

A Short Bi=Bi Bond Supported by a Metalloid Group 13 Ligand**

Ganesan Prabusankar, Christian Gemel, Pattiyil Parameswaran, Charity Flener, Gernot Frenking,* and Roland A. Fischer*

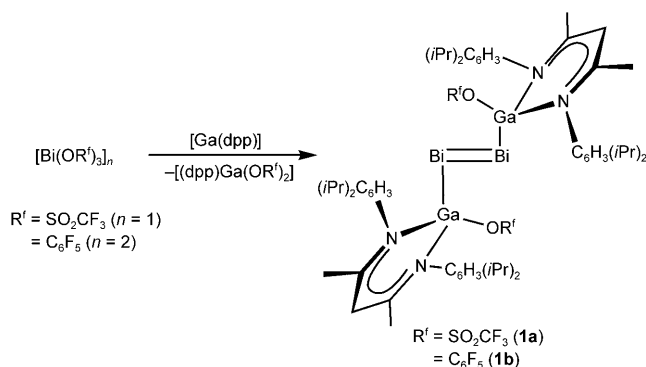
Multiple bonds between main-group metals have brought much attention for more than the last two decades owing to both inherent fundamental chemistry and applications in synthesis.^[1] Particularly the isolation and structural characterization of multiply bonded Group 15 elements has posed a challenge to synthetic chemists. The first structurally characterized compound with a bismuth–bismuth double bond was discovered by Tokitoh et al. in 1997; it was prepared by treating sterically crowded tbtBiCl_2 ($\text{tbt} = 2,4,6\text{-(Me}_3\text{Si)}_2\text{CH}_3\text{C}_6\text{H}_2$) with Li_2Se and subsequent reduction of resulting $(\text{tbtBiSe})_3$ with three equivalents of $(\text{Me}_2\text{N})_3\text{P}$.^[2] Subsequently, it was shown that RBi=BiR ($\text{R} = 2,6\text{-(2,4,6-Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$ or bbt , $4\text{-(SiMe}_3)_3\text{C-2,6-[(Me}_3\text{Si)}_2\text{CH}_2\text{C}_6\text{H}_2]$) can also be obtained by the controlled reduction of the corresponding monoorganyl bismuth dihalides with magnesium.^[3]

The “next generation”^[4] of molecules with metal–metal multiple bonds between main-group elements was introduced by the recent and most notable reports on $(\text{NHC})\text{E=E}(\text{NHC})$ species ($\text{E} = \text{Si}^{[5a]}$ or $\text{BH}^{[5b,c]}$, $\text{NHC} = [\text{CH}(2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{-N})_2\text{C}]$). These unusual molecules were obtained by reduction of the adducts $(\text{NHC})\text{SiCl}_4$ and $(\text{NHC})\text{BBr}_3$ with KC_8 . Similar reduction of $(\text{NHC})\text{PCl}_3$ or $(\text{NHC}')\text{PCl}_3$ ($\text{NHC}' = [\text{CH}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{N})_2\text{C}]$) resulted in a singly bonded diposphorus moiety supported by NHC or NHC' ligands.^[6] However, NHC-stabilized multiple bonds of heavier main-group elements have not yet been realized. Nevertheless, fine tuning of NHC-type ligands could well be a successful synthetic strategy to access molecules with such units.^[1]

It has been shown that the Group 13 metal-substituted NHC analogue $[\text{Ga}(\text{ddp})]$ ($\text{ddp} = \text{CH}[\text{MeC}(2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{N})_2]$ ^[7,8]) reacts as a selective, yet very potent, reducing agent. At the same time, it acts as a strong σ -

donor ligand, quite compatible with the electrophilic nature of heavy main-group metals. For example, the synthesis of the Zintl type clusters $[(\text{ddp})\text{Ga}(\text{Cl})]_2\text{Sn}_7$ and $[(\text{ddp})\text{Ga}(\text{Cl})]_4\text{Sn}_{17}$ involves the reduction and coordination of SnCl_2 by $[\text{Ga}(\text{ddp})]$.^[9] According to this strategy, we have now achieved the reduction of $\text{Bi}(\text{OSO}_2\text{CF}_3)_3$ and $[\text{Bi}(\text{OC}_6\text{F}_5)_3(\text{toluene})]_2$ ^[10] by $[\text{Ga}(\text{ddp})]$ to yield $[(\text{R}'\text{O})(\text{ddp})\text{GaBi=BiGa}(\text{ddp})(\text{OR}')]$ ($\text{R}' = \text{SO}_2\text{CF}_3$ (**1a**), C_6F_5 (**1b**)), which represents a new type of dibismuthene stabilized by NHC-related ligands.

The reactions between two equivalents of $[\text{Ga}(\text{ddp})]$ and $\text{Bi}(\text{OSO}_2\text{CF}_3)_3$ and between six equivalents of $[\text{Ga}(\text{ddp})]$ and $[\text{Bi}(\text{OC}_6\text{F}_5)_3(\text{toluene})]_2$ gave purple crystals of **1a** (yield 29–



Scheme 1. Synthesis of **1a** and **1b**.

32%) and **1b** (yield 63%; Scheme 1), respectively. The byproduct, which is generated in stoichiometric amounts, was characterized in each case as $[(\text{ddp})\text{Ga}(\text{OR}')_2]$. Molecules **1a** and **1b** are soluble in polar organic solvents. The purple color rapidly disappears when the solids or solutions are exposed to air, owing to oxidation.^[2] Reaction of $[\text{Ga}(\text{ddp})]$ with other commercially available bismuth salts such as BiX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) under various conditions resulted in the reduction of Bi^{III} to metallic bismuth. Interestingly, the reduction of $[(\text{NHC})\text{Bi}(\text{OSO}_2\text{CF}_3)_3]$ using $[\text{Co}(\text{C}_5\text{H}_5)_2]$ gives metallic bismuth, while $[\text{Ga}(\text{ddp})]$ as the reducing agent leads to **1a** in high yields.

The ^1H and ^{13}C NMR spectra of **1a** and **1b** show the expected signals for the β -diketiminato ligand.^[7] Additional signals for the triflate group in **1a** ($\delta = 171.4$ ppm) and the OC_6F_5 group in **1b** ($\delta = 173.61, 145.16, 144.0, 138.07$ ppm) were observed in the ^{13}C NMR spectra. In the IR spectrum of **1a**, the triflate vibrations were detected at $1386(\text{s})$ and $1200(\text{s}) \text{ cm}^{-1}$, suggesting the presence of covalently linked monodentate triflate groups.^[11] Solution and solid-state UV/

[*] Dr. G. Prabusankar, Dr. C. Gemel, Prof. Dr. R. A. Fischer
Inorganic Chemistry II—Organometallics & Materials
Faculty of Chemistry and Biochemistry, Ruhr University Bochum
44870 Bochum (Germany)
Fax: (+49) 234-321-4174
E-mail: roland.fischer@rub.de
Homepage: <http://www.ruhr-uni-bochum.de/aci2/>
P. Parameswaran, C. Flener, Prof. Dr. G. Frenking
Department of Chemistry, Philipps-University Marburg
35032 Marburg (Germany)
E-mail: frenking@staff.uni-marburg.de

[**] Organo Group 13 complexes of d-block elements 59. For 58, see:
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Vis spectra of **1a** (see the Supporting Information for details) exhibit two absorption bands, each showing a distinct shoulder, while in **1b** only the weaker band shows this splitting. The UV/Vis absorptions of **1a** and **1b** are in the range of those of known aryl dibismuthenes.^[1a] Compound **1a** was selected for electrochemical characterization. A THF solution containing (Bu₄N)PF₆ was studied by cyclic voltammetry (CV) and showed only one completely reversible redox wave with a half-wave potential $E_{1/2} = -1.2$ V versus Ag⁺/Ag (see the Supporting Information). These data indicate that **1a** is more easily reduced than the series of dipnictenes (bbt)E=E(bbt) (E=P −1.84 V, Sb −1.65 V, Bi −1.79 V).^[12] In contrast, **1b** is not easily reduced at this potential (reversible $E_{1/2} = -2.60$ V vs. Ag⁺/Ag; irreversible $E_{pc} = -2.31$ V vs. Ag⁺/Ag).

The structural features of **1a** and **1b** are very similar (Figure 1).^[13,14] Therefore, only the solid-state structure of **1a** is discussed. It reveals a monomeric molecule with a bismuth–bismuth double bond in which each bismuth center is tethered by a Ga(ddp)(OSO₂CF₃) ligand. The GaBi=BiGa moiety is

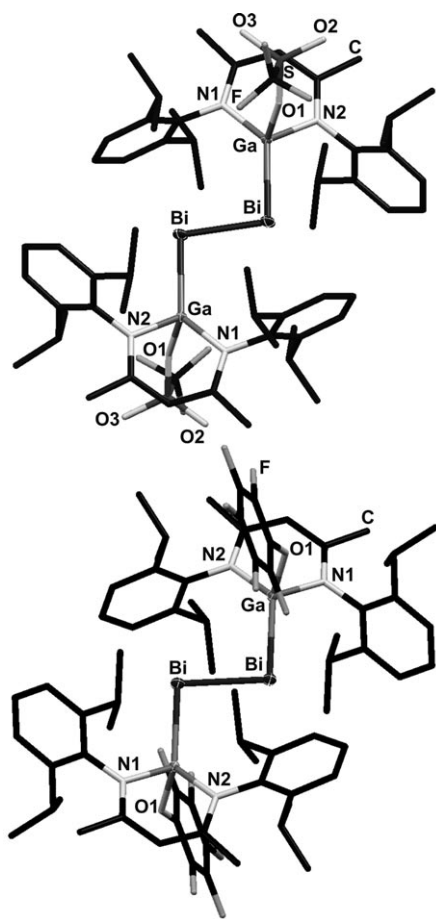


Figure 1. Molecular structure of **1a** (top) and **1b** (bottom). Selected bond lengths [Å] and angles [°] for **1a**: Bi=Bi 2.8111(2), Ga–Bi 2.655(1), Ga–N2 1.933(1), Ga–N1 1.922(1), Ga–O1 2.027(1); Ga–Bi–Bi 90.56(1), N1–Ga–N2 97.59(2), N1–Ga–Bi 133.437(1), N2–Ga–Bi 118.141(1), Bi–Ga–O1 103.63(2). Selected bond lengths [Å] and angles [°] for **1b**: Bi=Bi 2.8182(4), Ga–Bi 2.6930(6), Ga–N1 1.944(4), Ga–N2 1.961(4), Ga–O 1.897(39); Ga–Bi–Bi 95.521(16), N1–Ga–N2 95.43(17), N1–Ga–Bi 127.81(12), N2–Ga–Bi 114.86(13), Bi–Ga–O1 117.33(11).

planar and contains a center of inversion. The two Ga(ddp)-(OSO₂CF₃) ligands are located *trans* to each other. The aromatic groups in the β-diketiminato ligands are positioned above and below the GaBi=BiGa backbone. The gallium atom is connected to the two nitrogen atoms of the β-diketiminato ligand, one triflate oxygen atom, and one bismuth center in a distorted tetrahedral fashion. The triflate groups are found *trans* to each other with respect to the approximate plane generated by the {(ddp)GaBi=BiGa(ddp)} moiety. Note that the triflate and OC₆F₅ groups have no interaction with the bismuth center, as confirmed by the chemical shift values of these groups in the ¹³C NMR spectra (see above). However, some π interaction of the C₆H₃(iPr)₂ rings of the ddp ligand with the bismuth centers may be present in the solid state, with average Bi–C distances of 3.673 Å for **1a** and 3.869 Å for **1b**. The Bi=Bi bond lengths in **1a** (2.8111(2) Å) and **1b** (2.8182(4) Å) are slightly shorter than those in the series of aryl dibismuthenes ArBi=BiAr (2.8206(8)–2.8699(6) Å; Ar = 2,4,6-[(SiMe₃)₂CH]₃C₆H₂,^[2] 4-(SiMe₃)₃C-2,6-[(SiMe₃)₂CH]₂C₆H₂,^[3c] 2,6-(2,4,6-Me₃C₆H₂)₂-C₆H₃,^[3a]). The Bi=Bi bond in **1a** is 0.1789 Å (**1b** 0.1718 Å) shorter than the Bi–Bi single bond of Ph₂Bi–BiPh₂ (2.990(2) Å).^[15] The Ga–Bi bonds (2.655(1) Å (**1a**), 2.693(6) Å (**1b**)) are considerably shorter than the sum of the covalent radii for Ga and Bi (2.76 Å) and than the corresponding bond in the covalently linked Ga/Bi molecule [(Me₂GaBi(SiMe₃)₂]₃] (2.744(1)–2.783(1) Å).^[16] The Ga–Bi–Bi bond angle (90.56(1)°) in **1a** is smaller than in **1b** (95.521(16)°). These angles in **1a** and **1b** are only slightly lower than the C–Bi–Bi bond angle reported for ArBi=BiAr^[2,3] and are comparable to the C–Si–Si bond angle (93.37(5)°) of (NHC)Si=Si(NHC).^[5a] The torsion angles Ga–Bi–Bi–Ga in **1a** (180.0(1)°) and **1b** (180.0(18)°) are similar to those reported for C–Bi–Bi–C (180°).^[2,3] The metrics of the Ga(ddp) backbone are typical of those found in other Ga(ddp) complexes.^[8] The Ga–O1 bond in **1a** (2.027(1) Å) is somewhat longer than that of **1b** (1.897(39) Å) and is more comparable to the distance observed in [(ddp)Ga(OSO₂CF₃)-(PPh₂)] (1.979(6) Å).^[17] The fluoride atoms of the triflate and C₆F₅ groups show weak F⋯H interactions with the aryl and iPr C–H groups (see the Supporting Information).

Geometry optimizations (BP86/TZ2P level) for the *cis* and *trans* isomers of the model dibismuthenes [LBi=BiL] (L = Ga(F)(C₃H₅N₂); **1-L**), [LBi=BiL]²⁺ (L = Ga(C₃H₅N₂); **1-L**²⁺), [C₆H₅Bi=BiC₆H₅] (**1-Ph**), and [CH₃Bi=BiCH₃] (**1-Me**) were performed to elucidate the bonding situation in **1a** and **1b**.^[18] The optimized geometries and the full set of calculated data are given in the Supporting Information. The most stable forms of **1-L**, **1-L**²⁺, **1-Ph**, and **1-Me** lie in the *trans* orientations. Notably, the molecule **1-L** exhibits two types of *trans* isomers (*C*₁ and *C*_s) owing to a slight twist in the Bi–Ga bond; the *C*_s isomer is slightly higher in energy (ca. 0.7 kcal mol^{−1}) than the *C*₁ isomer. The optimized structural parameters for the *C*₁ isomer of **1-L** are in good agreement with the experimentally determined data of **1a** and **1b**. The calculated Wiberg bond orders *P*(Bi–Bi) of the compounds in the *trans* conformation **1-L** (1.91), **1-L**²⁺ (1.90), **1-Ph** (1.91), and **1-Me** (1.96) suggest Bi–Bi double bonds, while the *P*(Ga–Bi) values, which are between 0.99 for **1-L** and 0.86 for **1-Ph**,

indicate Bi–Ga single bonds. The contour line diagram of the Laplacian distribution $\nabla^2\rho(r)$ ^[24] of **1-L** at the GaBiBiGa plane depicts bond-critical points for Ga–Bi and Bi=Bi bonds (Figure 2). The calculated energy density at the Ga–Bi bond-

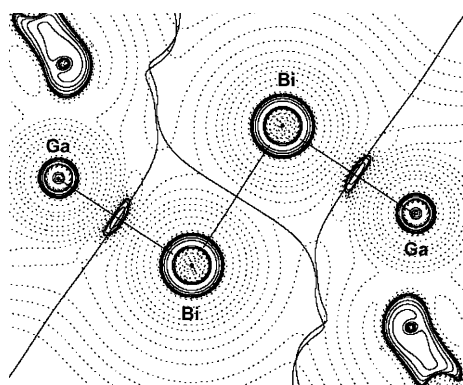


Figure 2. Contour line diagrams $\nabla^2\rho(r)$ of the *trans* (C_1) isomer of **1-L** at the GaBiBiGa plane. Solid lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$), while dashed lines show areas of charge depletion ($\nabla^2\rho(r) > 0$).

critical point ($H(r_b) = -0.022$ Hartree $\text{\AA}^{-3}$) is higher than the Bi=Bi bond-critical point ($H(r_b) = -0.016$ Hartree $\text{\AA}^{-3}$). Figure 2 shows that there is an area of charge concentration ($\nabla^2\rho(r) < 0$; solid lines) in the middle of the Ga–Bi bonds in **1-L**, which suggests rather nonpolar bonds. Energy decomposition analyses (EDA)^[25] for the bismuth–bismuth bond in the *trans* isomers of **1-L**, **1-L**²⁺, **1-Ph**, and **1-Me** show a consistent picture for the orbital term, with approximately 78% σ and 22% π bonding. The calculated data clearly support a typical covalent bonding situation between Ga and Bi and preclude a description as a contact ion pair $[\text{Bi}=\text{Bi}]^{2-}[\text{Ga}(\text{OR}^f)\text{ddp}]^{2+}$ corresponding to a Bi^{I} , Ga^{III} formulation. We favor a description as Bi^{I} , in agreement with the general bonding situation of known aryl dibismuthenes $\text{ArBi}=\text{BiAr}$. From this point of view, the Bi_2^{2+} units of **1a** and **1b** are stabilized by two neutral $[\text{Ga}(\text{ddp})]$ ligands in which the Ga centers are made electrophilic by the formation of the Bi–Ga donor–acceptor bond. The two counteranions OR^f coordinate to the Ga centers and contribute to the overall steric shielding of the central dibismuthene unit. This coordination, however, does not change the formal oxidation state Ga^{I} . The species $[(\text{NHC})\text{Bi}=\text{Bi}(\text{NHC})]^{2+}$ proved to be elusive, at least in our hands to date, which may be due to the much less electrophilic character of coordinated carbene carbon atoms of NHC ligands in comparison to the Group 13 metal congeners.^[26]

In summary, the new dibismuthenes **1a** and **1b** were derived from the commercially available bismuth triflate and bismuth aryloxide in acceptable yields by employing $[\text{Ga}(\text{ddp})]$ as both an efficient reducing agent and a stabilizing or trapping ligand for reactive species. Apart from the shortest known dibismuthene bond, the title compounds demonstrate the unique synthetic potential of low-coordinate Group 13 NHC analogues in main-group chemistry.

Experimental Section

1a: A Schlenk tube was charged with $[\text{Ga}(\text{ddp})]$ (0.1 g, 0.2052 mmol) and $\text{Bi}(\text{OSO}_2\text{CF}_3)_3$ (0.067 g, 0.1028 mmol). Fluorobenzene (2 mL) was added to this solid mixture at room temperature under vigorous stirring. The color of the reaction mixture immediately changed from yellow to purple. The mixture was stirred for 15 min, heated to 50 °C, cooled to room temperature, filtered, and the filtrate layered with hexane (2 mL) to yield purple crystals of **1a**. Yield: 29–32% (based on $\text{Bi}(\text{OSO}_2\text{CF}_3)_3$). IR (KBr): $\tilde{\nu}_{\text{OSO}_2\text{CF}_3} = 1386(\text{s})$ and $1200(\text{s}) \text{ cm}^{-1}$. ^1H NMR (C_6D_6 , 250 MHz): $\delta = 7.08\text{--}7.04$, $6.87\text{--}6.81$ (m, 12 H, Ar CH), 5.20 (s, 2 H, $\gamma\text{-CH}$), 3.84 (sept, 4 H, $\text{CH}(\text{Me})_2$), 2.66 (sept, 4 H, $\text{CH}(\text{Me})_2$), 1.68 (s, 12 H, CH_3), 1.37 (d), 1.21 (d), 0.89 ppm (dd) (48 H, $\text{CH}(\text{Me})_2$); ^{13}C NMR (C_6D_6 , 62.8952 MHz): $\delta = 171.38$ (OSO_2CF_3), 146.75 ($\text{C}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{-N}$), 143.13 (CMe), 140.46 [$o\text{-C}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)$], 126.25 [$p\text{-C}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)$], 124.86 [$m\text{-C}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)$], 101.87 ($\gamma\text{-C}$), 29.25 , 28.61 , 28.07 , 27.44 (CHMe_2), 25.79 (CHMe_2), 24.96 , 24.89 (CMe), 24.44 , 24.40 ppm (CHMe_2). UV/Vis (toluene): λ (ϵ) = 515 (1889), 482 (1793), 685 (321), 631 nm ($300 \text{ m}^{-1}\text{cm}^{-1}$). UV/Vis (solid): λ = 408, 498, 628, 676. Elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{82}\text{Bi}_2\text{F}_6\text{Ga}_2\text{N}_4\text{O}_6\text{S}_2$ (1690.87): C 42.62, H 4.89, N 3.31, S 3.79; found: C 44.14, H 4.94, N 4.20, S 3.63; the comparatively high deviation of the carbon value is explained by the disturbing influence of fluorine.

1b: Hexane (2 mL) was added to a mixture of $[\text{Ga}(\text{ddp})]$ (0.1 g, 0.2052 mmol) and $[\text{Bi}(\text{OC}_6\text{F}_5)_3(\text{toluene})_2]$ (0.058 g, 0.0342 mmol) cooled at -30°C for 30 min. The resulting yellow turbid solution was stirred at this temperature for 30 min and then allowed to warm slowly to room temperature. The color of the reaction mixture changed to purple. The mixture was stirred at room temperature for 1 h, toluene (0.5 mL) was added, the mixture was filtered, and the clear purple filtrate was stored at 8 °C to give purple crystals of **1b**. Yield: 63% (based on $[\text{Bi}(\text{OC}_6\text{F}_5)_3(\text{toluene})_2]$). ^1H NMR (C_6D_6 , 250 MHz): $\delta = 7.12$ (s), 7.09 (s), 7.00 (d), 6.97 (m, 12 H, Ar CH), 5.03 (s, 2 H, $\gamma\text{-CH}$), 3.48 (sept, 4 H, $\text{CH}(\text{Me})_2$), 2.70 (sept, 4 H, $\text{CH}(\text{Me})_2$), 1.62 (s, 12 H, CH_3), 1.10 (dd), 0.97 (d), 0.89 ppm (dd, 48 H, $\text{CH}(\text{Me})_2$); ^{13}C NMR (C_6D_6 , 62.8952 MHz): $\delta = 173.61$ ($\text{O-C}(\text{C}_6\text{F}_5)$), 169.14 ($\text{C}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{-N}$), 145.16 ($o\text{-C}(\text{C}_6\text{F}_5)$), 144.0 ($m\text{-C}(\text{C}_6\text{F}_5)$), 143.08 (CMe), 141.78 [$o\text{-C}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)$], 138.07 ($p\text{-C}(\text{C}_6\text{F}_5)$), 125.60 [$p\text{-C}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)$], 124.88 , 124.72 [$m\text{-C}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)$], 99.38 , 98.30 ($\gamma\text{-C}$), 29.64 , 28.57 , 27.92 (CHMe_2), 26.03 , 25.92 (CHMe_2), 24.79 , 24.41 , 24.38 , 24.27 (CMe), 23.98 , 23.63 ppm (CHMe_2). UV/Vis (toluene): λ (ϵ) = 512 (4422), 658 (152), 701 nm ($155 \text{ m}^{-1}\text{cm}^{-1}$). UV/Vis (solid): λ = 506, 643, 694 nm. Elemental analysis calcd (%) for $\text{C}_{70}\text{H}_{82}\text{Bi}_2\text{F}_{10}\text{Ga}_2\text{N}_4\text{O}_2$ (1758.84): C 47.80, H 4.70, N 3.19; found: C 52.09, H 5.15, N 3.12; the comparatively high deviation of the carbon value is explained by the disturbing influence of fluorine.

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