syn stereochemistry with respect to the diene fragment presumably reduces steric interactions between bulky coordinated $Fe(CO)_3$ and $PtCl_2$ units.

An underlying reason for the facile and rather selective coupling of acetylenes observed here is that in complexes of type I the alkynes, when forced into close proximity by bulky groups in the coordination sphere of the platinum atom, exhibit intramolecular interactions.[3,11] It is possible that the nature of these intramolecular alkyne–alkyne contacts influences the direction of acetylene coupling since for R = Ph, Cy, and $SiMe_3$ coupling affords predominantly cyclopentadienones whereas for R = *t*-Bu, there is high specificity for cyclobutadiene synthesis. It is also significant to note that these metal carbonyl mediated cyclizations stand in sharp contrast to the corresponding thermal reactions where disubstituted naphthalenes are the principal products for R = Ph.[3] The overall ramifications of these observations for the synthesis of new substituted carbocycles and ligands are under investigation.

Registry No. I (X = Cl, R = *t*-Bu), 42847-18-7; I (X = Cl, R = Ph), 42847-16-5; I (X = Br, R = Ph), 71755-68-5; I (X = 2-MeC_6H_4, R = Ph), 91390-55-5; I (X = C_6F_5, R = Ph), 91409-33-5; I (X = CF_3, R = Ph), 91390-56-6; I (X = Cl, R = Cy), 91390-57-7; I (X = Cl, R = $SiMe_3$), 91390-58-8; II, 91390-50-0; III, 91390-48-6; IV (X = Br, R = Ph), 91390-41-9; IV (X = 2-MeC_6H_4, R = Ph), 91390-42-0; IV (X = C_6F_5, R = Ph), 91409-31-3; IV (X = Cl, R = Cy), 91390-44-2; IV (X = Cl, R = $SiMe_3$), 91390-45-3; IV (X = Cl, R = Ph), 91390-52-2; V (X = Cl, R = Cy), 91390-43-1; V (X = Br, R = Ph), 91390-46-4; V (X = 2-MeC_6H_4, R = Ph), 91390-47-5; V (X = C_6F_5, R = Ph), 91409-32-4; V (X = Cl, R = Ph) $Fe_2(CO)_9$, 91390-54-4; (η^5-C_5H_5)$Co(CO)_2$, 12078-25-0.

Supplementary Material Available: Details of collection, reduction, and refinement and tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles and structure factor amplitudes for all three compounds, II, IV, and V (102 pages). Ordering information is given on any current masthead page.

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(10) Comparison of the structures of IV (X = Cl, R = Ph) and V (X = C_6F_5, R = Ph) reveals that both molecules contain nonplanar C_6O ring systems. In IV the dihedral angle between the plane defined by the four diene carbon atoms C(4), C(5), C(7), and C(8) and the plane defined by C(5), C(7) and the carbonyl carbon C(6) is 16.9°. For V the same dihedral angle is only 5.1°. In IV the enone oxygen atom and the diene carbon atoms C(4) and C(8) have an anti stereochemistry with respect to the plane C(5), C(6), C(7) whereas in V, the corresponding diene carbon atoms C(13) and C(17) are syn to the carbonyl oxygen atom. The ketonic C=O bond length of 1.232 (14) Å in IV is arguably longer than in the non-π-complexed compound V (C(15)–O = 1.203 (9) Å).

(11) Forced intramolecular interactions in acetylenes frequently lead to unusual reactivity. See, for example: Misumi, S.; Kaneda, T. In "The Chemistry of the Carbon-Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978; Chapter 16. Also: Muller, E.; Luppold, E.; Winter, W. *Synthesis* 1975, 265 and references therein.

Interaction of Fischer Carbene Complexes of the Type $W(CO)_5[C(OMe)R]$ ($R = CH_3, C_2H_5$) with Acetylenes

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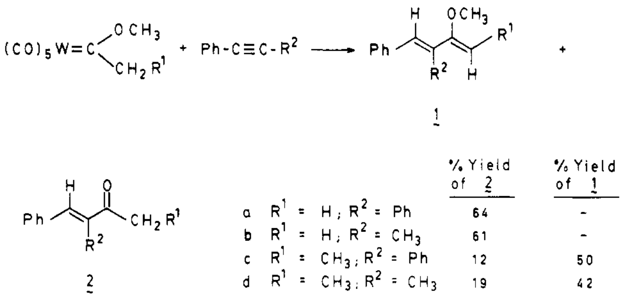
Summary: $W(CO)_5[C(OMe)CH_2R^1]$ ($R^1 = H, CH_3$) reacts with PhC_2R^2 ($R^2 = Ph, CH_3$) in toluene at 100 °C to give vinyl ethers and enones. The formation of these products can be explained by an exocyclic β-hydride elimination reaction of a metallacyclobutene intermediate.

Scheme I



	% Yield of 2	% Yield of 1
a $R^1 = H; R^2 = Ph$	64	-
b $R^1 = H; R^2 = CH_3$	61	-
c $R^1 = CH_3; R^2 = Ph$	12	50
d $R^1 = CH_3; R^2 = CH_3$	19	42

The interaction of Fischer-type chromium carbene complexes and acetylenes has received considerable attention from several research groups.[1-3] These investigations include mechanistic as well as synthetic studies, indicating that chromium carbene complexes have synthetic utility in the preparation of many useful organic molecules, including vitamins K and E,[4] nanomycin A and deoxyfrenolicin,[2] and precursors to anthracyclinones.[3] Surprisingly, little work has appeared concerning the interaction of Fischer-type tungsten carbene complexes with acetylenes.[5,6] The most recent report by Geoffroy and co-workers focused on the photochemistry of $W(CO)_5[C(OMe)Ph]$ with several acetylenes, including PhC_2Ph, PhC_2Me, MeC_2Me, PhC_2H, and n-$C_4H_9C_2H$.[5] The isolation of the first alkyne–carbene complex at −30 °C was also described by a photolysis of $W(CO)_5[C(OMe)Ph]$ and PhC_2Ph in hexane solvent.[5] We wish to report here our findings on the interaction of $W(CO)_5[C(OMe)CH_2R^1]$ (R^1 = H, CH_3) with acetylenes.

The carbene complexes $W(CO)_5[C(OMe)CH_2R^1]$ (R^1 = H,[7] CH_3[8]) were reacted with PhC_2R^2 (R^2 = Ph, CH_3) in toluene at 100 °C to produce **1c**, **1d**, and **2a–d** (Scheme I).[9,10] Compounds **1c**, **1d**, and **2a–d** were isolated by

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(1) For a comprehensive review see: Dötz, K. H. *Pure Appl. Chem.* 1983, *55*, 1689.

(2) Semmelhack, M. F.; Bozell, J. J. *Tetrahedron Lett.* 1982, *23*, 2931. Semmelhack, M. F.; Bozell, J. J.; Sato, T.; Wulff, W.; Spiess, E.; Zask, A. *J. Am. Chem. Soc.* 1982, *104*, 5850.

(3) Wulff, W.; Peng-Cho, T.; McCallum, J. S. *J. Am. Chem. Soc.* 1981, *103*, 7677. Wulff, W.; Peng-Cho, T. *Ibid.* 1984, *106*, 434. Peng-Cho, T.; Wulff, W. *Ibid.* 1984, *106*, 1132.

(4) Dötz, K. H. *J. Organomet. Chem.* 1977, *140*, 177. Dötz, K. H.; Pruskil, I.; Mühlemeier, J. *Chem. Ber.* 1982, *115*, 1278.

(5) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* 1983, *105*, 3064.

(6) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* 1980, *102*, 422. Katz, T. J.; Lee, S. J.; Shippey, M. A. *Ibid.* 1980, *102*, 7940. Katz, T. J.; Lee, S. J. Shippey, M. A. *J. Mol. Catal.* 1980, *8*, 219.

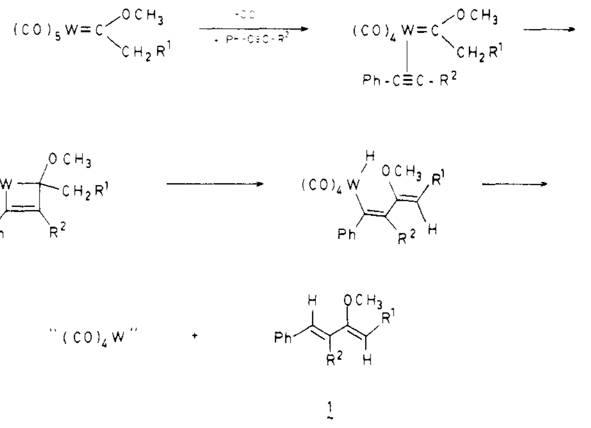
(7) Fischer, E. O.; Maasböl, A. *Chem. Ber.* 1967, *100*, 2445. Aumann, R.; Fischer, E. O. *Ibid.* 1968, *101*, 954.

(8) $W(CO)_5[C(OMe)C_2H_5]$ was prepared in 56% yield from ethyllithium and $W(CO)_6$ by using the same methods described in ref 7. The carbene prepared in this manner gave NMR and IR spectra in agreement with literature values. Winter, S. R.; Cornett, G. W.; Thompson, E. A. *J. Organomet. Chem.* 1977, *133*, 339.

(9) All isolated compounds were characterized by ^1H NMR (400 MHz), ^{13}C NMR (100.6 MHz), MS, IR, and physical properties (mp, bp, R_f), which agreed with reported literature values. **2a**: Fine, S. A.; Pulaski, P. D. *J. Org. Chem.* 1973, *38*, 1747. Zimmerman, H. E.; Singer, L.; Thyagarajan, B. S. *J. Am. Chem. Soc.* 1959, *81*, 108. Veprek-Bilinski, V.; Narasimhand, K.; Dreiding, A. S. *Helv. Chim. Acta* 1978, *61*, 3018. **2b** and **2d**: Roustan, J. L.; Guinot, A.; Cadiot, P. *J. Organomet. Chem.* 1980, *194*, 367. **2c**: Unterhalt, B. *Arch. Pharm. Ber. Dtsch. Pharm.* 1967, *300*, 748.

(10) Typically, 1.0 mmol of the tungsten carbene complex and 1.5–2.0 equiv of acetylene were used. The reactions were carried out in dry toluene under a nitrogen atmosphere. The reactions were terminated when the starting carbene complex had completely reacted as determined by TLC analysis.

Scheme II

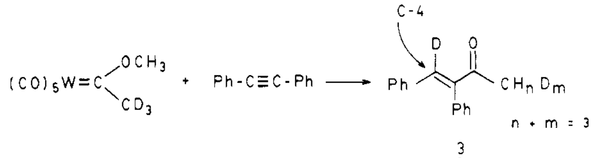


evaporating the toluene under vacuum followed by flash chromatography[11] of the residue. These reactions were also carried out in toluene-d_8, at 100 °C, and the progress of each was monitored by ^{1}H and ^{13}C NMR. The disappearance of the NMR signals of the starting carbene and acetylene could be followed easily with concomitant appearance of the NMR signals corresponding to the vinyl ethers **1a–d**. A signal at δ 191.15, which corresponds to $W(CO)_6$, was observed during the course of these experiments. Upon completion of the reaction $W(CO)_6$ could be isolated.[12] In each case, vinyl ethers **1a–d** formed prior to the appearance of the corresponding enones **2a–d**.[13] Vinyl ethers **1a** and **1b** (R^1 = H) could not be isolated from the reaction mixture. Their conversion to the corresponding enones **2a** and **2b** occurred under the reaction conditions or upon isolation or both. The formation of enones **2a–d** probably occurs via hydrolysis of the corresponding vinyl ethers **1a–d** during chromatographic workup.[11]

The reaction of $W(CO)_5[C(OMe)CH_3]$ with PhC_2Ph follows a different course than the analogous reaction with $Cr(CO)_5[C(OMe)CH_3]$, which affords a cyclobutenone in which one of the phenyl rings is coordinated to a $Cr(CO)_3$ group.[14] The fundamental difference between these reactions is that Fischer-type chromium carbene complexes, upon treatment with acetylenes, usually incorporate a CO ligand into the final product.[1-3] According to these results as well as work by Geoffroy and co-workers,[5] it appears that Fischer-type tungsten carbene complexes do not incorporate CO. This may be in part due to the greater strength of tungsten–carbonyl bonds as compared to chromium–carbonyl bonds.[5]

Both $W(CO)_5[C(OMe)CH_2R^1]$ and $W(CO)_5[C(OMe)Ph]$ exhibit the same regiochemistry in their reactions with PhC_2CH_3.[5] In each case (R^1 = H, CH_3), this preference is demonstrated by the isolation of only one of the two possible regioisomers, **2b** and **2d**. Additional information about the configuration of **1d** was obtained from a NOE difference experiment.[15] The results suggest that **1d** exists in the s-trans configuration and that the carbon–carbon double bond bearing the methoxy and methyl group has the *Z* configuration.

To account for the formation of the observed products from the reactions of $W(CO)_5[C(OMe)CH_2R^1]$ (R^1 = H, CH_3) with PhC_2Ph and PhC_2Me, we have proposed the mechanism outlined in Scheme II.[16] The first two steps in this mechanism (i.e., replacement of a coordinated CO ligand with an external acetylene, followed by metallacyclobutene formation) have been proposed in several mechanisms to date.[1-6] The last two steps involve an *exocyclic β-hydride elimination* followed by reductive elimination. We believe this represents the first example of an exocyclic β-hydride elimination reaction from a metallocyclobutene intermediate. Semmelhack and Tamura have recently proposed a similar sequence to explain the products arising from a reaction between Fischer-type iron carbene complexes and alkenes.[17] To gain further insight into this proposed mechanism, we prepared $W(CO)_5[C(OMe)CD_3]$[18] and studied its reactivity with PhC_2Ph. The results are summarized in eq 1. The reaction was conducted at 100 °C in toluene and compound **3** isolated by flash chromatography. The mass spectrum of **3** showed deuterium content of C-4 >98% as indicated by the fragment $[C_6H_5CD{=}C(C_6H_5)CO]^+$ (*m/e* 208). The deuterium content at C-1 had the following distribution: D_0 26% (*m/e* 223), D_1 38% (*m/e* 224), and D_2 35% (*m/e* 225). Presumably this distribution at C-1 arises from proton–deuterium exchange during isolation by chromatography. A comparison of the ^{1}H NMR of **2a** and **3** shows that product **3**, which results from a reaction between $W(CO)_5[C(OMe)CD_3]$ and PhC_2Ph, has only deuterium at



(1)

3

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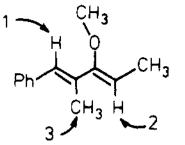
[11] Chromatography conditions: E. Merck silica gel 60 (40–63 μm), ethyl acetate/hexane 1:20. Still, W. C.; Kahn, M.; Metra, A. *J. Org. Chem.* **1978**, *43*, 2923.

[12] IR (hexane) ν_{CO} 1980 cm^{-1}; MS (*m/e*, ^{184}W) 352.

[13] NMR spectral data for **1a** (toluene-d_8): ^{1}H NMR δ 4.16 (d, 1 H, J_{HH} = 2.3 Hz), 4.03 (d, 1 H, J_{HH} = 2.3 Hz), 3.37 (s, 3 H); ^{13}C NMR δ 162.78 (s), 87.86 (dd, J_{CH} = 158.0 Hz), 54.91 (q). **1b** (toluene-d_8): ^{1}H NMR δ 4.36 (d, 1 H, J_{HH} = 2.6 Hz), 4.07 (d, 1 H, J_{HH} = 2.6 Hz), 3.34 (s, 3 H), 1.95 (d, 3 H, J_{HH} = 1.6 Hz); ^{13}C NMR δ 162.52 (s), 82.91 (dd, J_{CH} = 166.3 Hz), 54.73 (q), 14.90 (q).

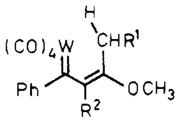
[14] Dötz, K. H.; Dietz R. *J. Organomet. Chem.* **1978**, *157*, C55.

[15] Irradiation of methyl group 3 shows a 26% enhancement in the intensity of vinyl hydrogen 2. Likewise, irradiation of the methoxy group shows a 12% enhancement in the intensity of vinyl hydrogen 1.



1d

[16] An alternative mechanism which accounts for the formation of **1a–d** includes the rearrangement of a metallacyclobutene to the carbene **4** followed by a [1,5] hydrogen shift and reductive elimination. Rearranged carbene complexes analogous to **4** but containing five CO ligands have been previously isolated. Dötz, K. H.; Kreiter, C. G. *J. Organomet. Chem.* **1975**, *99*, 309. Dötz, K. H. *Chem. Ber.* **1978**, *110*, 78. Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.



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[17] Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 6750.

[18] The tungsten carbene complex was prepared according to a procedure outlined for the analogous chromium carbene complex: Kreiter, C. G.; Fischer, E. O. *Chem. Ber.* **1970**, *103*, 1561.

C-4. The ^{1}H NMR of **2a** exhibits a singlet (δ 7.64) for the unique hydrogen at C-4. This resonance was not observed in the ^{1}H NMR of compound **3**. Likewise, a comparison of the $^{13}C\{^1H\}$ NMR of **2a** and **3** shows complete deuterium substitution at C-4. The $^{13}C\{^1H\}$ NMR of **3** exhibits a triplet (J_{CD} = 23.2 Hz) for the carbon at C-4.[19] The chemical shift of C-4 (δ 138.49) for **3** is slightly upfield of C-4 (δ 138.81) for **2a**. There have been many examples of this upfield deuterium isotope shift in ^{13}C NMR reported.[20]

These findings indicate that Fischer-type tungsten carbene complexes react with acetylenes under thermal conditions to give vinyl ethers and enones. The formation of these compounds can be explained by an exocyclic β-hydride elimination reaction followed by reductive elimination. We are continuing to investigate the reactions of tungsten carbene complexes with acetylenes and to develop their application in organic synthesis.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and Professor J. Paukstelis for assistance with the NOE experiment. We thank the National Science Foundation for financial support to purchase the 400-MHz NMR spectrometer.

Registry No. **1a**, 91711-62-5; **1b**, 91711-63-6; **1c**, 91711-64-7; **1d**, 91711-65-8; **2a**, 38661-88-0; **2b**, 42968-14-9; **2c**, 91711-66-9; **2d**, 75391-07-0; **3**-*d*, 91711-67-0; **3**-d_2, 91711-68-1; **3**-d_3, 91711-69-2; $W(CO)_6$, 14040-11-0; $W(CO)_5[C(OMe)CH_3]$, 20540-70-9; $W(CO)_5[C(OMe)CH_2CH_3]$, 37956-78-8; $W(CO)_5[C(OMe)CO_3]$, 64784-31-2; PhC≡CMe, 673-32-5; PhC≡CPh, 501-65-5.

Supplementary Material Available: Partial ^{1}H NMR (400 MHz) and $^{13}C\{^1H\}$ NMR (100.6 MHz) spectra for compounds **2a** and **3** (2 pages). Ordering information is given on any current masthead page.

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[19] The magnitude of the ^{13}C–D coupling constant (J_{CD}) is equal to J_{CH}/6.5. "Interpretation of Carbon-13 NMR spectra"; Wehrli, F. W.; Wirthlin, T.; Heyden Press: New York, 1980; p 107. The observed ^{13}C–H coupling constant for C-4 of compound **2a** was 152.8 Hz.

[20] Feeney, J.; Partington, P.; Roberts, G. C. K. *J. Magn. Reson.* **1974**, *13*, 268. Stothers, J. B.; Tan, C. T.; Nickon, A.; Huana, F.; Sridhar, R.; Weylein, R. *J. Am. Chem. Soc.* **1972**, *94*, 8581. Bell, R. A.; Chan, C. L.; Sayer, B. G. *J. Chem. Soc., Chem. Commun.* **1972**, 67. Dodrell, D.; Burfitt, I. *Aust. J. Chem.* **1972**, *25*, 2239.

Cluster Mimetics. 2. The Preparation and Characterization of $(\mu\text{-}H)(\mu\text{-}CO)Fe_3(CO)_9BH_2$, $(\mu\text{-}CO)Fe_3(CO)_9BH_2^-$, and $Fe_3(CO)_9BH_4^-$

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Summary: The preparation and characterization of $HFe_3(CO)_{10}BH_2$ and the related anions $Fe_3(CO)_{10}BH_2^-$ and $Fe_3(CO)_9BH_4^-$ are described. Measured ^{11}B NMR parameters demonstrate that the capping boron in $HFe_3(CO)_{10}BH_2$ is similar to the capping carbon in the isoelectronic $HFe_3(CO)_{10}CH$ cluster. However, in contrast to the CCH_3 derivative of this hydrocarbyl cluster, neither the neutral ferraborane nor the deprotonated anion undergoes ready reaction with H_2. The arrangement of hydrogens on $HFe_3(CO)_{10}BH_2$, compared to that in the analogous $H_3Os_3(CO)_9BCO$, emphasizes the important role of the M–H–M bond energy in these systems.

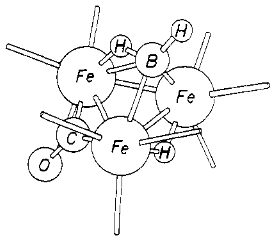
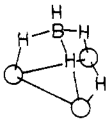
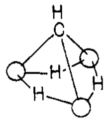


Figure 1. Proposed structure of $HFe_3(CO)_{10}BH_2$.

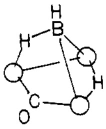
Isoelectronic compounds have provided a rich source of information upon which to base models of bonding. Examples of such compounds, differing only in the location of a single type of proton, are particularly fascinating in that the perturbation caused by moving a proton relative to the nuclear framework lends itself to simple physical descriptions.[1] In this vein, we have previously compared compounds in which BH replaces C in small systems, e.g., HBS vs. CS[2] as well as very large, e.g., $HFe_4(CO)_{12}BH_2$ vs. $HFe_4(CO)_{12}CH$.[3] Most recently we have described $HFe_3(Co)_9BH_4$,[4] I, and have contrasted its structure and properties to those of $H_3Fe_3(CO)_9CH$ (I′).[5] Herein we report the preparation and properties of $HFe_3(CO)_{10}BH_2$ (II). This particular cluster mimic is isoelectronic with $HFe_3(CO)_{10}CH$ (II′)[6] and is analogous to $H_3Os_3(CO)_9BCO$.[7] As such II, along with I, constitutes a perturbation of the reaction by which I′ and II′ (CCH_3 rather than CH) are interconverted in the presence of CO and H_2[8] and II defines one role of the transition metal in determining cluster isomer stability.



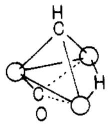
I



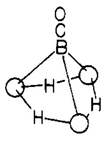
I′



II



II′



III

○ ≡ $Fe(CO)_3$

The reaction of $Na[Fe(CO)_4C(O)CH_3]$ in THF with 2 equiv of commercial $BH_3\cdot THF$[9] and 2 equiv of $Fe(CO)_5$ at 70 °C for 1 h yields a red mixture of anionic ferraboranes and iron carbonyl hydrocarbyls. Removal of the solvent, followed by treatment with 80% aqueous H_3PO_4 and extraction with hexane, yields a brown extract. Compound II is a major component of this mixture and is isolated in 14% yield (based on total iron) by chromatography as a brown solid that is modestly air stable. The molecular composition of this material was established by mass spectrometry as $C_{10}H_3O_{10}BFe_3$.[10] The fragmentation be-

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[1] See, for example: Ballard, R. E. *Appl. Spectrosc. Rev.* **1973**, *7*, 183.

[2] Fehlner, T. P.; Turner, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 7175.

[3] Fehlner, T. P.; Housecroft, C. E.; Scheidt, W. R.; Wong, K. S. *Organometallics* **1983**, *2*, 825.

[4] Vites, J.; Eigenbrot, C.; Fehlner, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4633.

[5] The ethylidyne derivative $H_3Fe_3(CO)_9CCH_3$ has been fully described (Wong, K. S.: Haller, K. J.; Dutta, T. K.; Chipman, D. M.; Fehlner, T. P. *Inorg. Chem.* **1982**, *21*, 3197. DeKock, R. L.; Wong, K. S.; Fehlner, T. P. *Ibid.* **1982**, *21*, 3203) and we have now fully characterized the methylidyne. Vites, J. C.; Jacobsen, G. B.; Fehlner, T. P., to be submitted for publication.

[6] Although we have prepared this compound, it has already been reported. Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307.

[7] Shore, S. G.; Jan, D.-Y.; Hsu, L.-Y.; Hsu, W.-L. *J. Am. Chem. Soc.* **1983**, *105*, 5923.

[8] Vites, J.; Fehlner, T. P. *Organometallics* **1984**, *3*, 491.

[9] A method for the in situ generation of reactive iron carbonyl anion fragments. Vites, J. C., unpublished observations.

[10] $^{56}Fe_3{}^{10}B^{12}C_{10}{}^{16}O_{10}{}^1H_3$: calcd 460.790 amu; obsd 460.788 amu. Sequential loss of 10 CO molecules from the parent ion is observed as well as a p − 1 ion (peak matched) of 25% of the intensity of the parent ion.

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