References and Notes

1. A number of experimental studies describe growth via oriented aggregation. For example, this has been reported in anatase (TiO_2) under hydrothermal conditions [R. L. Penn and J. F. Banfield, *Geochim. Cosmochim. Acta* **63**, 1549 (1999)]. Also see (*2–7*).
2. Aggregation-based grown has been demonstrated in hematite (α-Fe_2O_3) formed by aging of $FeCl_3$ in the presence of KH_2PO_4 [J. K. Bailey, C. J. Brinker, M. L Mecartney, *J Colloid. Interface Sci.* **157**, 1 (1993)].
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9. A mine-trained SCUBA diving team led by T. T. Ebert collected samples of water and biofilms into sterile syringes. Samples were kept on ice until returned to the laboratory, where they were stored at 4°C before examination by optical and electron microscopy.
10. Cells were detected by staining their DNA with 4′,6-diamidino-2-phenylindole (DAPI). Stained cells were visualized with epifluorescence microscopy. Population analyses with 16*S* ribosomal RNA gene sequencing are underway. Results will be reported separately.
11. High-resolution TEM (HRTEM) images show cross-fringes (periodicities not detected by SAED) in orientations that indicate 3D order in two-line ferrihydrite (see Fig. 3). In some regions, additional diffraction maxima indicate feroxyhite (*12*) and, less commonly, six-line ferrihydrite. Results are consistent with previous studies (*13*, *14*), which provide structural details.
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15. H. L. Zhu and R. S. Averback [*Philos. Mag.* **73**, 27 (1996)] demonstrated rotation of copper particles to achieve parallel orientations with molecular dynamics simulation. The homogeneous sizes of the initial nanoparticles and their clear separation into distinct 2- to 3-nm diameter entities rule out an alternative interpretation that oriented aggregates arise from sequential nucleation of seeds on earlier formed particles. No damage (such as creation of porosity) was detected during examination with the HRTEM operated at 200 kV. No microstructures suggestive of contact epitaxy were observed.
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20. Oriented aggregation requires coherency in the 2D plane of the interface. In addition to attachment that generates perfect 3D structure, coherent {100} and {110} interfaces with structural characteristics intermediate between ferrihydrite and goethite can be created. These regions may nucleate transformation reactions. We reported analogous phenomena in titania; see (*4*, *5*).
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22. For example, see O. Y. Pykhteev, A. A. Efimov, L. N. Moskvin, *Russ. J. Appl. Chem.* **72**, 9 (1999). Although some data supporting the formation of polynuclear hydrolysis products have been reported, Schwertmann *et al.* (*21*) maintain that there is no good evidence for intermediates between trimers and solids.
23. Subnanometer-scale porosity within ferrihydrite (*7*) may be generated if ferrihydrite itself forms by aggregation of protocrystals. Protocrystals could consist of three oxygen planes that sandwich pairs of face-sharing octahedra (to our knowledge, no small aqueous clusters containing face-sharing units are known, so face-sharing must be introduced by aggregation of smaller corner- and edge-linked molecules). Formation of ferrihydrite could proceed via sequential elimination of n(OH), following aggregation of pairs of $\{\sim n[O_{0.25}\,(OH)_{0.75}\,(Fe_{2/3})\,O_{0.5}(OH)_{0.5}(Fe_{2/3})\,O_{0.25}\,(OH_{0.75})$or $n(FeOOH)_4{\cdot}H_2O]$ units}. If some factor favors joining of alternate nuclei that are rotated by 180°, ferrihydrite ABAC oxygen closest packing would result.
24. Web figures 1 through 3 are available at *Science* Online at www.sciencemag.org/feature/data/1050910.shl.
25. We thank V. Dritts and A. Manceau for their comments on a longer report describing structural aspects of iron oxyhydroxides and W. H. Casey for discussion of multinuclear clusters. Supported by NSF grants EAR 9317082 and EAR 9814333 and the NASA Astrobiology Institute (JPL-Caltech). We also thank T. O'Connor for permission to reproduce Fig. 1.

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A Cyclic Carbanionic Valence Isomer of a Carbocation: Diphosphino Analogs of Diaminocarbocations

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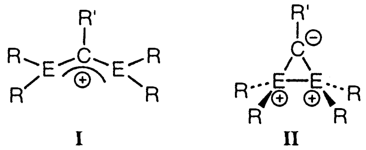
Diaminocarbocations (or amidinium salts) feature a three-center 4π electron system with an open planar structure. Their 2π electron three-membered cyclic valence isomers, in which the carbon atom bears a negative charge, are predicted to be about 541 kilojoules per mole higher in energy than the open form. This isomer has not been identified yet. In contrast, the attempted synthesis of a diphosphorus analog of amidinium salts leads to the cyclic carbanionic form. There is no precedent for such a transformation of a carbocationic center into a carbanionic center, but with the help of heavier main-group elements, numerous examples can be imagined. This approach will enable the preparation of many unknown structural moieties that are difficult or even impossible to access in the corresponding carbon and nitrogen series.

In 1972, Olah suggested that cations of carbon compounds be termed "carbocations" (*1*); the corresponding anionic compounds are called "carbanions." Because they are not tetravalent, carbocations are usually very reactive, and in his Nobel lecture, Olah added, "it should be clear that in carbocationic systems varying degrees of delocalization always exist. This can involve participation by neighboring n-donor atoms, π-donor groups, or σ-donor C–H or C–C bonds" (*2*, p. 1401). The long-known synthetically and biologically important amidinium salts, $\mathbf{I_N}$, can thus be considered as diamino-substituted carbocations (*3–9*). Here, we report the synthesis of a diphosphorus analog, which adopts a cyclic structure $\mathbf{II_P}$, with the carbon atom bearing a negative charge (Fig. 1).

Quantum chemical calculations at the B3LYP/6-31g* level with additional zero-point vibrational energy correction (*10*) predict the amidinium salt $\mathbf{I_N}$ (R = R′ = H) to be 541 kJ/mol more stable than its unknown cyclic valence isomer $\mathbf{II_N}$. Several factors indicated that the difference in energy between the valence isomers $\mathbf{I_P}$ and $\mathbf{II_P}$ should be much smaller than in the nitrogen series. (i) A stable allylic structure of type **I** (a three-center 4π electron system) implies a large singlet-triplet energy separation, which amounts to 379 kJ/mol for the parent compound $\mathbf{I_N}$ but only 163 kJ/mol for $\mathbf{I_P}$ (R = R′ = H). This is due mainly to the much smaller inversion barrier at nitrogen (21 kJ/mol) than at phosphorus (146 kJ/mol), which favors π bonding. In addition, π bonds between phosphorus and carbon are much weaker than those for nitrogen (P=C, 188 kJ/mol; N=C, 271 kJ/mol), which disfavors the allylic structure $\mathbf{I_P}$. (ii) Phosphorus-carbon bonds are longer than



I **II**

$\mathbf{I_N, II_N : E = N}$

$\mathbf{I_P, II_P : E = P}$

Fig. 1. Diamino- and diphosphino-substituted carbocations **I** and their cyclic valence isomers **II**.

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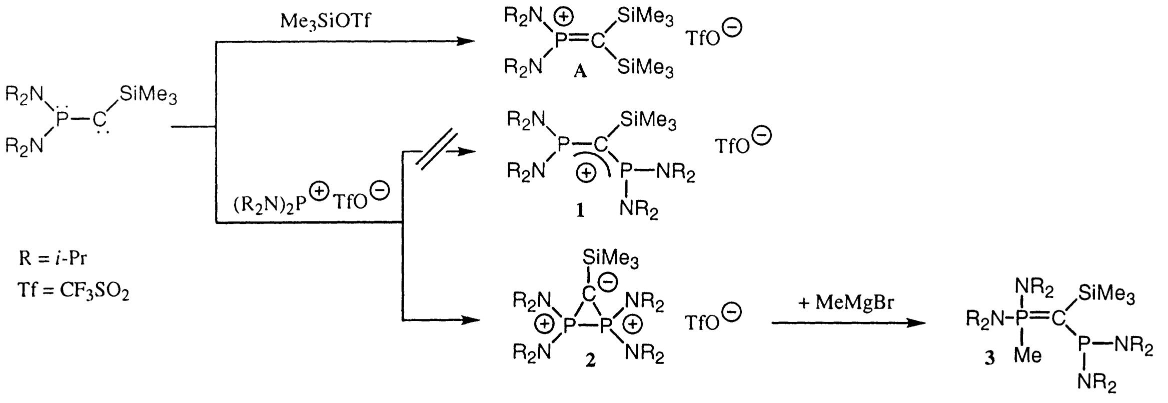
Fig. 2. Synthesis and reactivity of **2**.



nitrogen-carbon bonds (P–C, 1.89 Å; N–C, 1.47 Å), and thus, the ring strain energy in **II**$_{\mathrm{P}}$ should be smaller than that in **II**$_{\mathrm{N}}$. (iii) Because of the presence of an accessible σ* orbital at phosphorus, compound **II**$_{\mathrm{P}}$ could benefit from σ* aromaticity (*11*), although this type of stabilization is far weaker than that resulting from π aromaticity, which is present in the well-known cyclopropenium salts (*12*).

Previously, we have shown that the stable [bis(diisopropylamino)phosphino](silyl)carbene (*13*) reacts with trimethylsilyl trifluoromethane sulfonate to form the phosphinocarbocation **A** (*14*), one of the very few stable phosphorus analogs of an iminium salt (*15*) (Fig. 2). The same synthetic strategy was adopted to prepare the diphosphinocarbocation **1** or its valence isomer **2**. A dichloromethane solution of bis(diisopropylamino)phosphenium triflate (*16*) was added at 0°C to a pentane solution of the carbene (all manipulations were performed under argon). After evaporation of the solvent, the residue was washed with ether, and the resulting white powder recrystallized from tetrahydrofurane at −5°C. The adduct **2** was isolated in 66% yield as white crystals that are extremely sensitive to air (melting point 89° to 90°C).

The ionic nature of **2** was indicated by its very low solubility in nonpolar solvents. A triplet in the ^{29}Si nuclear magnetic resonance (NMR) spectrum [$\delta_{\mathrm{Si}} = -10.7$ parts per million (ppm), $J_{\mathrm{PSi}} = 10$ Hz (δ is the chemical shift and *J* the spin-spin coupling constant)] suggested the presence of two magnetically equivalent phosphorus nuclei. A three-membered ring structure was indicated by the high-field ^{31}P NMR signal ($\delta_{\mathrm{P}} = +7.3$ ppm) (*17*). The ^{13}C NMR signal corresponding to the carbon bonded to the two phosphorus atoms appears at 49.6 ppm (triplet, $J_{\mathrm{PC}} = 7.3$ Hz). This chemical shift is at far too high field for a carbocationic center but is well within the range expected for a carbanion (*18*). A single-crystal x-ray diffraction analysis (*19*) (Fig. 3) shows that **2** has pseudo C_{2v} symmetry. The carbon center is planar (sum of the bond angles is 359.8°), and the P–P (2.12 Å) and P–C (1.73 and 1.71 Å) bond lengths are slightly shorter than would be expected for single bonds.

To gain more insight into the electronic structure of **2**, we performed ab initio calculations (*10*) on the model compound **2′** (Fig. 4). The calculated geometric parameters (P–P, 2.102 Å; P–C, 1.726 and 1.727 Å) compare well with those found experimentally for the sterically encumbered derivative **2**. The analysis of the electron densities of each of the constituents of **2′** is of particular interest. Each diaminophosphenium unit carries a charge of approximately +1, whereas the carbon bears a charge of −1.6 [−1.2 in the σ space and −0.4 in the (formal) p orbital]. At first glance, this large value seems rather surprising, but if one subtracts a charge of −0.5, which is provided by the silyl unit, it leaves a charge of −1.1 at the carbon. There is a simple explanation for this observation. The angular compression at the carbon makes it extremely electronegative. It therefore withdraws considerable electron density from the neighboring phosphorus and silyl groups. This view is corroborated by the chemical behavior of **2**. For example, methyl magnesium bromide does not react at the carbon center but at phosphorus, leading to the

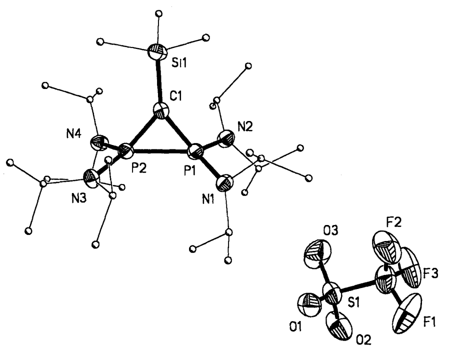
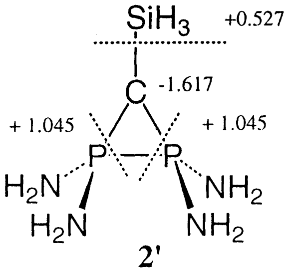


Fig. 3. Molecular view of **2** in the solid state (thermal ellipsoids at the 50% probability level). Isopropyl and methyl groups are simplified for clarity. Selected bond lengths (in angstroms) are as follows: C(1)–P(1), 1.731(3); C(1)–P(2), 1.710(3); C(1)–Si(1), 1.859(3); P(1)–P(2), 2.1195(11); P(1)–N(1), 1.651(3); P(1)–N(2), 1.659(3); P(2)–N(3), 1.651(2); and P(2)–N(4), 1.642(2). Selected bond angles (in degrees) are as follows: P(1)–C(1)–P(2), 76.04(13); P(1)–C(1)–Si(1), 146.00(18); P(2)–C(1)–Si(1), 137.79(18); C(1)–P(1)–P(2), 51.53(10); and C(1)–P(2)–P(1), 52.42(10).



2′

Fig. 4. Charges of fragments for **2′**.

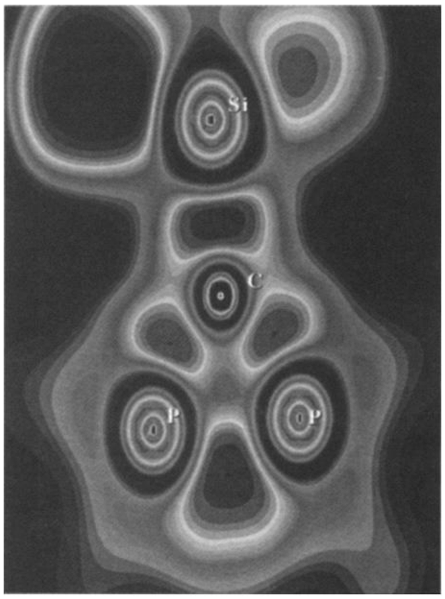


Fig. 5. Electron localization function analysis for **2′** (ring bonds in plane of paper).

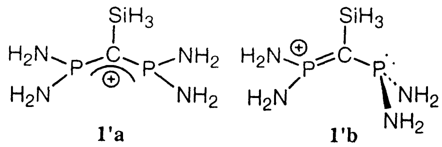


Fig. 6. Open forms of diphosphinocarbocation **1′**.

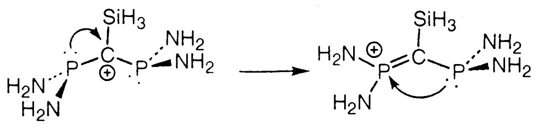


Fig. 7. Cascade stabilization in diphosphino-substituted carbocations.

corresponding *P*-methyl phosphorus ylide **3** in near-quantitative yield (an ylide is a compound in which a positively charged atom from group 15 or 16 is connected to a carbon atom carrying a negative charge) (Fig. 2). Further investigation of **2′** through analysis of the Laplacian of the electron density (*20*) and the electron localization function (*21*) reveals a strong "banana" P–P bond with large p character (the bond ellipticity is 0.45) in the plane of the ring and partial double-bond character (Wiberg bond indices = 1.2) for the P–C bonds (Fig. 5).

The calculations found that the open planar form (C_{2v} symmetry) of type **1′a**, analogous to that of amidinium salts, is not a minimum on the potential energy surface. This illustrates the striking difference between phosphorus and nitrogen chemistry (Fig. 6). However, pyramidalization at one of the phosphorus atoms leads to **1′b**, which is not only an energy minimum, but is also lower in energy by 24 kJ/mol than the cyclic form **2′**. The experimental observation of **2** can be explained by the presence of bulky diisopropylamino groups because the steric demand in the linear form is larger than in the cyclic system.

Derivative **2** can be considered as resulting from a "cascade stabilization" of the electron-deficient carbocation center. As in the case of monophosphinocarbenium ions such as **A**, the first phosphorus atom gives electrons to the carbocationic center and becomes positively charged and, therefore, highly electrophilic (*22*). The second phosphorus atom then acts as a Lewis base toward the first (Fig. 7).

This type of transformation of a cationic center into an anionic center is unlikely to be unique and should be of important synthetic utility. For example, preliminary calculations predict that the corresponding diphosphinonitrenium ions should exist in the cyclic form, with a negatively charged nitrogen atom. The synthesis of **2**, combined with the recent preparation of a tricyclic tetraphosphabenzene valence isomer (*23*) (calculated in the carbon series to be 933 kJ/mol less stable than benzene), also suggests that the unique electronic properties of heavier main-group elements will allow for the preparation of many new structural moieties that are difficult or impossible to access in the corresponding carbon and nitrogen series.

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19. Crystal data for **2** is as follows. Cell constants and an orientation matrix for data collection correspond to the monoclinic space group $P2_1/c$, with the following cell parameters: a = 15.031(2) Å, b = 10.218(1) Å, c = 24.906(3) Å, β = 100.99(1)°, and V (cell volume) = 3755.1(8) Å^3. There is one molecule, $C_{29}H_{65}F_3N_4O_3P_2SSi$, per asymmetric unit (number of formula units per cell = 4), giving a formula weight of 696.94 and a calculated density D_c of 1.233 Mg m^{-3}. The data of the structure were collected on a STOE Imaging Plate Diffraction System diffractometer at a temperature of 173(2) K with graphite-monochromated Mo Kα radiation (wavelength = 0.71073 Å) by using φ scans. We solved the structure by direct methods, using SHELXS-97 [G. M. Sheldrick, *Acta Crystallogr.* **A46**, 467 (1990)]. The linear absorption coefficient, μ, for Mo Kα radiation is 0.252 mm^{-1}. The structure was refined with all data on F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o{}^2) + (g1 \cdot P)^2 + (g2 \cdot P)$ with $P = (F_o{}^2 + 2F_c{}^2)/3$ using SHELXL-97 [G. M. Sheldrick, *Program for Crystal Structure Refinement* (Universität Göttingen, Göttingen, 1997)] [g is the weighting factor ($g1$ = 0.069100 and $g2$ = 3.406500), and F_o and F_c are the observed and calculated structure factors, respectively]. All nonhydrogen atoms were treated anisotropically. The hydrogen atoms were located by difference Fourier maps and refined with a riding model. The final cycle of full-matrix least squares refinement was based on 21,874 measured (5180 unique) reflections and 407 variable parameters and converged with the unweighted agreement factor equal to $R1$ [$I > 2\sigma(I)$ = 0.0484 (I is the observed reflection intensity)] and the weighted factor $wR2$ = 0.1328 for all data. Crystallographic details are available at www.sciencemag.org/feature/data/1051650.shl.
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24. We are grateful to the French Embassy in Japan for a grant to T.K. and to the Centre National de la Recherche Scientifique and Deutsche Forschungsgemeinschaft for financial support of this work.

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Atmospheric Influence of Earth's Earliest Sulfur Cycle

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Mass-independent isotopic signatures for $\delta^{33}S$, $\delta^{34}S$, and $\delta^{36}S$ from sulfide and sulfate in Precambrian rocks indicate that a change occurred in the sulfur cycle between 2090 and 2450 million years ago (Ma). Before 2450 Ma, the cycle was influenced by gas-phase atmospheric reactions. These atmospheric reactions also played a role in determining the oxidation state of sulfur, implying that atmospheric oxygen partial pressures were low and that the roles of oxidative weathering and of microbial oxidation and reduction of sulfur were minimal. Atmospheric fractionation processes should be considered in the use of sulfur isotopes to study the onset and consequences of microbial fractionation processes in Earth's early history.

The present-day sulfur cycle is strongly influenced by anthropogenic emissions, biological processes, and oxidative weathering of continental sulfides (*1–3*). It has been debated whether the sulfur cycle early in Earth's history was significantly different from the preanthropogenic sulfur cycle (*4–9*). Here we report sulfur multiple-isotope measurements (of $\delta^{33}S$, $\delta^{34}S$, and $\delta^{36}S$) of sulfide and sulfate minerals from Precambrian sedimentary and metasedimentary rocks and use them to document that a profound change occurred in the sulfur cycle between 2090 and 2450 Ma.

Thermodynamic, kinetic, and biological processes produce isotopic fractionations that depend on the relative mass differences be-

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