nonequilibrium defect is short when a crystal is small. (That small perfect crystals are easier to make than large ones is confirmed by a quick check of the size dependence of prices for diamonds at a jewelry store!)

Can small but highly perfect nanocrystals be assembled into pure extended solids? Until recently, it seemed that aggregation of nanocrystals would always lead to disordered (albeit very interesting) solids. For example, Matijevic and coworkers demonstrated exquisite shape control of polycrystalline micrometer-sized particles prepared by nanocrystal aggregation (*7*). Gleiter showed that ceramics derived from the random consolidation of nanoparticles are particularly resistant to fracture (*8*). The discovery that aggregation of nanocrystals can yield an ordered crystal thus comes as a surprise.

Penn and Banfield previously showed that long chains of highly ordered titania can emerge from a solution of primary titania nanoparticles (*9*) (see the figure). This chain can only arise if each nanocrystal "docks" with the next, such that the two crystals are fully aligned, a process the authors call "oriented attachment." There is certainly a strong thermodynamic driving force for oriented attachment, because the surface energy is reduced substantially when the interface is eliminated. The surprise is that two crystals can align, dock, and fuse without first getting stuck in any one of an almost innumerable set of misoriented arrangements.

One possible explanation for this behavior comes from Averback and coworkers (*10*), who independently and simultaneously discovered the same type of nanocrystal addition process. They studied the deposition of a silver nanoparticle onto a copper substrate and observed a process they called "contact epitaxy." The Ag nanocrystals were initially randomly oriented but subsequently aligned epitaxially with the substrate. Once aligned with the substrate, the nanocrystals are also aligned with each other. In a series of simulations, Averback *et al.* showed that this could arise if, after the nanocrystal lands on the substrate, the stress between the nanocrystal and the substrate creates a dislocation within the nanoparticle. As this dislocation moves toward the nanocrystal surface, the particle "rotates," resulting in full alignment with the substrate. Similar phenomena occur in simulations studying the docking of two nanocrystals (*11*).

Three aspects of oriented attachment are of particular interest: (i) it occurs naturally, (ii) it provides a convenient explanation for certain types of defects in solids, and (iii) it may be a useful method for creating advanced artificial materials.

Banfield *et al.* present a strong case for some naturally occurring materials arising through oriented attachment (*1*). They examine iron oxyhydroxide minerals recovered from a flooded mine and find both primary particles with diameters of 2 to 3 nm and oriented nanoparticle chains and sheets. They conclude that the latter have arisen during natural biomineralization as a consequence of oriented attachment. It remains to be seen, however, how common this type of mineral growth is in nature.

Oriented attachment provides a simple set of explanations for how particular types of defects may arise in extended solids (*12*). Nanocrystals, if well formed, have facets, separated by regions where step faces are exposed. If the face of one nanocrystal docks against the steps of another, the two crystallites will naturally be oriented at a particular angle. Depending on the orientation, further oriented attachment will yield various types of dislocations or screw axes (*13*). Impurity incorporation may also be more facile under conditions where crystals grow by nanocrystal attachment rather than atom by atom.

Oriented attachment may enable the preparation of interesting artificial materials. One of the most advanced methods of crystal growth, molecular beam epitaxy, involves deposition of atomic or molecular precursors onto a hot substrate. Manipulation of the stress and strain at the interface between two solids can be used to control particle size and shape, as in the growth of quantum dots, or to create metastable materials. The use of preformed nanoparticles as precursors in molecular beam epitaxy may generate new and interesting artificial materials. Likewise, the growth of nanorods and other specially shaped nanostructures with controlled defects may be possible by exploiting and controlling oriented attachment.

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PERSPECTIVES: CHEMISTRY

New Chemical Bricks Made Through Phosphorus Tricks

Hansjörg Grützmacher

The columns of the Periodic Table help chemists systematize their thinking about chemical reactivity of groups of elements based on their valence. This approach is useful so long as one is aware of the "first-row anomaly": the very different reactivity of first-row elements such as carbon (C) and nitrogen (N) relative to silicon and phosphorus (P). The first-row elements tend to form hybrids from s and p orbitals that lead to the familiar trigonal and tetrahedral bonding geometries. Second-row elements avoid hybrization (*1*). This tendency can be seen in their elemental forms—for example, nitrogen (N≡N) contains a multiple bond, whereas phosphorus adopts P–P single bonds in the tetrahedral P_4 molecule.

For organic reactions, differences in electronegativity—the relative ability of atoms in molecules to attract electrons—is also important. Whereas N is more electronegative than C, P is slightly electropositive. These differences can be exploited to stabilize P-containing species that would be transient or unknown as the N analog. On page 754 of this issue, Kato *et al.* (*2*) show that replacing N or C centers with P can lead to versatile new reagents. Two recent related studies are also discussed below (*3*, *4*). The three studies not only help identify new reagents, but also expand our understanding of the chemical bonding and reactivity of main group elements.

Carbenium ions like amidinium ions $[\mathrm{CR(NR'_2)_2}]^{\oplus}$ **1** play a prominent role in synthetic chemistry because a new chemical bond between the electrophilic carbon center and an electron-rich entity, or nucleophile, is easily formed. The amino

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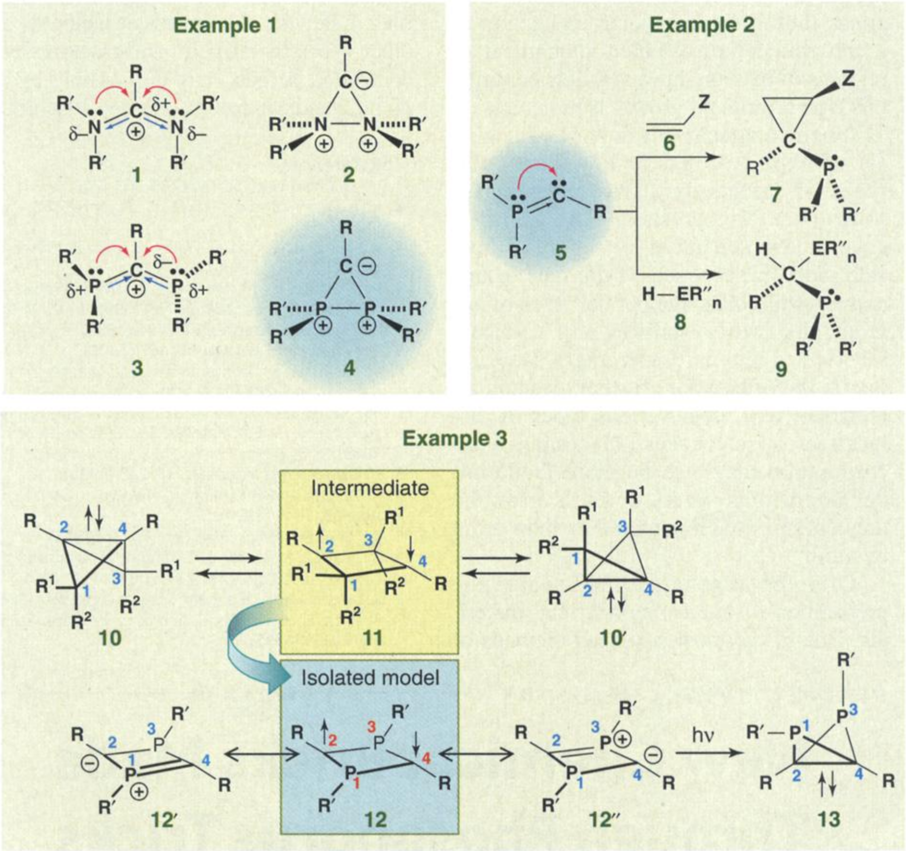
group, NR'_2, stabilizes the central trivalent and electron-deficient carbon center by electron donation from the N lone pairs, as is indicated in example 1 in the figure. However, electronegativity caused the N atoms to remain negatively charged (δ–) and the C atoms positively charged (δ+).

Replacement of NR'_2 with phosphanyl groups, PR'_2, dramatically changes the properties of the resulting carbenium ions **3** and **4**. First, the bond polarities in **3** and **4** are reversed because P donates electron density from its lone pairs but is more electropositive than C (*5*). Second, other structural alternatives not imaginable for N compounds can be realized. The cyclic isomer **2** is separated from the open amidinium form **1** by an energy gap of 540 kJ/mol. However, the cyclic, P-containing carbenium ion **4** is much closer to **3** in energy (a gap of only 115 kJ/mol) (*5*). Therefore, **4** can be isolated (*2*) because P avoids the formation of multiple bonds (*1*) and trigonal planar c-ordination spheres (note that the P centers in the open form **3** are pyramidal).



Exploiting the "phosphorus trick." Three examples illustrate the effect of phosphorus centers in carbenium ions **3** and **4** **(upper left)**, carbenes **5** **(upper right)**, and singlet biradicals **12** **(bottom).** Various substituents are denoted R on carbon and R′ on phosphorus; E stands for an element center (Si, Ge), and Z denotes an electron withdrawing group (COOR, CN, etc.). Red arrows indicate electron donation through lone pairs, and blue arrows indicate electron donation caused by differences of the electronegativities. ⊕ and Ψ indicate Lewis charges; δ+ and δ– denote the physical charges. The energy of a photon is represented as *h*ν.

This "phosphorus trick" has also been used to extend the lifetime of carbenes, CR_2 (see example 2 in the figure). Like carbenium ions, these divalent carbon compounds are highly reactive electrophilic species. Binding an electron-donating phosphanyl group PR'_2 to the C center in **5** makes the carbene nucleophilic (*3*). Furthermore, the trivalent P center in **5** is forced into an inconvenient trigonal planar configuration. Thus, unlike other stable nitrogen-substituted carbenes (*6*), **5** still shows typical carbene reactivity that makes it a synthetically useful "chemical brick" for attacking electrophilic centers. The Bertrand carbenes **5** react with electron-poor olefins **6** to give cyclopropanes **7** in a stereoselective reaction, or insert into the E–H bond in **8** to give highly functionalized methanes **9** (E = Si, Ge).

The physical and chemical properties of strained hydrocarbons can teach us much about bond formation and cleavage. Consider the inversion of bicyclobutane **10** (see example 3 in the figure), in which the substituents R^1 and R^2 are exchanged. In the intermediate **11** (*7*), a C–C bond is stretched to a nonbonding distance, but the electrons (shown as black arrows) still carry the same spin and form singlet biradicals.

Phosphorus chemistry allows the isolation of singlet biradicals. A recent example is the isolation of benzene valence isomer that contained one-electron P–P bonds (*8*). The more elusive "bond-stretch" isomer (*9*) was obtained when the CR^1R^2 groups in 1 and 3 position of **10** were replaced by isoelectronic PR′ groups. The Niecke biradicals of type **12** (*4*) owe their stability (up to 100°C!) to the effect of the PR′ groups. The resonance structures **12′** and **12″** indicate that electron donation from the P lone pairs balances the electron deficiency at the radical C centers in the biradical structure **12**. Furthermore, the thermal formation of a bond between carbon atoms 2 and 4 is a forbidden process, but the 1,3-diphosphabicyclobutane **13** forms almost quantitatively through a photochemical route (*10*).

The stabilizing electron donation by P causes its coordination sphere to flatten, which consumes energy. This energy is relaxed when species like **4**, **5**, and **12** are used in chemical reactions. Therefore, application of the "phosphorus trick" allows the isolation of species otherwise difficult to handle without making them unreactive. Furthermore, the unwillingness of trivalent phosphorus to adopt a planar configuration can be used to stabilize valence isomers or even "freeze out" transition states where strong pyramidalization at some centers occurs.

The compounds cited here mark only the beginning of a scientific endeavor. The results to be obtained will go far beyond the approach of systematically replacing CR groups or N atoms by isoelectronic P atoms and should have a broad impact on chemical synthesis, reaction mechanisms, and bonding theory.

References and Notes

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