Hypervalent Carbon Atoms in a Ferrocene Dication Derivative - $[Fe(Si_2C_5H_2)_2]^{2+}$

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Abstract: Pentacoordinate carbon atoms are theoretically predicted here in a ferrocene dication derivative in both staggered-$[Fe(Si_2C_5H_2)_2]^{2+}$(**1**; C_{2h}) and eclipsed-$[Fe(Si_2C_5H_2)_2]^{2+}$(**2**; C_{2v}) forms for the first time. Relative energy difference between these two ranges from -40.34 to 2.47 kJ mol^{-1} at different levels. The planar tetracoordinate carbon atom in the ligand $Si_2C_5H_2$ becomes a hypervalent pentacoordinate carbon upon complexation.

Carbon showing hypervalent behavior - either penta or hexa - is rare but not very new to chemists.[1–8] Non-planar pentacoordination to carbon has already been well established in systems such as CH_5^+,[1,9,10] CLi_5,[11] $C(CH_3)_5^+$,[12] $[(Ph_3PAu)_5C]^+$,[13] and $Si_2(CH_3)_7^+$.[14] Likewise, non-planar hexacoordination to carbon has been proven in CLi_6,[11,15] $[(Ph_3PAu)_6C]^{2+}$,[16] and $C_6(CH_3)_6^{2+}$.[17,18] Carbon atom having heptavalency is theoretically predicted in trophylium trication, $C_7H_7^{3+}$.[19] Ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2$, is an eminent molecule over the last seven decades.[20–23] It opened a new avenue called organometallic chemistry, which is continuously growing since 1951.[20,24,25] Here, using $Si_2C_5H_2$ as a ligand, two ferrocene derivative dication structures are theoretically identified – staggered-$[Fe(Si_2C_5H_2)_2]^{2+}$(**1**; C_{2h}) and eclipsed-$[Fe(Si_2C_5H_2)_2]^{2+}$(**2**; C_{2v}) – that shows hypervalent nature (pentacoordination) to its ligand carbon atom (see Figure 1). The latter was previously a planar tetracoordinate carbon (ptC) atom[26,27] in the absence of Fe^{2+} ion. Both **1** and **2** exhibit two hypervalent pentacoordinate carbon atoms due to the formation of a metallocene complex.

In our earlier theoretical work, various isomers of $Si_2C_5H_2$ have been theoretically identified and it was concluded that the molecule with a ptC atom, 2,7-disilatricyclo[4.1.0.0^{1,3}]hept-2,4,6-trien-2,7-diyl, is the most stable structure thermodynamically.[28] The global minimum geometry for $Si_2C_5H_2$ has also been theoretically verified elsewhere through search algorithms.[29] The kinetic stability of the latter through appropriate dissociation pathways has been analyzed by us in detail recently.[30] It was proven theoretically that the global minimum isomer of $Si_2C_5H_2$ with a ptC atom is not only thermodynamically stable but also kinetically stable.[30]

Considering the fact that both **1** and **2** are dications with a net charge of 2+, it was speculated that Fe is in +4 oxidation state ([Ar] 3d^4) as in decamethylferrocene dication.[31] However, the electronic ground states in both **1** and **2** are not triplets and they are singlets. Moreover, the triplets are 38.05 and 41.11 kJ mol^{-1} above singlets in **1** and **2**, respectively, at the ωB97X-D[32]/def2-TZVP[33] level of theory. Thus, the oxidation state of Fe in both **1** and **2** is +2 ([Ar] 3d^6) and the ligands ($Si_2C_5H_2$) are neutral with 6π electrons. Thus, these complexes do attain the 18-electron

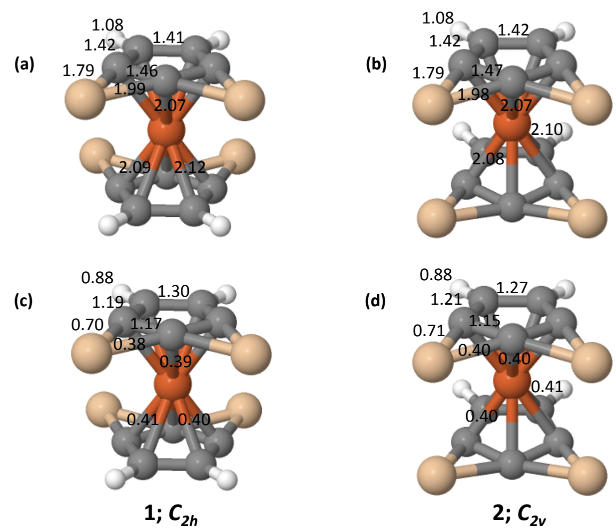

Figure 1. Optimized structures of (a) staggered- and (b) eclipsed-$[Fe(Si_2C_5H_2)_2]^{2+}$(Fe:orange; Si:bisque; C:gray; H:white). Bond lengths are indicated in Å. Wiberg bond indices are given in (c) and (d), respectively. Calculations are done at the ωB97X-D/def2-TZVP level of theory.

configuration or to put it in simpler terms they do follow the effective atomic number (EAN) rule (EAN = 36) and attain the electron configuration of Kr. Therefore, we believe that these complexes could effectively be identified in the laboratory sooner than later provided if $Si_2C_5H_2$ ligand could be prepared.

The C-C bond length in **1** range from 1.41 to 1.46 Å (see Figure 1 (a)) whereas in **2** it varies from 1.42 to 1.47 Å (see Figure 1 (b)). Compared to ferrocene,[34] where the mean C-C bond length is equal to 1.431 Å, these bond lengths are slightly varied, which is reasonable due to the ionic character (dication) in these complexes apart from the presence of silicon atoms. Likewise, the Fe-C bond length in **1** range from 2.07 to 2.12 Å whereas in **2** it varies from 2.07 to 2.10 Å. In ferrocene, the mean Fe-C bond length is equal to 2.059 Å and here they are slightly longer. The Si-C bond length connected to the hypervalent carbon is 1.99 Å in **1** and 1.98 Å in **2**, which reflects its single bond characteristics whereas the Si-C bond on the sides are shorter with a bond length of 1.79 Å in both the cases. This shows its double bond characteristics. In principle, the isolated $Si_2C_5H_2$ ligand almost behaves like cyclopentadienyl anion ($C_5H_5^-$) with a slight exception that the former contains 3c-2e σ bond around Si-C-Si region.[29,30] This is evidently seen even when it makes complexation with Fe^{2+}. The zero-point vibrational energy (ZPVE) corrected-relative energies and Gibbs free energies obtained for **1** and **2** at different levels are shown in Ta-

Table 1. ZPVE-corrected relative energies (ΔE_0) and thermally corrected Gibbs energies ($\Delta G_{298.15}$) of **2** relative to **1** at various levels[a]

	6-311++G(2d,2p)-SDD (Fe)		def2-TZVP	
Functional	ΔE_0	$\Delta G_{298.15}$	ΔE_0	$\Delta G_{298.15}$
B3LYP	4.90	6.44	2.47	4.59
B3LYP-D3BJ	-5.63	-3.11	-8.24	-5.51
M06-L	-38.11	-38.02	-40.34	-37.89
TPSSh	-29.08	-26.52	-30.78	-28.14
TPSSh-D3BJ	-30.44	-29.44	-32.29	-31.16
ωB97X-D	5.61	6.54	2.78	1.21

[a] All values are in kJ mol^{-1}.

ble 1. Like ferrocene, the relative energy difference between staggered and eclipsed forms is quite small. In the parent molecule, as per gas-phase calculations, the staggered form is a saddle-point (transition state) and the eclipsed form is a minimum.[25] In the derivatives studied here, both are minima at all levels.

All geometry optimization and frequency calculations for **1** and **2** were carried out using both 6-311++G(2d,2p)[35] and def2-TZVP basis sets.[33] In the former, for Fe, Stuttgart/Dresden effective core potential of MWF10 and the corresponding atomic natural orbital basis set were used in all calculations.[36] Various density functionals were used such as B3LYP,[37] TPSSh,[38] M06-L,[39] and ωB97X-D.[32] Calculations were also done with empirical dispersion corrections (D3)[40] with Becke-Johnson damping (BJ)[41,42] (i.e., B3LYP-D3BJ, TPSSh-D3BJ). Natural bond orbital analyses were done using ωB97X-D functional to obtain the natural atomic charges and Wiberg bond indices (WBIs).[43] All calculations were carried out using the Gaussian program package.[44]

Both **1** and **2** contain two hypervalent pentacoordinate carbons. This could be justified with the WBIs calculated (see Figures 1 (c) and (d)) for these two structures. For **1**, all WBI values for Fe-C are in the range of 0.39 to 0.41 whereas in **2** they are in the range of 0.40 to 0.41. This indicates that they are indeed single bonds. The hypervalent C-Si WBI values in **1** and **2** are 0.38 and 0.40, respectively, that reflect single bond characteristics. WBI values for all C-C bond lengths are greater than 1, which indicates resonance stabilization plus double bond characteristics. On the basis of these values, one could certainly conclude that the central carbon atoms are hypervalent (penta) in both the cases. It is emphasized here that each hypervalent carbon obeys the octet-rule as the total WBI for each hypervalent carbon is 3.49 for **1** and 3.50 for **2**. However, some of the bonds (Si-C and C-Fe) are electron-deficient bonds with fewer than two electrons as mentioned elsewhere in the example of $C(CH_3)_5^+$.[12] Nevertheless, with appropriate counter ions, it is quite likely that these new ferrocene derivatives could be isolated in the laboratory opening an avenue for "hypervalent metallocenes".

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Supporting Information Available: Cartesian coordinates of the optimized geometries, total electronic energies, and zero-point vibrational energies (ZPVE), ZPVE-corrected total energies, number of imaginary frequencies (NImag), relative energies, thermal correction parameters, and natural charges obtained at different levels for staggered-$[Fe(Si_2C_5H_2)_2]^{2+}$ (**1**; C_{2h}) and eclipsed-$[Fe(Si_2C_5H_2)_2]^{2+}$ (**2**; C_{2v}) forms. This material is available free of charge via the Internet at `http://pubs.acs.org/`.

References

(1) Tal'rose, V. L.; Lyubimova, A. K. Secondary Processes in the Ion Source of the Mass Spectrometer. *Dokl. Akad. Nauk SSSR* **1952**, *86*, 909–912.

(2) Akiba, K.-y.; Yamashita, M.; Yamamoto, Y.; Nagase, S. Synthesis and Isolation of Stable Hypervalent Carbon Compound (10-C-5) Bearing a 1,8-Dimethoxyanthracene Ligand. *J. Am. Chem. Soc.* **1999**, *121*, 10644–10645.

(3) Yamashita, M.; Yamamoto, Y.; Akiba, K.-y.; Hashizume, D.; Iwasaki, F.; Takagi, N.; Nagase, S. Syntheses and Structures of Hypervalent Pentacoordinate Carbon and Boron Compounds Bearing an Anthracene Skeleton Elucidation of Hypervalent Interaction Based on X-ray Analysis and DFT Calculation. *J. Am. Chem. Soc.* **2005**, *127*, 4354.

(4) Akiba, K.-y.; Moriyama, Y.; Mizozoe, M.; Inohara, H.; Nishii, T.; Yamamoto, Y.; Minoura, M.; Hashizume, D.; Iwasaki, F.; Takagi, N.; Ishimura, K.; Nagase, S. Synthesis and Characterization of Stable Hypervalent Carbon Compounds (10-C-5) Bearing a 2,6-Bis(p-substituted phenyloxymethyl)benzene Ligand. *J. Am. Chem. Soc.* **2005**, *127*, 5893.

(5) Fernández, I.; Uggerud, E.; Frenking, G. Stable Pentacoordinate Carbocations: Structure and Bonding. *Chem. Eur. J.* **2007**, *13*, 8620–8626.

(6) Yamaguchi, T.; Yamamoto, Y.; Kinoshita, D.; Akiba, K.-y.; Zhang, Y.; Reed, C. A.; Hashizume, D.; Iwasaki, F. Synthesis and Structure of a Hexacoordinate Carbon Compound. *J. Am. Chem. Soc.* **2008**, *130*, 6894–6895.

(7) Lancaster, K. M.; Roemelt, M.; Ettenhuber, P.; Hu, Y.; Ribbe, M. W.; Neese, F.; Bergmann, U.; DeBeer, S. X-ray Emission Spectroscopy Evidences a Central Carbon in the Nitrogenase Iron-Molybdenum Cofactor. *Science* **2011**, *334*, 974–977.

(8) Thimmakondu, V. S. Hypervalent Carbon Atoms in a Ferrocene Dication Derivative - $[Fe(Si_2C_5H_2)_2]^{2+}$. *ChemRxiv* **2021**,

(9) Olah, G. A.; White, A. M.; O'Brien, D. H. Protonated Heteroaliphatic Compounds. *Chem. Rev.* **1970**, *70*, 561.

(10) White, E. T.; Tang, J.; Oka, T. CH_5^+: The Infrared Spectrum Observed. *Science* **1999**, *284*, 135–137.

(11) Schleyer, P. v. R.; Würthwein, E.-U.; Kaufmann, E.; Clark, T.; Pople, J. A. Effectively Hypervalent Molecules. 2. Lithium Carbide (CLi_5), Lithium Carbide (CLi_6), and the Related Effectively Hypervalent First Row Molecules, CLi_5-nHn and CLi_6-nHn. *J. Am. Chem. Soc.* **1983**, *105*, 5930.

(12) McKee, W. C.; Agarwal, J.; Schaefer III, H. F.; Schleyer, P. v. R. Covalent Hypercoordination: Can Carbon Bind Five Methyl Ligands? *Angew. Chem., Int. Ed.* **2014**, *53*, 7875–7878.

(13) Scherbaum, F.; Grohmann, A.; Müller, G.; Schmidbaur, H. Synthesis, Structure, and Bonding of the Cation $[(C_6H_5)_3PAu_5C]^{\oplus}$. *Angew. Chem., Int. Ed.* **1989**, *28*, 463–465.

(14) Dávalos, J. A.; Herrero, R.; Abboud, J.-L. M.; Mó, O.; Yáez, M. How Can a Carbon Atom Be Covalently Bound to Five Ligands? The Case of $Si_2(CH_3)_7^+$. *Angew. Chem., Int. Ed.* **2007**, *46*, 381.

(15) Kudo, H. Observation of Hypervalent CLi_6 by Knudsen-Effusion Mass Spectrometry. *Nature* **1992**, *355*, 432.

(16) Scherbaum, F.; Grohmann, A.; Huber, B.; Krüger, C.; Schmidbaur, H. Aurophilicity as a Consequence of Relativistic Effects: The Hexakis(triphenylphosphaneaurio)methane Dication $[(Ph_3PAu)_6C]^{2\oplus}$. *Angew. Chem., Int. Ed.* **1988**, *27*, 1544–1546.

(17) Hogeveen, H.; Kwant, P. Direct Observation of a Remarkably

Stable Dication of Unusual Structure: $(CCH_3)_6^{2+}$. *Tetrahedron Lett.* **1973**, *14*, 1665–1670.
(18) Malischewski, M.; Seppelt, K. Crystal Structure Determination of the Pentagonal-Pyramidal Hexamethylbenzene Dication $C_6(CH_3)_6^{2+}$. *Angew. Chem., Int. Ed.* **2017**, *56*, 368–370.
(19) Wang, G.; Rahman, A. K. F.; Wang, B. Ab Initio Calculations of Ionic Hydrocarbon Compounds with Heptacoordinate Carbon. *J. Mol. Model.* **2018**, *24*, 116.
(20) Kealy, T. J.; Pauson, P. L. A New Type of Organo-Iron Compound. *Nature* **1951**, *168*, 1039–1040.
(21) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. The Structure of Iron Bis-Cyclopentadienyl. *J. Am. Chem. Soc.* **1952**, *74*, 2125–2126.
(22) Fischer, E. O.; Pfab, W. Cyclopentadien-Metallkomplexe, Ein Neuer Typ Metallorganischer Verbindungen. *Z. Naturforschg B* **1952**, *7*, 377–379.
(23) Pfab, W.; Fischer, E. O. Zur Kristallstruktur der Dicyclopentadienyl-Verbindungen des Zweiwertigen Eisens, Kobalts und Nickels. *Z. Anorg. Allg. Chem.* **1953**, *274*, 316–322.
(24) Werner, H. At Least 60Years of Ferrocene: The Discovery and Rediscovery of the Sandwich Complexes. *Angew. Chem., Int. Ed.* **2012**, *51*, 6052–6058.
(25) Mohammadi, N.; Ganesan, A.; Chantler, C. T.; Wang, F. Differentiation of Ferrocene D_{5d} and D_{5h} Conformers Using IR Spectroscopy. *J. Organomet. Chem.* **2012**, *713*, 51–59.
(26) Monkhorst, H. J. Activation Energy for Interconversion of Enantiomers Containing an Asymmetric Carbon Atom without Breaking Bonds. *Chem. Commun. (London)* **1968**, 1111–1112.
(27) Hoffmann, R.; Alder, R. W.; Wilcox, C. F. Planar Tetracoordinate Carbon. *J. Am. Chem. Soc.* **1970**, *92*, 4992–4993.
(28) Thirumoorthy, K.; Cooksy, A. L.; Thimmakondu, V. S. $Si_2C_5H_2$ Isomers - Search Algorithms versus Chemical Intuition. *Phys. Chem. Chem. Phys.* **2020**, *22*, 5865–5872.
(29) Yañez, O.; Vásquez-Espinal, A.; Pino-Rios, R.; Ferraro, F.; Pan, S.; Osorio, E.; Merino, G.; Tiznado, W. Exploiting Electronic Strategies to Stabilize A Planar Tetracoordinate Carbon in Cyclic Aromatic Hydrocarbons. *Chem. Commun.* **2017**, *53*, 12112–12115.
(30) Thirumoorthy, K.; Chandrasekaran, V.; Cooksy, A. L.; Thimmakondu, V. S. Kinetic Stability of $Si_2C_5H_2$ Isomer with a Planar Tetracoordinate Carbon Atom. *Chemistry* **2021**, *3*, 13–27.
(31) Malischewski, M.; Adelhardt, M.; Sutter, J.; Meyer, K.; Seppelt, K. Isolation and Structural and Electronic Characterization of Salts of the Decamethylferrocene Dication. *Science* **2016**, *353*, 678–682.
(32) Chai, J.-D.; Head-Gordon, M. Long-Range Corrected Hybrid Density Functionals with Damped Atom-Atom Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.
(33) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
(34) Seiler, P.; Dunitz, J. D. Low-Temperature Crystallization of Orthorhombic Ferrocene: Structure Analysis at 98 K. *Acta Cryst. B* **1982**, *38*, 1741–1745.
(35) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. Efficient Diffuse Function-Augmented Basis Sets for Anion Calculations. III. The 3-21+G Basis Set for First-Row Elements, Li-F. *J. Comput. Chem.* **1983**, *4*, 294–301.
(36) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. Energy-Adjusted Ab Initio Pseudopotentials for the First Row Transition Elements. *J. Chem. Phys.* **1987**, *86*, 866–872.
(37) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula Into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.
(38) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the Density Functional Ladder: Nonempirical Meta–Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.
(39) Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Phys.* **2006**, *125*, 194101.
(40) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
(41) Becke, A. D.; Johnson, E. R. Exchange-Hole Dipole Moment and the Dispersion Interaction. *J. Chem. Phys.* **2005**, *122*, 154104.
(42) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.
(43) Glendening, E. D.; Weinhold, F. Natural Resonance Theory: I. General Formalism. *J. Comput. Chem.* **1998**, *19*, 593–609.
(44) Frisch, M. J. et al. Gaussian 16 Revision B.01. 2016; Gaussian Inc. Wallingford CT.

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