

keeping with the generalization that the order of basicity is terminal CO  $\gg$   $\mu_2$ -CO  $<$   $\mu_3$ -CO.<sup>24</sup> This alkylation does not change the electron count of the cluster valence electrons; however, it does bring about a redistribution of electron density away from existing metal framework MO's and into the alkylated CO. Evidence for this electron redistribution includes the shift of all terminal CO stretching absorption modes to higher frequencies, the lengthening of the  $\mu_3$ -CO bond and shortening of the Fe-C bonds to the  $\mu_3$ -CO, and a variety of physical evidence on other compounds containing an electrophile attached to a CO oxygen.<sup>24-27</sup> It is presumably this electron density shift that brings about a rearrangement of the semibridging CO ligands from the three semibridging COs in the parent anion,  $[\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-CO})]^{2-}$  (I), to one in the alkylated product. From the chemical evidence cited above and a variety of physical data, bridging and semibridging CO ligands appear to withdraw more electron density than terminal CO; therefore, a semibridging disposition is favored for several CO ligands in the electron-rich cluster I, and the decrease in cluster electron density in the alkylated product V in electron-poor clusters causes a shift to terminal positions. One previous example of the shift of CO from bridging to terminal positions induced by an electrophile is known.<sup>28</sup>

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The foregoing transformations are summarized along with some of the previously reported chemistry on these compounds in Scheme I. For simple tri- and tetranuclear dianionic iron carbonyl cluster compounds, O-alkylation occurs with strong carbocation reagents, whereas protonation occurs on the metal bonds. Presumably, the different site preference arises from the bulk of  $\text{CH}_3$ , which inhibits interaction with the metal centers. The protonation of the tetrahedral ions I and V has the remarkable effect of inducing a framework geometry change from tetrahedral to a butterfly array. One possible rationalization for this conversion is that the steric requirements of the H, while small, induce a more open structure.<sup>2</sup> This open (butterfly) structure requires two more cluster valence electrons, which is attained in the product by a shift of one CO into a dihapto configuration, converting it from a two-electron donor to a four-electron donor.

**Acknowledgment.** The portion of this research conducted at Northwestern University was supported by the NSF, through Grant CHE-7918010. E.M.H. thanks Dr. Chuck Campana of Nicolet-XRD for his assistance with the data collection on compound IV.

**Registry No.** [PPN][ $\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-COCH}_3)$ ], 79075-54-0; [PPN]- $[\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-CCH}_3)]$ , 82865-65-4; [PPN]<sub>2</sub>[ $\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-CO})$ ], 69665-30-1; [PPN]<sub>2</sub>[ $\text{Fe}_4(\text{CO})_{12}\text{C}$ ], 74792-05-5;  $\text{CH}_3\text{SO}_3\text{CF}_3$ , 333-27-7.

**Supplementary Material Available:** Positional and thermal parameters and observed and calculated structure factors (97 pages). Ordering information is given on any current masthead page.

## Reactivity of Metal Carbide Clusters: Alkylation and Protonation of $[\text{Fe}_5(\text{CO})_{14}\text{C}]^{2-}$

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**Abstract:** The alkylation of  $[\text{Fe}_5(\text{CO})_{14}\text{C}]^{2-}$  was performed, and <sup>13</sup>C NMR indicates that alkylation occurs on a bridging carbonyl and not on the carbide. As judged by <sup>1</sup>H NMR, subsequent protonation occurs on the metal framework. This lack of reactivity of the carbide atom in the five-coordinate carbide cluster contrasts with reports of the protonation and alkylation of the four-coordinate carbide in  $\text{Fe}_4\text{C}$  clusters. Metal cluster carbides were investigated by extended Hückel calculations, which indicate a correlation between reactivity and the position of C-rich MO's relative to the HOMO and LUMO levels in the cluster. Model calculations on octahedral  $(\text{HFe})_6\text{C}$  and square-pyramidal  $(\text{HFe})_5\text{C}$  which lack reactivity at the carbide atom show a very large separation of molecular orbitals having significant carbon atomic orbital contributions. This MO separation is much smaller for the butterfly  $\text{Fe}_4\text{C}$  array and correlates well with the reactivity of this type of molecule. The MO calculations indicate that species of the type  $\text{M}_3\text{C}$ , having  $\text{C}_{3v}$  symmetry, are likely to be detectable.

The chemistry of metal carbide cluster compounds is an interesting and relatively unexplored area that may provide useful parallels with the chemistry of the surface carbides believed to be intermediates in the reduction of CO to hydrocarbons on Fe, Ru, and Ni.<sup>1</sup> In the present paper we explore the reactions of electrophiles, the proton and the methyl carbocation, toward the anionic iron carbonyl cluster  $[\text{Fe}_5(\text{CO})_{14}\text{C}]^{2-}$ . This is one member of the series of anionic iron carbide clusters ranging from the octahedral  $\text{Fe}_6(\text{CO})_{16}\text{C}^{2-}$ , which contains an enclosed octahedrally coordinated C,<sup>2</sup> to  $[\text{Fe}_5(\text{CO})_{14}\text{C}]^{2-}$ , which has square-pyramidal

coordination around the C atom;<sup>3</sup> to  $[\text{Fe}_4(\text{CO})_{12}\text{C}]^{2-}$ , which has a four-coordinated C cradled between the wing tips of a butterfly

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Table I. Extended Hückel Parameters

orbital	$H_{ii}$ , eV	$\xi_1$	$\xi_2$	$c_1$	$c_2$
H 1s	-13.60	1.30			
C 2s	-21.40	1.625			
C 2p	-11.40	1.628			
O 2s	-32.20	2.275			
O 2p	-14.80	2.275			
Fe 3d	-12.70	5.35	1.80	0.5366	0.6678
Fe 4s	-9.17	1.90			
Fe 4p	-5.37	1.90			

Wolfsberg-Helmholtz coefficient = 1.75  
 distances Fe-H = 1.60 Å; Fe-C = 1.89 Å;  
 Fe-Fe = 2.67 Å; C-O = 1.13 Å

array of iron atoms;<sup>4,5</sup> to the as yet unisolated  $[\text{Fe}_3(\text{CO})_{10}\text{C}]^{2-}$ , the deprotonated analogue of  $[\text{Fe}_3(\text{CO})_{10}(\text{CH})]^-$ , which contains a C atom coordinated to the three iron atoms.<sup>6</sup> The potential sites for the attack of electrophiles in these clusters are the carbide, metal atoms, or carbonyl oxygens.<sup>7,8</sup>

### Experiments and Calculations

**General Procedures.** All manipulations were carried out by using either Schlenck techniques under an inert atmosphere or a vacuum line. Solvents were dried by standard methods, distilled, and purged with prepurified  $\text{N}_2$  before use. Solids were manipulated in an inert-atmosphere glovebox. IR spectra were recorded on a Perkin-Elmer 399 and measured in  $\text{cm}^{-1}$ . Proton NMR were recorded on a Perkin-Elmer R-20B.  $^{13}\text{C}$  NMR were recorded in a Nicolet NT-360 at  $-95^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$  solvent. Mass spectra were recorded on a Hewlett-Packard 5985. Elemental analysis were performed by Galbraith Laboratories.

**General Syntheses.** A 5-g sample of  $\text{K}_2[\text{Fe}_4(\text{CO})_{13}]^9$  was dissolved in 80 mL of diglyme, 2.5 mL of degassed  $\text{Fe}(\text{CO})_5$  was added, and the mixture was heated to  $160^\circ\text{C}$  for 5 h.<sup>10</sup> The resulting deep red solution containing  $\text{K}_2\text{Fe}_6(\text{CO})_{16}\text{C}$  was converted to  $\text{Fe}_5(\text{CO})_{15}\text{C}$  by oxidation with  $\text{Fe}^{3+}$ .<sup>3</sup>  $[\text{Et}_4\text{N}][\text{Fe}_5(\text{CO})_{14}\text{C}]$  was prepared by the reaction of Na/Hg on  $\text{Fe}_5(\text{CO})_{15}\text{C}$ .<sup>11</sup>

$[\text{Et}_4\text{N}][\text{Fe}_5(\text{CO})_{13}(\text{COCH}_3)\text{C}]$ . A 0.2-g sample of  $[\text{Et}_4\text{N}]_2[\text{Fe}_5(\text{CO})_{14}\text{C}]$  was dissolved in 15 mL of  $\text{CH}_2\text{Cl}_2$ , and 0.08 mL of  $\text{CH}_3\text{SO}_3\text{F}$  was added via syringe. The solution was stirred for 8 h and the solvent removed under vacuum. The deep red solid was exposed to vacuum overnight to remove traces of  $\text{CH}_3\text{SO}_3\text{F}$ . The solid was redissolved in 10 mL of  $\text{CH}_2\text{Cl}_2$ , 30 mL of  $\text{Et}_2\text{O}$  added, and the resulting white solid removed by filtration. Slow evaporation of the solvent produced dark purple-black crystals of the product. Anal. Calcd for  $\text{Fe}_5\text{C}_24\text{H}_{23}\text{NO}_{14}$ : C, 34.79; H, 2.80; N, 1.69. Found: C, 34.84; H, 2.82; N, 1.83. IR ( $\text{CH}_2\text{Cl}_2$ ): 2050 (w), 1995 (s), 1988 (s), 1930 (sh).

$\text{HFe}_5(\text{CO})_{13}(\text{COCH}_3)\text{C}$ . A 0.1-g sample of  $[\text{Et}_4\text{N}][\text{Fe}_5(\text{CO})_{13}(\text{COCH}_3)\text{C}]$  was dissolved in 10 mL of  $\text{CH}_2\text{Cl}_2$  and the solution cooled to  $-37^\circ\text{C}$ .  $\text{HSO}_3\text{F}$  (0.01 mL) was added via syringe with rapid stirring, and stirring was continued for 10 min. The solvent was removed under vacuum, and the black tarry product was extracted with 15 mL of hexane. Black microcrystals were obtained by slow evaporation of this solution. IR (hexane): 2048 (m), 2030 (s), 2005 (mw); mass spectrum: parent ion at 699.5 (calcd 699.4) with successive loss of CO groups and methyl.

**Extended Hückel calculations** were performed by standard methods.<sup>12</sup> The parameters listed in Table I were used by Hoffmann in another study of iron-iron bonded systems.<sup>13</sup> The iron-carbon distance was set at 1.89 Å, which is the average of Fe-C distances in several iron carbide clusters, and the resulting Fe-Fe distance, 2.67 Å, was held constant for all systems. An initial set of calculations was performed on the bare  $\text{Fe}_n\text{C}$

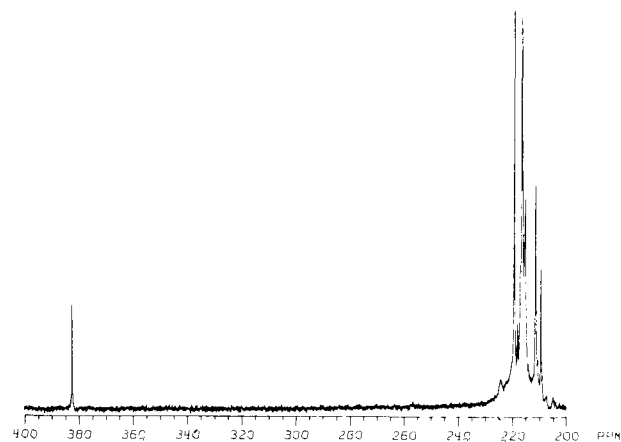


Figure 1.  $^{13}\text{C}$  NMR spectrum of  $[\text{Et}_4\text{N}][\text{Fe}_5(\text{CO})_{13}(\text{COCH}_3)\text{C}]$  obtained at 90 MHz. Shifts are in ppm relative to  $\text{Me}_4\text{Si}$ .

clusters and later repeated with  $(\text{HFe})_n\text{C}$  clusters. Mingos<sup>14</sup> has shown that the CoH is isolobal with  $\text{Co}(\text{CO})_3$ , and similar results were observed here for iron; however, there is a reversal of energy-level ordering, with FeH having  $e_1 > a_1$  vs.  $a_1 > e_1$  for  $\text{Fe}(\text{CO})_3$ . No charge iterations or geometry optimizations were performed. In keeping with Wade-Mingos-Lauher<sup>15-17</sup> rules, the position of the HOMO's and values of Mulliken overlap populations were determined by using the following number of valence electrons for each of the clusters: triangular  $\text{M}_3$ , 48; tetrahedral  $\text{M}_4$ , 60; butterfly  $\text{M}_4$ , 62; square pyramidal  $\text{M}_5$ , 74; and octahedral  $\text{M}_6$ , 86.

### Results and Discussion

**Reactions of Carbide Cluster Anions with Electrophiles.** The skeleton of  $[\text{Fe}_5(\text{CO})_{14}\text{C}]^{2-}$  is undoubtedly a square-based pyramid such as that found<sup>16</sup> for  $\text{Fe}_5(\text{CO})_{15}\text{C}$ , but the disposition of the CO ligands in the dianion is not known. In addition to terminal CO bands around  $1965\text{ cm}^{-1}$ , the IR of the dianion contains a band at  $1735\text{ cm}^{-1}$ , which is characteristic of an edge-bridging CO. These data in conjunction with the 3:11 pattern in the  $^{13}\text{C}$  NMR indicate a structure of 3 apical CO's and 11 basal CO's with one or more of these in edge-bridging positions along the base of the iron pyramid.<sup>1a</sup> An IR spectrum in KBr contains a band at  $815\text{ cm}^{-1}$  that may be assigned to a metal-carbide stretch. This is comparable to the Fe-C stretches in the parent  $\text{Fe}_5(\text{CO})_{15}\text{C}$  that are at  $790$  and  $770\text{ cm}^{-1}$ .<sup>18</sup>

Upon treatment of the dianion with strong alkylating agents, the terminal CO bands shift  $40\text{ cm}^{-1}$  to higher energy, which is expected for the conversion of a dianion to a monoanion, and the bridging CO band disappears, indicating a bridging to terminal CO shift similar to the CO rearrangement found for  $[\text{Fe}_4(\text{C}-\text{O})_{12}(\text{COCH}_3)]^-$ . In this latter compound, bridging CO's move to terminal positions upon alkylation of a CO.<sup>19b,c,f</sup> IR bands also appear at  $1291$  and  $835\text{ cm}^{-1}$  for  $[\text{Fe}_5(\text{CO})_{13}(\text{COCH}_3)\text{C}]^-$  in KBr, which can be assigned to the ether-type stretch of an alkylated CO and the initial carbide stretch, respectively.

**NMR Spectra and Structures.** The  $^1\text{H}$  NMR of this alkylated species in  $\text{CD}_2\text{Cl}_2$  contains a singlet at  $4.92\text{ ppm}$  that is comparable to other alkylated species,<sup>19</sup> Table II. The  $^{13}\text{C}$  NMR of  $[\text{Fe}_5(\text{CO})_{13}(\text{COCH}_3)\text{C}]^-$  containing 10% enriched  $^{13}\text{C}$ O shows a singlet at  $382.2\text{ ppm}$  and a series of five peaks between  $219.0$  and  $209.0$

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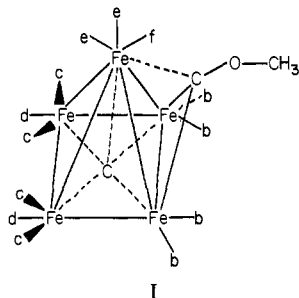
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Table II. Summary of  $^1\text{H}$  and  $^{13}\text{C}$  NMR Shifts of O-Alkylated Clusters

compound	solvent	$^1\text{H}$ shifts, ppm		$^{13}\text{C}$ shifts	ref
		aliphatic	hydride		
[PPN] $[\text{Fe}_3(\text{CO})_{13}(\text{COCH}_3)]$	$\text{CD}_2\text{Cl}_2$	4.33		336.8	8a
$\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$	$\text{C}_6\text{D}_6$	4.23	-18.20	356.5	8a
[PPN] $[\text{Fe}_3(\text{CO})_{10}\text{COC}_2\text{H}_5]$	$\text{CD}_2\text{Cl}_2$	4.49 (q), 1.52 (t)			8a
$\text{HFe}_3(\text{CO})_{10}\text{COC}_2\text{H}_5$	$\text{C}_6\text{D}_6$	4.54 (q), 1.24 (t)	-18.26		8a
[PPN] $[\text{Fe}_4(\text{CO})_{12}\text{COCH}_3]$	$\text{CD}_2\text{Cl}_2$	4.49		361.2	19b
$\text{HFe}_4(\text{CO})_{12}(\text{COCH}_3)$	$\text{CD}_2\text{Cl}_2$	4.08	-26.24	301	4
$\text{HRu}_3(\text{CO})_{10}(\text{COCH}_3)$	$\text{CD}_2\text{Cl}_2$	4.46	-14.85	366.5	19d
$\text{HOs}_3(\text{CO})_{10}(\text{COCH}_3)$	$\text{CD}_2\text{Cl}_2$	4.60	-16.2	352.2	19e
$[\text{Et}_4\text{N}][\text{Fe}_5(\text{CO})_{13}\text{C}(\text{COCH}_3)]^-$	$\text{CD}_2\text{Cl}_2$	4.92		381.2	this work
$\text{HFe}_5(\text{CO})_{13}\text{C}(\text{COCH}_3)$	$\text{CD}_2\text{Cl}_2$	4.87	-24.2	377.7	this work

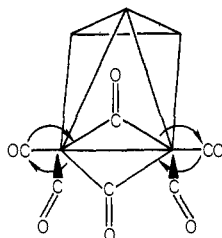
ppm in the ratio of 1:4:4:2:2:1 (Figure 1).<sup>20</sup> The distinctive, large downfield shift of one CO is characteristic of a bridging CO that has been alkylated at oxygen to form an ether-type linkage, Table II. The partial rigidity observed for the CO's in the terminal region of the alkylated species is consistent with the increase in stereochemical rigidity previously observed upon the O-alkylation of other iron carbonyl anions.<sup>8</sup>

The spectroscopic evidence is quite strong for attachment of the  $\text{CH}_3^+$  electrophile to the oxygen of an edge-bridging CO. The apparent lack of a peak of intensity 3 indicates that the apical CO's are not equivalent. This may arise from through-space steric interaction or direct bonding of the alkylated CO to the apical iron as shown in I. A similar structure has been proposed<sup>8a</sup> for



I

$[\text{Fe}_3(\text{CO})_{10}(\text{COCH}_3)]^-$ . As illustrated in II, CO's labeled c may



II

exchange via a bridging process which may make them distinct from the CO's labeled d.

The anion  $[\text{Fe}_5(\text{CO})_{13}\text{C}(\text{COCH}_3)]^-$  can be protonated to yield the unstable hydride  $\text{HFe}_5(\text{CO})_{13}\text{C}(\text{COCH}_3)$ . The  $^1\text{H}$  NMR provides clear evidence for the metal-bound proton (hydride) in this compound. Two  $^1\text{H}$  NMR peaks at 4.87 and -24.2 ppm of intensity ca. 3:1 are observed. The high-field resonance is in the region characteristic of edge-bridging Fe-H-Fe, and the methyl peak is essentially unshifted by the protonation.

The low-temperature  $^{13}\text{C}$  spectrum of  $\text{HFe}_5(\text{CO})_{13}(\text{COCH}_3)\text{C}$  again contains a distinctive downfield CO, 377.7 ppm, and a series of five singlets in the terminal region between 212.6 and 207.2 ppm of intensity ca. 1:2:2:2:3:2 (Figures 2 and 3). The similarity of the spectra with the alkylated monoanion implies that no major structural rearrangement has taken place upon protonation. Integration of the NMR peaks could not be performed with great

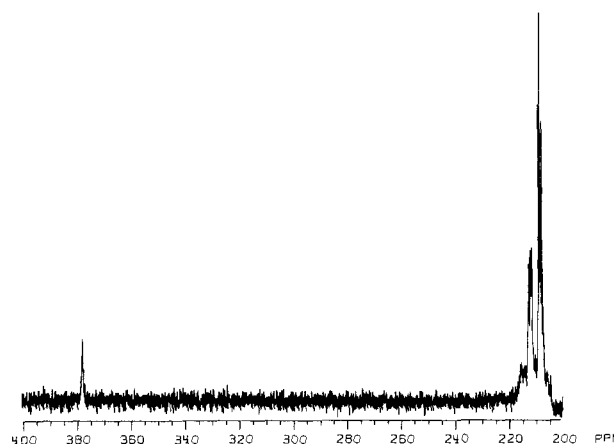


Figure 2.  $^{13}\text{C}$  NMR spectrum of  $\text{HFe}_5(\text{CO})_{13}(\text{COCH}_3)\text{C}$  obtained at 90 MHz. Shifts referenced as in Figure 1.

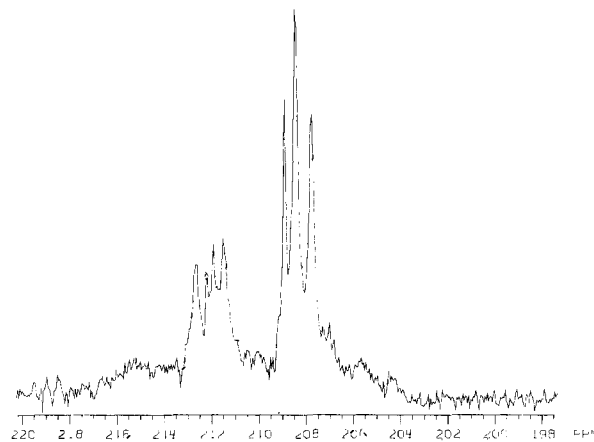
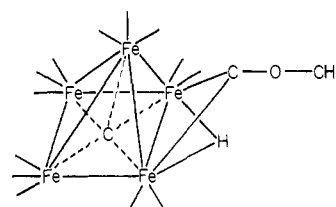


Figure 3. Detail of the 200-ppm region of  $^{13}\text{C}$  NMR of  $\text{HFe}_5(\text{CO})_{13}(\text{COCH}_3)\text{C}$ . Peaks marked with  $\times$  are spurious.

accuracy because of interference from signals of the impurity  $\text{HFe}_4(\text{CO})_{12}(\text{CH})$ . The appearance of a peak of intensity about 3 implies that the apical CO's are now exchanging and that the alkylated CO has assumed an edge-bridging position (III). This



III

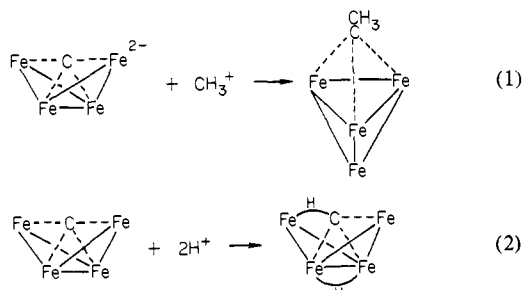
model is analogous to that for the structurally characterized<sup>8b</sup>  $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$ .

The attack of the electrophilic methyl carbocation on  $[\text{Fe}_5(\text{CO})_{14}\text{C}]^{2-}$  occurs at the oxygen of a bridging CO rather than at

(20) A solution of  $[\text{Et}_4\text{N}]_2[\text{Fe}_5(\text{CO})_{14}\text{C}]$  was stirred under a  $^{13}\text{CO}$  atmosphere overnight to isotopically label the carbonyl carbons but not the carbide. This  $^{13}\text{CO}$ -enriched material was then alkylated.

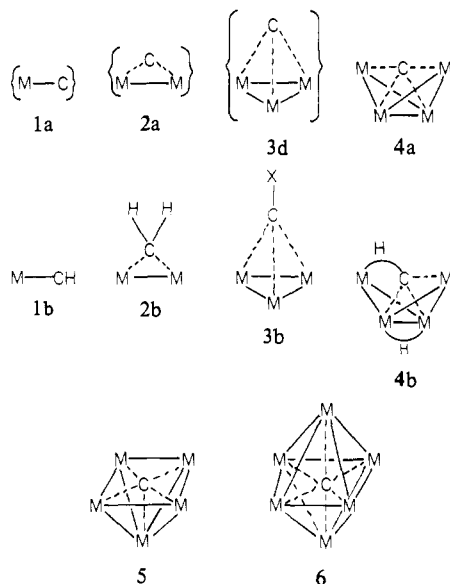
the exposed carbide atom. The reaction yields an O-alkylated COCH<sub>3</sub> group analogous to that in other cluster anions.<sup>8,19</sup> Also it has been shown by others<sup>21</sup> that monoprotection of [Fe<sub>5</sub>(CO)<sub>14</sub>C]<sup>2-</sup> occurs on the iron skeleton and not at the carbide. Similarly, the carbide atom in the neutral cluster Fe<sub>5</sub>(CO)<sub>15</sub>C has proved to be quite inert to attack by strong electrophiles such as H<sub>2</sub>SO<sub>4</sub>.<sup>11</sup>

**Correlations of Reactivity with Structure.** The lack of reactivity of the carbon atom in the 5-iron carbide with a strong carbocation reagent or with the proton contrasts with the carbide reactivity in the 4-iron species [Fe<sub>4</sub>(CO)<sub>12</sub>C]<sup>2-</sup> (eq 1 and 2). One clear



distinction between these clusters is the disposition of the carbide atom. Bradley and co-workers<sup>22</sup> and Muettterties and co-workers<sup>1</sup> have discussed the correlation of carbide reactivity with the degree of carbide exposure.

The chemistry of the known metal carbon compounds demonstrates that the reactivity of the carbide ligand-metal complexes depends very strongly on the number of attached metal atoms. For example, no terminal carbides attached to a single metal center, **1a**, are known at present, although there is a methylidyne



{ } = unknown species

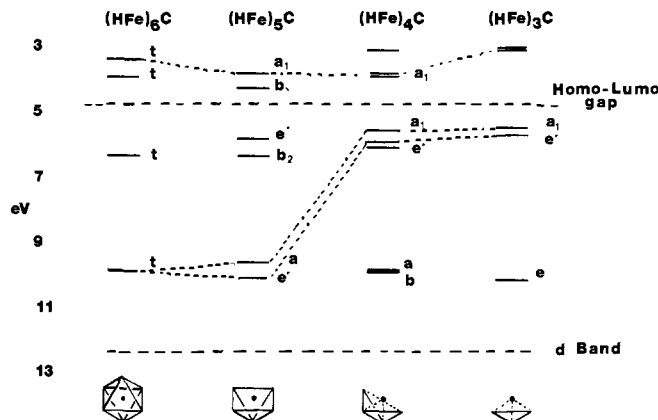
species known as M-CH, **1b**.<sup>23</sup> Similarly, a C bridge between two metals to form a closed triangle, **2a**, is unknown, but methylene bridges are, **2b**. Even with three attached metal atoms, the carbon atom appears to be so reactive that to date there is no known exposed carbide, **3a**, but a methyne that has a fourth group attached to the carbon atom is known, **3b**. The first example of a simple carbide in this series is observed with four metal atoms attached to carbon in the butterfly carbide **4**. As discussed above,

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**Figure 4.** Correlation of MO energies for the cluster carbides (HFe)<sub>x</sub>C, x = 3-6. Many of the Fe-Fe and Fe-C bonding orbitals have been omitted for clarity. The correlation indicated by ... connects the higher filled MO's and the lowest vacant MO's that contain large contributions from carbon atomic orbitals. The HFe moiety was used as an isolobal approximation to Fe(CO)<sub>3</sub>.

this type of carbide ligand in an anionic cluster is reactive with electrophiles. With five or six iron atoms around carbon, **5** and **6**, the carbide is highly stable, and the carbon atoms have so far proven to be devoid of reactivity.

**Correlation of Reactivity and Orbital Energies.** The skeleton of each member in the above series of metal carbides can be derived conceptually by successive removal of metal atoms from the octahedral carbide **6**. Initially, extended Hückel calculations were performed on the bare metal clusters.<sup>15</sup> In a second set of calculations, the influence of ligands was simulated by an approximation used by Mingos<sup>14</sup> in which the M(CO)<sub>3</sub> group is mimicked by MH. This approach is motivated by the observation that the framework orbitals generated for M(CO)<sub>3</sub> and MH are isolobal. The results of our Fe<sub>n</sub>C and (HFe)<sub>n</sub>C calculations are similar, but the latter model is preferred because it leads to stronger and apparently more realistic metal-metal interaction. The most important results from these calculations are displayed in the MO energy correlation diagram (Figure 4). For (HFe)<sub>6</sub>C, there is a large energy gap, 2.4 eV, between the HOMO and LUMO molecular orbitals for an 86 valence electron cluster, as expected from Wade-Mingos-Lauher rules.<sup>15-17</sup> The MO's containing substantial C atomic orbital contributions are well separated from the HOMO-LUMO gap, Figure 4. This energy ordering arises from strong interaction between the C valence orbitals and s and d orbitals of the surrounding Fe atoms that are well disposed to overlap with all of the C orbitals. According to our extended Hückel results, interactions of the metal p orbitals with carbide orbitals are negligible. (For previous discussion of this point, see ref 15). Whether the observed lack of reactivity of the carbon in the Fe<sub>6</sub>C cluster compounds arises from this energy ordering or from steric factors is a moot point. With the (HFe)<sub>5</sub>C cluster, a similar gross ordering of energies is observed, as illustrated in Figure 4. The Fe-C interaction is still sufficiently large to leave virtually no C atomic orbital contribution to the MO's most likely to partake in chemical reaction, i.e., those at or near the HOMO or the LUMO. This result correlates with the observed lack of protonation or alkylation of the carbide carbon on the 5-iron carbide compounds, which are observed in this and previous studies.<sup>21</sup> It also is possible that steric factors account for the lack of carbide reactivity of [Fe<sub>5</sub>(CO)<sub>14</sub>C]<sup>2-</sup> toward CH<sub>3</sub>SO<sub>3</sub>F; however, steric repulsion will not explain the lack of carbide reactivity of this ion toward H<sup>+</sup>. Furthermore, some simple estimates suggest that there is sufficient room to accommodate a CH<sub>3</sub> group.<sup>3</sup>

A qualitatively different situation is observed for MO energy ordering in the (HFe)<sub>4</sub>C and (HFe)<sub>3</sub>C clusters. For the former, the HOMO-LUMO energy gap is somewhat smaller than for the larger clusters, but still substantial, 1.6 eV. The new feature in the 4-iron butterfly array is the significant contribution of the carbide atomic orbitals to the HOMO, the LUMO, and other nearby orbitals. This feature correlates well with the reactivity

that is observed at the carbide carbon in this cluster system. The positions of the HOMO and LUMO metal orbitals are somewhat artificial because of the omission of CO ligands. The significant result of these calculations is the great decrease in the gap between filled and empty carbide-containing orbitals on going from the 5- and 6-metal cluster carbides down to 3- and 4-metal carbides. In the low-coordinate carbides, the carbon p orbitals form molecular orbitals that are not as stabilized and lie near the frontier orbital interface.

Removal of one more FeH vertex from the cluster generates (HFe)<sub>3</sub>C, in which a triangular array of iron atoms is capped on one face by a carbide. In this case, the large gap in energy occurs for 50 valence electrons, which superficially appears to be at variance with the 48-electron count expected for a 3-metal cluster. On closer inspection it is noted that there is a nonbonding carbide orbital of a<sub>1</sub> symmetry, which is 5 e<sub>u</sub> below the HOMO and is nearly pure C(p<sub>z</sub>). The C(p<sub>z</sub>) coefficient in this orbital is 0.80, and the largest bonding iron d orbital coefficient is 0.29; so the interaction is small with the framework. Therefore, this is best considered to be a carbon nonbonding lone-pair orbital, which should not be included in arriving at the cluster valence electron count. With this reassignment, the number of cluster valence electrons is the expected 48. This situation is reminiscent of the nonbonding "exodeltahedral" sulfur orbitals that Rudolph and co-workers<sup>25</sup> have described for sulfur-containing carboranes. Clearly, the existence of a carbon lone pair in the (HFe)<sub>3</sub>C moiety should confer reactivity at the carbon, but the substantial HOMO-LUMO gap indicates that the detection of a μ<sub>3</sub>-carbide may not be out of the question. As with the other clusters considered above and recent calculations on Co<sub>3</sub>(CO)<sub>9</sub>CX molecules,<sup>24</sup> the carbide carbon is strongly bonded to the metal triangle. The prospects seem particularly good for the isolation of Fe<sub>3</sub>C species in which the carbide is "stabilized" by coordination to main-group

or transition-metal acceptor species.

### Conclusions

The simple MO results correlate well with the observed reactivity of the carbide atom in the iron carbonyl carbides. In the octahedral Fe<sub>6</sub>C species and square-pyramidal Fe<sub>5</sub>C, strong interaction between all of the carbon p orbitals and the metal framework results in a large separation of the highest filled and lowest empty orbitals having significant carbide contributions. This result is in harmony with the observation that neither of these cluster types displays reactivity at the carbide. For the more exposed carbide of the butterfly Fe<sub>4</sub>C species, the gap between highest filled and lowest empty carbide orbitals is greatly reduced, in agreement with the observed carbide atom reactivity. The Fe<sub>3</sub>C species has a somewhat smaller carbide orbital energy gap. In addition, it contains an orbital with relatively little cluster interaction, which is best described as a carbide lone pair. These features of the electronic structure parallel the lack of observation of a simple μ<sub>3</sub>-carbide, although derivatives of the type M<sub>3</sub>CR are well-known. Despite experimental and theoretical indications of great reactivity at the μ<sub>3</sub>-carbide, the extended Hückel results do show a significant energy gap between empty and filled carbide-containing molecular orbitals, so the detection of a μ<sub>3</sub>-carbide remains a distinct possibility. The MO calculations were based on idealized geometries close to those in observed known clusters. Large distortions of the M<sub>n</sub>C array such as pulling the C atom significantly out of the basal plane in an M<sub>4</sub>C or away from the M<sub>4</sub> butterfly array will significantly alter the metal-carbon interactions and should therefore affect the reactivity of the carbide.

**Acknowledgment.** This research was supported by the National Science Foundation through Grant CHE-798010. We appreciate fruitful discussions with Drs. John Bradley and Ken Whitmire concerning the reactivity of cluster carbides. High-field <sup>13</sup>NMR measurements were made at the University of Illinois NSF Regional Instrumentation Facility (Grant CHE 97-16100).

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## Proton-Induced Reduction of CO to CH<sub>4</sub> in Homonuclear and Heteronuclear Metal Carbonyls: A Survey of the Influence of the Metal and Nuclearity

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**Abstract:** The reactions of mononuclear, dinuclear, trinuclear, tetranuclear, and hexanuclear metal carbonyls with HSO<sub>3</sub>CF<sub>3</sub> have been studied. Mononuclear through trinuclear metal carbonyls produce no appreciable amounts of CH<sub>4</sub>. Trace amounts of methane, which were sometimes generated from these low-nuclearity systems, are attributed to small amounts of higher nuclearity cluster. Methane production in the case of the tetranuclear clusters increases in the order Co<sub>4</sub>(CO)<sub>12</sub> < [FeCo<sub>3</sub>(CO)<sub>12</sub>]<sup>-</sup> < [Ru<sub>3</sub>Co(CO)<sub>13</sub>]<sup>-</sup> < [Fe<sub>3</sub>Co(CO)<sub>13</sub>]<sup>-</sup> < [Ru<sub>4</sub>(CO)<sub>13</sub>]<sup>2-</sup> < [Fe<sub>4</sub>(CO)<sub>13</sub>]<sup>2-</sup>. The indication from these studies is that polynuclear metal centers are required for the proton-induced reduction of CO to methane.

A distinctive feature of the conversion of CO to hydrocarbons on Fe, Ru, and Ni surfaces appears to be the scission of the CO bond and subsequent hydrogenation of the surface carbide.<sup>2-4</sup> By contrast, CO activation and reduction by mononuclear metal

complexes are thought to be dominated by CO migratory insertion as the primary step.<sup>5-7</sup> It is probable that the differing patterns of reactivity arise because surface interactions with several metal atoms promote CO bond cleavage and formation of surface intermediates, whereas these multimetal interactions are not possible in homogeneous reactions at single-metal complex centers.<sup>8</sup>

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