulomb repulsion, resulting in a much greater extent of cyclic delocalization and aromaticity of the system.[5] According to their calculations, the dilithium cyclobutadiene dianion $[Li^+]_2[C_4H_4]^{2-}$ is a planar D_{4h} "inverse sandwich" (Scheme 1, **C**, R = H).[5] Such a delocalized 6π-electron aromatic structure was experimentally realized by the synthesis of the dilithium derivative of the tetrakis(trimethylsilyl)-cyclobutadiene dianion $[Li^+]_2[(Me_3Si)_4C_4]^{2-}$ stabilized by the four π-accepting trimethylsilyl groups (Scheme 1, **C**, R = $SiMe_3$).[6a] A computational study on the three-dimensional aromaticity of **C** was recently reported.[7] We also prepared alkali metal derivatives of the heavy analogs of the cyclobutadiene dianion, namely $[M^+]_2[(tBu_2MeSi)_4Si_4]^{2-}$ and $[M^+]_2[(tBu_2MeSi)_4Si_2Ge_2]^{2-}$ (M = Li, Na, K), which were found to be nonaromatic species, in contrast to

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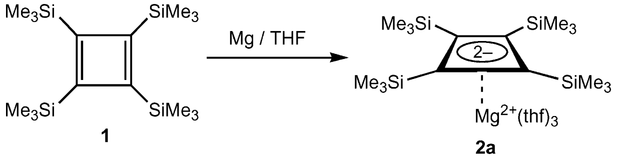
[a] Department of Chemistry, Graduated School of Pure and Applied Sciences, University of Tsukuba
Tsukuba, Ibaraki 305-8571, Japan
Fax: +81-29-853-4314
E-mail: sekiguch@chem.tsukuba.ac.jp

their organic counterparts.[8] Surprisingly, the alkaline earth metal salts of the same derivative, $[M^{2+}][(tBu_2MeSi)_4Si_2Ge_2]^{2-}$ (M = Mg, Ca, Sr), possess totally different structures, namely bicyclo[1.1.0]butane skeletons.[9] In this paper we report the reduction of tetrakis(trimethylsilyl)cyclobutadiene (**1**) with alkaline earth metals (Mg, Ca), resulting in the formation of 6π-electron aromatic derivatives, both featuring a half-sandwich as a novel structural motif among the (cyclobutadiene)metal complexes. One should note that the sandwich complexes of the main group elements, including alkaline earth metals, are still rare, while those having cyclobutadiene as a ligand are unknown.[10]

Results and Discussion

The target alkaline earth metal derivative of the tetrakis(trimethylsilyl)cyclobutadiene dianion, $[Mg]^{2+}[(Me_3Si)_4C_4]^{2-}$ (**2a**), was prepared by treatment of tetrakis(trimethylsilyl)cyclobutadiene (**1**)[11] with excess magnesium metal in THF for 2 d and isolated as pale yellow crystals in 60% yield (Scheme 2).[12]



Scheme 2. Synthesis of the magnesium salt **2a** of the tetrakis(trimethylsilyl)cyclobutadiene dianion.

Because of its highly symmetrical structure, **2a** shows only one signal in both ^1H and ^{29}Si NMR spectra. Thus, the resonance of the substituent silicon atoms in **2a** are observed at δ = –24.7 ppm, a value similar to that of the dilithium derivative **C** (R = $SiMe_3$) (δ = –23.7 ppm).[6a] Such noticeable shielding could be rationalized in terms of the significant transfer of the extra negative charges from the four-membered ring to the electropositive silyl substituents through π–σ* orbital mixing, thus providing an overall stabilization of the system.[6d] The signal of the skeletal carbon atoms in **2a** is observed at δ = 109.2 ppm, demonstrating a marked shielding compared with the value for **1** of δ = 172.1 ppm.[11] Overall, the NMR spectroscopic data provide solid evidence for the presence of a delocalized half-sandwich cyclobutadiene dianion magnesium salt **2a**, in which the cyclobutadiene dianion moiety is isostructural to that of the aromatic dilithium salt **C** (R = $SiMe_3$).

The crystal structure of the magnesium salt **2a** was determined by X-ray crystallographic analysis. Two independent structurally very similar molecules were found in the unit cell, of which only one is shown in Figure 1, and for which the structural parameters are listed in Table 1. The four-membered C_4 ring of **2a** features a diagnostic η^4-coordination to the magnesium ion, which in turn is bonded to the three thf molecules. The Mg–C bonds of 2.235(3)–2.345(4) Å (av. 2.295 Å) are similar to those in bis(cyclopentadienyl)magnesium $[Mg(H_5C_5)_2]$ of 2.283(3)–2.324(7) Å (av. 2.304 Å).[13]

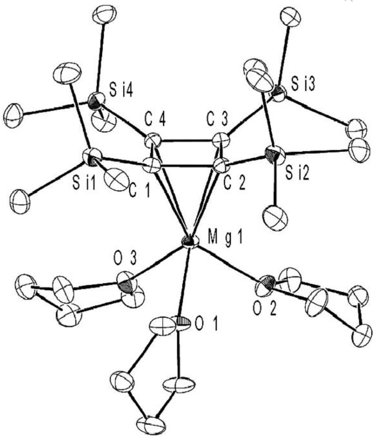


Figure 1. ORTEP drawing of **2a** (hydrogen atoms are not shown). Selected bond lengths [Å]: C1–C2 1.513(5), C2–C3 1.511(4), C3–C4 1.474(5), C1–C4 1.482(4), C1–Mg1 2.289(4), C2–Mg1 2.235(3), C3–Mg1 2.311(4), C4–Mg1 2.345(4), C1–Si1 1.833(3), C2–Si2 1.828(3), C3–Si3 1.827(4), C4–Si4 1.833(3). Selected bond angles [°]: C2–C1–C4 89.4(2), C1–C2–C3 89.1(2), C2–C3–C4 89.7(3), C1–C4–C3 91.8(3). Dihedral angle [°]: C1–C2–C3/C1–C3–C4 0.55(2).

Table 1. Geometrical parameters of the experimental $\{[Mg(thf)_3]^{2+}[(Me_3Si)_4C_4]^{2-}$ (**2a**)} and calculated {**2a** and $[Mg(Me_2O)_3]^{2+}[(H_3Si)_4C_4]^{2-}$ (**2a′**)} structures.

		2a experimental	**2a** calculated	**2a′** calculated
Bond lengths [Å]	C1–C2	1.513(5)	1.513	1.502
	C2–C3	1.511(4)	1.500	1.478
	C3–C4	1.474(5)	1.484	1.469
	C1–C4	1.482(4)	1.492	1.488
	C1–Mg1	2.289(4)	2.272	2.219
	C2–Mg1	2.235(3)	2.244	2.250
	C3–Mg1	2.311(4)	2.300	2.322
	C4–Mg1	2.345(4)	2.329	2.291
Distances of Si substituents above the C_4 plane [Å]	Si1–C_4 plane	0.6414(10)	0.654	0.586
	Si2–C_4 plane	0.7116(10)	0.668	0.524
	Si3–C_4 plane	0.6323(10)	0.603	0.348
	Si4–C_4 plane	0.4237(10)	0.471	0.261

The cyclic π-delocalization was further manifested in the planarity (negligible folding of 0.55°) of the four-membered ring with the sum of the interior bond angles being 360°. The lengths of all endocyclic C–C bonds in **2a** well fit the range between typical C–C single (1.54 Å) and C=C double (1.34 Å) bonds: C1–C2 1.513(5), C2–C3 1.511(4), C3–C4 1.474(5), C1–C4 1.482(4) Å. Interestingly, the distances between the skeletal C atoms and the Si atoms of the substituents [C1–Si1 1.833(3), C2–Si2 1.828(3), C3–Si3 1.827(4), C4–Si4 1.833(3) Å] in **2a** are shorter than the Si–CH_3 (substituent) bonds (av. 1.886 Å) in the same compound, which could be taken as further evidence for the above-mentioned π–σ* hyperconjugation. Structural parameters such as the planarity of the C_4 ring and the lengths of the skeletal C–C bonds, are similar to those in the dilithium salt **C** (R = $SiMe_3$): folding angle 0.89°, cyclic C–C bond lengths 1.485(10), 1.493(4), 1.496(3), 1.507(9) Å.[6a] In contrast, the direction of the silyl substituents is different in the magnesium salt **2a** and the dilithium salt **C** (R = $SiMe_3$). Thus, whereas the Me_3Si substituents in **C** (R = $SiMe_3$) occupy alternating up (0.275 and 0.252 Å) and down (0.297 and 0.267 Å) positions,[6a] the silicon atoms of all four silyl substituents in **2a** are located at 0.4237(10)–0.7116(10) Å above the four-membered carbon ring.

To obtain a deeper insight into the bonding situation of **2a**, we have performed a DFT computational study on the real molecule $[Mg(thf)_3]^{2+}[(Me_3Si)_4C_4]^{2-}$ at the B3LYP/6-31G(d) level of theory.[14] For comparison, the geometrical parameters of the experimental and calculated structures of **2a** are summarized in Table 1. The experimental structural features of **2a** were well reproduced computationally: C–C bond lengths of 1.484–1.513 Å, C–Mg bond lengths of 2.244–2.329 Å, the silicon atoms of all four silyl substituents at 0.471–0.668 Å above the four-membered ring. Because both **2a** and **C** (R = $SiMe_3$) bear the same Me_3Si substituents, the steric repulsion between the substituents and $Mg(thf)_3$ unit in **2a** seems to play a minor role in determining the overall orientation of the silyl groups. Instead, this should rather be attributed to the difference in the bonding modes of the magnesium and lithium salts of **2a** and **C** caused by the difference in the 3p(Mg) and 2p(Li) orbital sizes, which forces the silyl substituents in **2a** to be bent outwards in order to achieve the optimum overlap of the $\pi(C_4)$–3p(Mg) orbitals as depicted in Figure 2. Indeed, the optimized structure of the model $[Mg(OMe_2)_3]^{2+}$-$[(H_3Si)_4C_4]^{2-}$ (**2a′**) bearing less bulky SiH_3 groups shows structural features similar to both experimental and calculated data for **2a**, namely, the location of all four SiH_3 substituents at 0.261–0.586 Å above the C_4 ring.

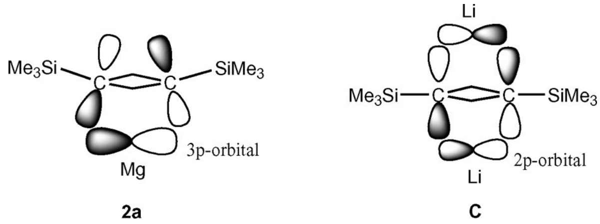


Figure 2. Molecular orbital interaction in the magnesium salt **2a** and the lithium salt **C** (R = $SiMe_3$).

Inspection of the frontier molecular orbitals of **2a** shows a pair of nearly degenerate HOMO (–4.61 eV) and HOMO–1 (–4.75 eV),[15] a situation that is expected for the aromatic cyclobutadiene dianion in its delocalized D_{4h} form. The NICS[16] values were calculated to be negative at 1 Å above and below the center of the ring: NICS(1) = –4.5 (on the side of the Mg center) and NICS(1) = –3.0 (on the opposite side from the Mg center) for **2a**, similar to NICS(1) = –4.5 for **C**.

Conclusions

New representatives of the family of 6π-electron aromatic compounds featuring a persilyl-substituted cyclobutadiene dianion fragment η^4-coordinated to the alkaline earth metal ions, namely the magnesium and calcium salts of the tetrakis(trimethylsilyl)cyclobutadiene dianion $[Mg(thf)_3]^{2+}$-$[(Me_3Si)_4C_4]^{2-}$ (**2a**) and $[Ca(thf)_n]^{2+}[(Me_3Si)_4C_4]^{2-}$ (**2b**), were synthesized by the reduction of tetrakis(trimethylsilyl)-cyclobutadiene [$(Me_3Si)_4C_4$, **1**] with metallic magnesium or calcium, respectively. The diagnostic structural features (ring planarity, lengths of the cyclic C–C bonds) and spectroscopic data, as well as theoretical calculations, of the cyclobutadiene dianion magnesium salt **2a** definitely indicate its 6π-electron cyclic delocalization, and consequently appreciable aromaticity.

Experimental Section

Magnesium Salt of Tetrakis(trimethylsilyl)cyclobutadiene Dianion {$[Mg(thf)_3]^{2+}[(Me_3Si)_4C_4]^{2-}$ (2a)}: Tetrakis(trimethylsilyl)cyclobutadiene (**1**) (80 mg, 0.24 mmol) and excess Mg (21 mg, 0.86 mmol) were placed in a reaction tube with a magnetic stirring bar. Oxygen-free dry thf (2 mL) was introduced into the reaction tube by vacuum transfer, and the reaction mixture was stirred at room temperature to produce a yellow solution over a period of 2 d. The reaction mixture was filtered to remove metallic magnesium, and the solution was cooled to 5 °C to produce pale yellow crystals of **2a** (72 mg, 60%); m.p. 92–94 °C. ^1H NMR (400 MHz, $[D_8]$thf): δ = 0.10 (s, 36 H) ppm. ^{13}C NMR (100.6 MHz, $[D_8]$thf): δ = 5.4, 109.2 (skeletal C) ppm. ^{29}Si NMR (79.5 MHz, $[D_8]$thf): δ = –24.7 ppm. UV/Vis (thf): λ (ε) = 252 (4200), 323 (4700) nm.

X-ray Diffraction Study and Crystal Data for 2a: A single crystal of **2a** suitable for X-ray diffraction was grown from a thf solution. The diffraction data were collected with a MacScience DIP2030 image plate diffractometer equipped with a rotation anode using graphite-monochromatized Mo-K_α radiation (λ = 0.71070 Å) at 150 K. The structure was solved by direct methods and refined by full-matrix least-squares methods using the SHELX-97 program.[17] $C_{28}H_{60}MgO_3Si_4$, M = 581.43, triclinic, $P\bar{1}$, a = 11.0120(7), b = 18.8020(11), c = 20.0050(6) Å, α = 116.643(3), β = 102.323(3), γ = 95.203(3)°, V = 3533.5(3) Å^3, Z = 4, $D_{calcd.}$ = 1.093 g/cm^3, R = 0.0655 (wR = 0.1930 for all data) for 9164 reflections with $I > 2\sigma(I)$, GOF = 1.023. CCDC-673965 contains 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

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[1] a) T. Sommerfeld, *J. Am. Chem. Soc.* **2002**, *124*, 1119; b) S. Feuerbacher, L. S. Cederbaum, *J. Am. Chem. Soc.* **2003**, *125*, 9531.

[2] V. I. Minkin, M. N. Glukhovtsev, B. A. Simkin, *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*, Wiley, New York, **1994**.

[3] B. A. Hess Jr, C. S. Ewig, L. J. Schaad, *J. Org. Chem.* **1985**, *50*, 5869.

[4] G. van Zandwijk, R. A. J. Janssen, H. M. Buck, *J. Am. Chem. Soc.* **1990**, *112*, 4155.

[5] a) A. J. Kos, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1980**, *102*, 7928; b) M. Balci, M. L. McKee, P. v. R. Schleyer, *J. Phys. Chem. A* **2000**, *104*, 1246; c) Y. Jung, T. Heine, P. v. R. Schleyer, *J. Am. Chem. Soc.* **2004**, *126*, 3132.

[6] a) A. Sekiguchi, T. Matsuo, H. Watanabe, *J. Am. Chem. Soc.* **2000**, *122*, 5652; b) T. Matsuo, T. Mizue, A. Sekiguchi, *Chem. Lett.* **2000**, 896; c) A. Sekiguchi, T. Matsuo, M. Tanaka, *Organometallics* **2002**, *21*, 1072; d) For review: A. Sekiguchi, T. Matsuo, *Synlett* **2006**, 2683.

[7] B. A. Shainyan, A. Sekiguchi, *THEOCHEM* **2005**, *728*, 1.

[8] a) V. Ya. Lee, K. Takanashi, T. Matsuno, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2004**, *126*, 4758; b) V. Ya. Lee, K. Takanashi, R. Kato, T. Matsuno, M. Ichinohe, A. Sekiguchi, *J. Organomet. Chem.* **2007**, *692*, 2800.

[9] V. Ya. Lee, K. Takanashi, M. Ichinohe, A. Sekiguchi, *Angew. Chem. Int. Ed.* **2004**, *43*, 6703.

[10] P. Jutzi, N. Burford, *Chem. Rev.* **1999**, *99*, 969.

[11] A. Sekiguchi, M. Tanaka, T. Matsuo, H. Watanabe, *Angew. Chem. Int. Ed.* **2001**, *40*, 1675.

[12] The calcium salt of the tetrakis(trimethylsilyl)cyclobutadiene dianion, $Ca^{2+}[(Me_3Si)_4C_4]^{2-}$ (**2b**) was also prepared by the reduction of the neutral cyclobutadiene **1** with calcium metal in thf for 8 h. Although **2b** was not isolated in pure form due to unavoidable decomposition at room temperature, its structure was proved by NMR spectroscopic data similar to those of **2a**: ^{1}H NMR (400 MHz, [D$_8$]thf): δ = 0.10 (s, 36 H) ppm. ^{13}C NMR (100.6 MHz, [D$_8$]thf): δ = 5.4, 119.7 (skeletal C) ppm. ^{29}Si NMR (79.5 MHz, [D$_8$]thf): δ = –27.4 ppm.

[13] W. Bünder, E. Weiss, *J. Organomet. Chem.* **1975**, *92*, 1.

[14] All DFT computations were performed at the B3LYP/6-31G(d) level with the *GAUSSIAN-03* program package: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian-03*, Revision D.01, Gaussian, Inc., Wallingford, CT, **2004**.

[15] The single-point MO calculations of the magnesium salt **2a** were performed using X-ray crystal structure coordinates (data for coordinated solvent thf was removed).

[16] a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317; b) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842.

[17] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

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