Structure and chemistry of a metal cluster with a four-coordinate carbide carbon atom

(metal cluster metal surface analogy/x-ray crystallographic study/reactivity of metal carbide carbon atoms)

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ABSTRACT   Molecular metal clusters with carbide carbon atoms of low coordination number have been prepared; they are the anionic $[HFe_4C(CO)_{12}^-]$ and $[Fe_4C(CO)_{12}^{2-}]$ clusters. An x-ray crystallographic analysis of a tetraaminozinc salt of the latter has established a butterfly array of iron atoms with the carbide carbon atom centered above the wings of the Fe_4 core. Each iron atom was bonded to three peripheral carbonyl ligands. The distances from the carbide carbon to iron were relatively short, particularly those to the apical iron atoms (1.80 Å average). Protonation of the anionic carbide clusters reversibly yielded $HFe_4(CH)(CO)_{12}$, and methylation of the dianion gave $\{Fe_4[CC(O)CH_3](CO)_{12}^-\}$. Oxidation of $[Fe_4C(CO)_{12}^{2-}]$ yielded the coordinately unsaturated $Fe_4C(CO)_{12}$ cluster, which was extremely reactive. Hydrogen addition to this iron cluster was rapid below 0°C, and a C–H bond was formed in this transformation.

Carbon atoms chemisorbed on metal surfaces possess a high chemical reactivity (1). In further exploring the analogy between metal surfaces and metal clusters (2), we have attempted to demonstrate similar high reactivity for a carbide carbon atom in a molecular metal carbide cluster. We anticipated two features to be critical to such high reactivity in a cluster: a low coordination number for the carbide carbon atom and coordination unsaturation for the molecular cluster (3, 4). These features have been realized (5, 6) in the following clusters with 4-coordinate carbide carbon atoms, $[Fe_4C(CO)_{12}^{2-}]$ and $[HFe_4C(CO)_{12}^-]$. We describe here the crystal structure of $[Zn(NH_3)_4^{2+}]$ $[Fe_4C(CO)_{12}^{2-}]$ and the chemistry of these unique clusters with low-coordinate carbide carbon atoms.

EXPERIMENTAL

Procedures. All manipulations were performed under argon or nitrogen by using modified Schlenk techniques, a Vacuum Atmospheres HE-43 DRI-LAB, or a glass vacuum system. All solvents were dried by distillation from P_4O_{10}, calcium hydride, or sodium/benzophenone. NMR spectra were recorded on a modified Bruker 42-kG multinuclear, pulse-Fourier transform NMR spectrometer equipped with Nicolet Technology Corporation software. All chemical shifts were referenced to tetramethylsilane. Microanalyses were performed by Vazenken Tashinian (University of California, Berkeley, Department of Chemistry Microanalytical Laboratory).

$[Zn(NH_3)_4^{2+}][Fe_4C(CO)_{12}^{2-}][OH_2]$. A methanolic solution of $HFe_4(CH)(CO)_{12}(5)$ (200 mg, 15 ml) was mixed with an aqueous ammonia solution of $Zn(NH_3)_4Br_2$ (120 mg, 20 ml). Water (50 ml) was layered over the water/methanol reaction system and allowed to diffuse slowly into the lower aqueous layer. After 2

days, large single crystals of $[Zn(NH_3)_4^{2+}][Fe_4C(CO)_{12}^{2-}]$ formed. The supernatant was removed by a siphon and the crystals were collected. Analysis: calculated for $[Zn(NH_3)_4^{2+}][Fe_4C(CO)_{12}^{2-}]$ $[OH_2]$: C, 21.39; H, 1.95; N, 7.75. Found: C, 21.84; H, 1.95; N, 8.05.

X-Ray Crystallographic Study. Single crystals of $[Zn(NH_3)_4^{2+}]$ $[Fe_4C(CO)_{12}^{2-}][OH_2]$ were orthorhombic, space group *Pnma* $(D_{2h}^{16}$, no. 62) with $a = 15.502(4)$ Å, $b = 10.918(3)$ Å, $c = 13.348(4)$ Å, $V_c = 2259(1)$ Å, and $Z = 4$ at $-100°C$. With a Syntex P2$_1$ automated diffractometer, a graphite monochromator, and MoKα radiation ($\lambda = 0.71073$ Å), 2746 independent reflections were collected ($4.0° \leq 2\theta \leq 50.0°$) at $-100°C$ by the θ–2θ scan technique; of these, 1801 had $F_o^2 \geq 3\sigma(F_o^2)$. Data were treated for Lorentz and polarization effects, and individual absorption corrections were applied ($\mu_c = 36.6$ cm^{-1}, $T_{min} = 0.49$, and $T_{max} = 0.67$). After the structure was solved by using Multan (7), the oxygen atom of the water molecule and all the hydrogen atoms (except those in the water molecule) were found in difference Fourier maps. Full matrix least-squares refinement (anisotropic temperature factors for all atoms except the hydrogens, which were fixed at $B_{iso} = 3.0$ Å^3) yielded $R(F_o) = 0.065$ (all data) = 0.042 [for $F_o^2 \geq 3\sigma(F_o^2)$]. Form factors for Zn, Fe, C, and O (and anomalous dispersion corrections for Zn and Fe) were taken from the International Tables (8, 9); form factors for the H atoms were from Stewart *et al.* (10).

Oxidation of $[Fe_4C(CO)_{12}^{2-}]$ with Ag$^+$ in the Presence of Hydrogen. Dichloromethane (5 ml) was vacuum transferred to a cooled ($-196°C$) reaction tube (100 ml, Kontes stopcock) containing $[(C_6H_5)_3PNP(C_6H_5)_3^+]_2[Fe_4C(CO)_{12}^{2-}]$ (1) (80 mg) and AgBF$_4$ (20 mg). Then hydrogen was admitted to a pressure of 1 atm (1 atm = 1.013×10^5 Pa). The reaction mixture was warmed to $-78°C$ with rapid stirring and then was allowed to warm to 20°C, at which temperature deposition of silver metal was evident. After 10 min at 20°C, the solvent was removed under vacuum. Extraction of the residue yielded $HFe_4(CH)(CO)_{12}$ (5), as shown by the infrared spectrum. The analogous reaction with $^2H_2$ yielded the same product but with a 45% deuterium enrichment.

Oxidation of $[Fe_4C(CO)_{12}^{2-}]$ by Ag$^+$ Under CO Atmosphere. The above procedure was followed except that carbon monoxide was substituted for hydrogen. In this reaction, silver metal deposition was accompanied by a color change of the solution to dark green. $Fe_4C(CO)_{13}$ was obtained from a hexane extract of the reaction residue. Infrared $\nu(CO)$ (hexane): 2063s, 2050vs, 2039m, 2031m, 1989w, 1898w, br. Mass spectrum: 600 for the parent ion (^{56}Fe) and ions formed from successive losses of 13 carbonyls. Analysis: calculated for $Fe_4C_{14}O_{13}$: C, 28.04; H, 0.00; N, 0.00; Fe, 37.3. Found: C, 28.30; H, 0.05; N, 0.01; Fe, 38.4. In the absence of a CO atmosphere, this compound was also ob-

tained when more than 2 equivalents of AgBF$_4$ were added, presumably due to generation of free carbon monoxide by oxidative decomposition of iron carbonyl clusters.

Oxidative Degradation of [Fe$_4$C(CO)$_{12}$$^{2-}$] by Ag$^+$. [(C$_6H_5$)$_3$PNP(C$_6H_5$)$_3$$^+$]$_2$[Fe$_4$C(CO)$_{12}$$^{2-}$] (100 mg) and 2 equivalents of AgBF$_4$ (23 mg) were placed in a 50-ml reaction tube; dichloromethane (≈3 ml) was vacuum condensed into the reaction tube at −196°C. The reaction tube was first warmed to −78°C with stirring; then it was warmed to room temperature. Removal of the solvent under vacuum was followed by hexane extraction of the residue. The extract was evaporated to give Fe$_3$C(CO)$_{11}$, which was then recrystallized from chloroform at −25°C. Infrared ν(CO) (dichloromethane): 2110w, 2053s, 2012w, 1720vw. Mass spectrum: 488 parent (^{56}Fe) and ions from successive losses of 11 carbonyls.

Preparation of [(C$_6$H$_5$)$_3$PNP(C$_6$H$_5$)$_3$$^+$]{Fe$_4$[CC(O)CH$_3$] (CO)$_{12}$$^-$}. [(C$_6H_5$)$_3$PNP(C$_6H_5$)$_3$$^+$]$_2$[Fe$_4$C(CO)$_{12}$] (150 mg) was placed in a 50-ml Schlenk flask equipped with a Kontes stopcock and a ball-joint. Dry dichloromethane (10 ml) was vacuum transferred into the flask followed by ≈0.2 ml of iodomethane. The solution was stirred at room temperature for 2 days, during which the solution turned from deep brown to green-black. The volume of the solvent was reduced to ≈1 ml; then 10 ml of ethyl acetate was added to precipitate white crystals. The solvent was removed from the supernatant, and the solid thus obtained was crystallized from ethanol at −25°C. Infrared ν(CO) (dichloromethane): 2021m, 1987vs, 1027sh, 1628w. ^{1}H NMR (δ CH$_2$Cl$_2$, +20°C and −90°C): 2.0 (s, 3H), 7.2–7.8 (m, ≈32H). CO ^{13}C NMR (ppm, tetrahydrofuran, −80°C): 196.7 (s, acetyl), 210.7 (s, 6CO), 219.1 (s, 3CO), 219.5 (s, 3CO). ^{13}C NMR (ppm, tetrahydrofuran, +27°C): 196.0 (s, acetyl), 214.6 (br.s, 12CO). Analysis: calculated for C$_{51}$H$_{33}$NFe$_4$P$_2$O$_{13}$: C, 53.12; H, 2.88; N, 1.21. Found: C, 52.96; H, 2.93; N, 1.20.

RESULTS AND DISCUSSION

The two related cluster ions [HFe$_4$C(CO)$_{12}$$^-$] and [Fe$_4$C(CO)$_{12}$$^{2-}$] are molecular carbide clusters with a carbide carbon atom of coordination number less than 5 (3–6); the previously established carbide clusters had carbide carbon atom coordination numbers of 5, 6, and 8 (3). Precise structural definition of the [Fe$_4$C(CO)$_{12}$$^{2-}$] ion is provided from our crystallographic data. Crystallographic analyses have been completed for a salt of [HFe$_4$C(CO)$_{12}$$^-$] by Shriver *et al.*[‡] and for a 4-coordinate carbide cluster, Fe$_4$C(CO)$_{13}$, by Bradley *et al.*[§] Thus, a comprehensive structural assessment can now be made for this new cluster carbide class. We use the term "carbide" as defined earlier in a
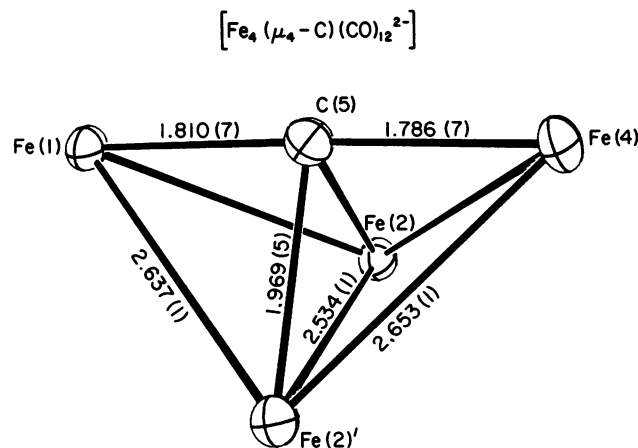

FIG. 1. Fe$_4$C core cluster structure for [Fe$_4$C(CO)$_{12}$$^{2-}$] in the hydrated tetraaminozinc salt is presented with values for all Fe–Fe and Fe–C (carbide) distances; a stereoscopic view of this cluster anion, shown in Fig. 2, depicts the stereochemistry of carbonyl ligand placement in the cluster. There is a crystallographic mirror plane that passes through Fe(1), C(5), and Fe(4) and bisects the Fe(2)–Fe(3) bond; the atom labeling scheme for the butterfly core structure is that used by Manassero *et al.* (12) and by us for related butterfly clusters (6) except that Fe(3) in the present structure above becomes Fe(2)' because of the crystallographic mirror plane.

connectivity context to avoid ambiguities associated with electronic or reactivity features (3, 5). A carbide carbon atom is one that is within bonding distance of only metal atoms. A carbide carbon atom that lies within a polyhedron of metal atoms is a *cage* (or interstitial) carbide, and those that lie in polyhedral faces or beyond are *peripheral* or exposed carbide carbon atoms (3, 5).

The crystal structure of [Zn(NH$_3$)$_4$$^{2+}$][Fe$_4$C(CO)$_{12}$$^{2-}$][OH$_2$] consisted of discrete cations, anions, and water of crystallization. The cations were the conventional tetrahedral [Zn(NH$_3$)$_4$$^{2+}$] aggregates. There appear to be interactions of the [Fe$_4$C(CO)$_{12}$$^{2-}$] anions with protons associated with the ammonia ligands of the cation. All these hydrogen-bond interactions were with oxygen

‡ Shriver, D. F., Holt, E. M. & Whitmire, K., 180th National Meeting, American Chemical Society (Las Vegas, NV, Aug. 25, 1980), *INOR* 003 (abstr.).

§ Bradley, J. S., Ansel, G. B., Leonowitz, M. & Hill, E., 180th National Meeting, American Chemical Society (Las Vegas, NV, Aug. 25, 1980), *INOR* 004 (abstr.).
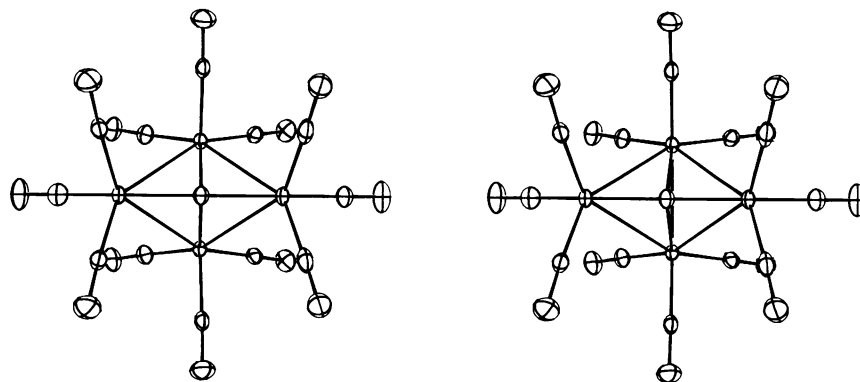

FIG. 2. This stereoscopic view of the [Fe$_4$(μ_4-C)(CO)$_{12}$$^{2-}$] anion clearly shows the crystallographic mirror plane cited in Fig. 1 and also illustrates the near C_{2v} symmetry of the molecule. Each iron atom has three terminal carbonyl ligands. Because of the near C_{2v} symmetry of the cluster, there are effectively only four types of CO environments—two associated with apical iron atoms and two with basal iron atoms.
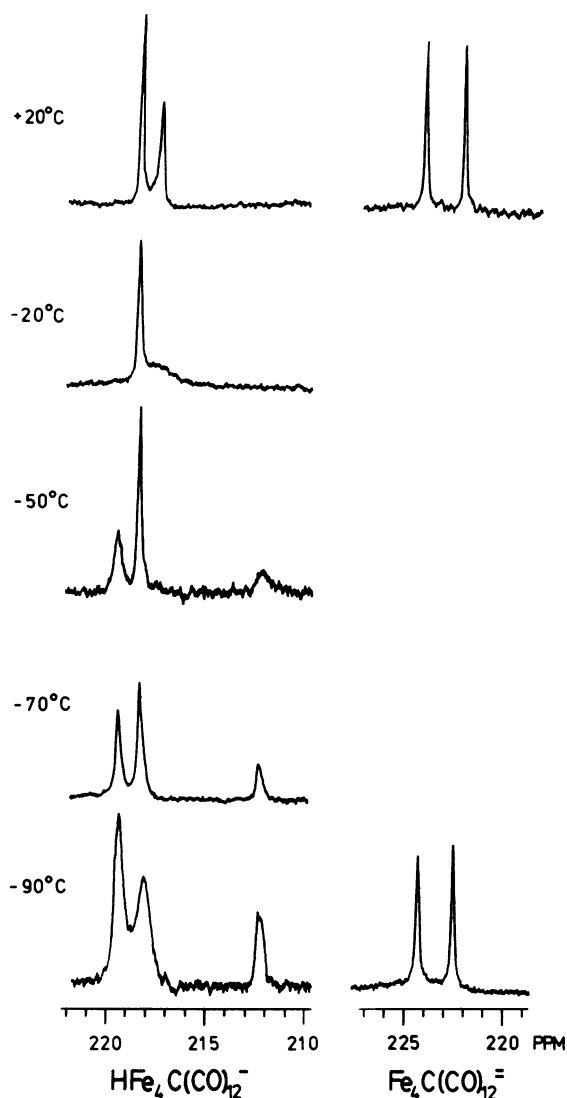
FIG. 3. ^{13}C CO NMR spectra for the two 4-coordinate carbide cluster anions. The spectrum of $[Fe_4C(CO)_{12}{}^{2-}]$ (*Right*) was essentially temperature independent over the temperature range of +20°C to −90°C; there were only two differentiable CO environments, ostensibly because of CO site exchange localized at the individual iron atoms. The spectra for $[HFe_4C(CO)_{12}{}^-]$ were temperature dependent (*Left*), with an approach to the limiting case of four resonances of relative intensities 2:1:2:1 at −90°C. At −70°C to −90°C, the observed relative intensities for three peaks are ≈2:3:1. The central, more intense resonance broadened substantially in going from −70°C to −90°C. This suggests that localized exchange at single iron atoms is still fast with respect to the NMR time scale at these temperatures for either the basal set or the apical set of iron atoms (and of course slow at the other set).

atoms of the carbonyl ligands of the anion and ostensibly did not substantially perturb the intrinsic structural or stereochemical features of the anion. The carbide cluster anion possessed the butterfly Fe_4C core expected (11) for a 62-electron cluster (Fig. 1), with the carbide carbon atom nearly centered above the wings. The cluster ion possessed a crystallographic plane of symmetry (Fig. 1) and nearly had C_{2v} symmetry, as is clearly shown in Fig. 2. Each iron atom had three terminal carbonyl ligands whose stereochemical disposition is illustrated in Fig. 2. All iron-carbon and carbon-oxygen bond distances associated with the carbonyl ligands were typical and require no comment.

The dianionic carbide cluster $[Fe_4C(CO)_{12}{}^{2-}]$ was derived from $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ by deprotonation. The structural de-

tails for the latter, parent methylidyne cluster have been established by x-ray (6) and neutron (13) crystallographic studies; it is instructive to compare these two clusters. Both have butterfly structures and the separations between the axial and basal iron atoms and between the carbide carbon atom and the basal iron atoms in both clusters are nondifferentiable within experimental error. The primary difference between the two structures results from the bridging three-center $Fe(1)\text{-}H_a\text{-}C(5)$ and $Fe(2)\text{-}H_b\text{-}Fe(3)$ bonds in the parent methylidyne cluster. Removal of these bridging hydrogen atoms explicably leads to a substantial decrease in the $Fe(1)\text{-}C(5)$ distance of ≈0.1 Å and in the $Fe(2)\text{-}Fe(2)'$ distance of ≈0.07 Å. [Note that the $Fe(2)\text{-}Fe(2)'$ labeling is $Fe(2)\text{-}Fe(3)$ in the parent cluster, as shown in Fig. 1.] The $Fe(1)\text{-}C(5)\text{-}Fe(4)$ angle is 170.5(1)° (molecule 1) in the parent methylidyne cluster and 177.6(5)° in $[Fe_4C(CO)_{12}{}^{2-}]$. A relatively characteristic shape parameter δ, the dihedral angle between the planes defined by the one apical iron atom and the two basal iron atoms and by the other apical iron atom and the two basal iron atoms, is 110.6° for the parent cluster and 101.5° for $[Fe_4C(CO)_{12}{}^{2-}]$; the angle reduction in going to the carbide dianion largely reflects the reduction in the $Fe(1)\text{-}C(5)$ separation.

The core Fe_4C structure in $[Fe_4C(CO)_{12}{}^{2-}]$ is similar to that in three isoelectronic iron carbide or nitride cluster butterfly structures—namely, $[HFe_4C(CO)_{12}{}^-]^\ddagger$, $[Fe_4C(CO)_{12}(\mu_2\text{-}CO)]^\S$, and $[HFe_4N(CO)_{12}]$ (14). The shape parameter δ is 104°, 101°, and 101.5°, respectively, for these three related clusters, values close to that for $[Fe_4C(CO)_{12}{}^{2-}]$. All Fe−Fe and Fe−C (carbide) or Fe−N (nitride) distances are similar to those reported here for $[Fe_4C(CO)_{12}{}^{2-}]$; the only experimentally significant parameter of variance is explicably the separation of the two basal iron atoms, which is dependent upon the presence or absence of a μ_2-bridging ligand at this site and the nature of the bridging ligand.

Both 4-coordinate carbide clusters, $[HFe_4C(CO)_{12}{}^-]$ and $[Fe_4C(CO)_{12}{}^{2-}]$, showed NMR evidence of facile intramolecular CO ligand site exchange. Each cluster anion should have C_{2v} or near C_{2v} symmetry in the solution state, and this stereochemistry requires two different CO environments for the CO ligands associated with the apical iron atoms and two for those associated with the basal iron atoms (Fig. 2). In fact, the dianionic cluster exhibited only two equal-intensity ^{13}C CO resonances from +20°C to −90°C, which is most realistically explained by a fast CO site exchange localized on individual iron atoms, a process commonly observed (15) for metal carbonyl clusters (Fig. 3). For the monoanion, $[HFe_4C(CO)_{12}{}^-]$, the ^{13}C CO spectra were temperature dependent, as shown in Fig. 3. At 20°C, the spectrum comprised two equal-intensity resonances analogous to that found for the dianion. Site exchange slowed sufficiently at lower temperatures (Fig. 3) so that the slow exchange limit of four resonances of 2:1:2:1 relative intensities, expected for C_{2v} symmetry, was approached at −90°C.

The $[Fe_4C(CO)_{12}{}^{2-}]$ anion was reversibly protonated to give first $[HFe_4C(CO)_{12}{}^-]$ and then $HFe_4(\eta^2\text{-}CH)(CO)_{12}$(5). Methylation followed a different course to ultimately form an apparently C-bonded acetyl cluster ion, $\{Fe_4[CC(O)CH_3](CO)_{12}{}^-\}$. Apparently, in methylation of the dianion, the methyl group was initially bonded to an iron atom(s) and then CO insertion to give an iron-bonded acetyl ligand occurred before migration of the methyl group to the carbide carbon atom could proceed. The final step was then migration of the acetyl ligand to the carbide carbon atom. The C-acetyl derivative is fluxional; the low-temperature ^{13}C NMR data indicate that there is a significant barrier to rotation of the acetyl group about the $Fe_4\text{-}C\text{-}C\text{-}(O)CH_3$ carbon-carbon bond. However, the proposed structure can only be considered tentative until a crystallographic analysis of a salt of the cluster is completed.

Chemistry: Davis *et al.*

The most significant chemistry associated with the 4-coordinate carbide cluster $[Fe_4C(CO)_{12}{}^{2-}]$ was in the oxidation to the transitory and coordinately unsaturated carbide cluster $Fe_4C(CO)_{12}$. Hydrogen reacted cleanly with this cluster with the formation of a C–H bond; specifically, $HFe_4(\eta^2\text{-CH})(CO)_{12}$ was formed. This is a definitive demonstration of high reactivity for a carbide carbon atom under mild conditions in a molecular cluster. Thus, the necessary conditions, as set out by us earlier (3, 4), of a coordinately unsaturated cluster with a low-coordinate carbide carbon atom have been realized in the putative $Fe_4C(CO)_{12}$ intermediate. The latter intermediate also reacted with carbon monoxide to form $Fe_4C(CO)_{12}(\mu_2\text{-CO})$, a cluster obtained through another reaction sequence by Bradley *et al.*,[§] but $Fe_4C(CO)_{12}$ did not complex with olefins or acetylenes. In the absence of effective reactants, oxidation of $[Fe_4C(CO)_{12}{}^{2-}]$ resulted in the formation of a trinuclear acylium type of cluster, $Fe_3(CCO)(CO)_{10}$.

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