Ask an American chemistry student, “Tell me what you know about carbides,” and here’s what I guess you’d get as an answer: “There’s calcium carbide, CaC₂, and I’ve heard of those long chains of carbon in John Gladysz’s organometallic molecules, and, yes, some transition metal carbide clusters, for instance the iron carbide carbonyl Fe₅C(CO)₁₅ [Figure 1].”

The realities: Calcium carbide, CaC₂, remains a major commercial chemical, though I suspect that few connect that molecule to the name of the one-time chemical giant, Union Carbide Corporation, now a subsidiary of Dow; WC—no, not the loo but tungsten carbide—in drilling bits and in “cemented” carbides is a major industry. Looming above these is steel, of weapons and at the core of large constructions. Steel is hardly uncommon, but I’d bet there is nary a word about this alloy of iron and carbon in the education of our students. Steel is a solid solution of carbon in iron mixed with compounds such as iron carbide, Fe₅C, and Hägg’s carbide, Fe₇C₂. Besides these three major players—CaC₂, WC and the carbides in steel—many other metal carbides have been made, more for curiosity than for profit.

The lacunae in the student’s answer—and professors will do no better—tell us much about education and fashions in science. I see in the answer (a) the triumph of molecular chemistry in the past century, so, for example, more people know the later and rarer discrete Fe₅C(CO)₁₅ cluster than the extended Fe₅C structure, and (b) the love affair people—subspecies chemists—have with simplicity; so both teachers and students would rather deal with a simple discrete molecule rather than the difficult to explain lanthanum nickel carbide, La₂Ni₅C₇, or, God forbid, messy steel.

Octahedra and Trigonal Prisms
In fact, the few hundred carbides known are a most remarkable and, as I will argue, inspiring group of compounds. First a brief on their macroscopic properties: These are all solid compounds, ceramic, sometimes metallic, often hard, often with high melting temperatures. They may be sensitive to moisture (Can anyone who has experienced it forget the smell of wet technical grade CaC₂?), but often are very resistant to water and air (those WC drilling bits). Their compositions may be simple—say, WC or NbC (niobium carbide)—or complex—Sc₅C₃ (scandium carbide) or Er₁₈Ru₁₉C₁₉ (an erbium ruthenium carbide).

Now to their microscopic structure. In the carbides known, carbon appears so far in only three forms. Most common are isolated carbon atoms, probably closer to being negatively charged ions. Figure 2, for instance, shows the structure of NbC—a layering of niobium and carbon, with an octahedron of niobiums around each carbon and an octahedron of carbons around each niobium. Does that sound familiar? These words describe the geometrical structure of rock salt or NaCl (sodium chloride), seen in our view of NbC from an atypical angle. The distances between niobium

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Figure 1. This carbide made of iron, carbon and oxygen, Fe₅C(CO)₁₅, is a molecular carbide cluster. In contrast, most carbides have extended structures that cannot be divided into discrete molecules.
atoms are a little longer than in niobium metal; the Nb-C distances are similar to those in discrete molecular NbC organometallic compounds. And there are no C-C bonds. Figure 2 also shows the WC structure, in which each carbon is surrounded by a trigonal prism of tungsten atoms and each tungsten by a trigonal prism of carbons. Interesting that the two structures should differ so much; I've written a paper with Sunil Wijeyesekeka teasing out an explanation for the different coordination preferences of NbC and WC. Cementite, Fe₃C (an important form of carbon in steel), is a variant of the WC structure. To get to it, imagine removing two-thirds of the carbon atoms and then collapsing the metal lattice, albeit in a complex way.

Incidentally, if you ask an inorganic chemist about the date of the first synthesis of molecules with a metal atom in a trigonal prismatic environment, the likely answer will be approximately 1965. But the WC structure has been known since 1928; it clearly has a trigonal prismatic coordinated metal atom, with W-C distances typical of those in organometallic molecules. That the molecular inorganic chemist doesn't point to WC (or to MoS₂—molybdenum sulfide—another structure with trigonal prismatic coordination of a metal, given to us by Linus Pauling in one of his early papers in 1923) illustrates the separation, persistent even as it is illogical, of molecular and extended inorganic chemistry over most of the 20th century. Talk of two cultures!

**C₂, C₃ and ... Nothing Simple**

There are many carbides that contain two linked carbon units. CaC₂ is one, a simple structure in which the C₁ units are close to C₂, like an acetylene (HCCH) with the two hydrogens ripped off as protons. Consistently, the C-C bond length in the C₂ units of CaC₂ is acetylenic, 1.19 angstroms. There’s a drawing of the atomic positions in calcium carbide in another article I’ve written (Marginalia, July–August 1995). C-C bond lengths in the C₂ units of other carbides range remarkably, from 1.19 to 1.48 angstroms, nearly matching the range of C-C bond lengths in organic molecules, from a triple bond to a single bond. This is not an accident.

The final and rare mode of C-C bonding in carbides is a C₃ unit. It occurs in Ca₃Cl₅C₃, but I'd
rather show you the phantasmaric Sc²C₄ structure of Pöttgen and Jeitschko (Figure 3). Like a smorgasbord of carbon forms in carbides, it has everything—C and C₂ and C₃ units in a complex arrangement whose repeat unit is Sc₉₀C₄₀ containing 12 C, 2 C₂, and 8 C₃. It is as if the metal atoms had torn apart a graphite lattice, forming little islands of organic matter in the metal.

Retreating just a bit from this vertiginous edge of complexity, consider Ca₅NiC₃, also made by the Jeitschko group at Münster in Germany. (Wolfgang Jeitschko is responsible for a great fraction of the carbides we have.) Figure 4 shows the one-dimensional Ni₃C₆⁺ ribbon cut out of the structure. It has vertex-sharing nickel squares, with C₂ wingtips. And smack in the middle of each square in this piecewise organic molecule—a square-planar (not tetrahedral) carbon!

Trapped in the Solid State
Consider still another Jeitschko structure, made of yttrium, cobalt, and carbon—YCoC (Figure 5). Through it run infinite [CoC]⁺⁻ needles, with a cobalt-carbon separation that is tied (with a discrete molecule) for the world’s record for shortest Co-C distance (1.85 angstroms). The Co-C separation in the naturally occurring molecule vitamin B₁₂ is substantially longer.

In YCoC there is a CoC⁻⁻ organometallic polymer, multiply bonded between Co and C, judging from that short distance. The polymer is trapped in the solid state. A theoretical chemist wishing to provoke his uppity experimental colleagues (that’s me) says, “Get it out of there, solubilize that polymer, give it—in a solvent—a better Lewis acid partner than Y⁺⁺.” Of course, they won’t get it out. But this structure should be an inspiration to molecular organometallic chemists making rodlike polymers; they’re possible, waiting to be made outside the solid.

Reasons to Be Interested in Carbides
As more carbon-rich carbides are synthesized, I think we will see other forms of C in them, and not only C, C₂, and C₃. In fact, I’m sure that little chunks of carbon will be made in solids in shapes that are so far unknown for carbon. Why? Well, every environment for the growth of an element (here carbon) creates its own “conditions of stability”—free in the gas phase or solution, on the surface of a metal, in the metal’s interior, at an interface. This is how I think about the fact that buckminsterfullerene, C₆₀, reached macroscopic stability—in the special reaction conditions of a carbon arc in a helium atmosphere. For most forms of carbon, survival after formation is guaranteed by the high barriers for breaking strong C-C bonds, even in strange, highly strained geometries. Based on what we know about the unusual geometrics of solid state borides (boron is next to carbon in the Periodic Table), it’s just a matter of time until we find weird C-C bonding in carbides.

Finally, a personal view of the importance of the carbides. It’s not in their economic value. Nor even in the simple to strange beauty of their structures, the paean to complexity they silently sing. No, their message is a spiritual one. The carbides are inorganic. Yet, ever so clearly, they are also organic—how else shall we think of those C-C bonds in many of them? Metal carbides are a bridge, the inherent link nature itself shows us, as we, in the simplicity of our minds, pigeonhole into one or another human-made category—organic, inorganic—the multifarious manifestations of one complex world.

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