Condensation of Aldehydes with μ-Alkylidyne Diiron Complexes: A New Synthesis of μ-Vinylcarbyne Complexes

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Cationic bridging alkylidyne diiron complexes were first prepared by Rosenblum by the reaction of RLi with [C$_5$H$_5$(CO)-Fe(μ-CO)]$_2$ followed by strong acid workup.[1] Recently, we developed a new synthesis of μ-alkylidyne diiron complexes by addition of the C—H bond of μ-methylidyne complex 2[2] across the C=C double bond of alkenes.[3,4] A wide range of μ-alkylidyne complexes are readily available by this new hydrocarbation procedure.

μ-Alkylidyne complexes can be reversibly deprotonated to give μ-alkenylidene complexes.[5] The ease with which μ-alkenylidene complexes can be protonated to give cationic μ-alkylidyne complexes prompted us to study their reactions with carbon electrophiles. Here we report that μ-alkylidyne complexes react with aldehydes and related substrates to produce new cationic vinylcarbyne complexes in a reaction that involves attack of a μ-alkenylidene complex on a protonated aldehyde.

When a suspension of μ-ethylidyne complex 1[1] (630 mg, 1.43 mmol) was stirred with p-tolualdehyde (3 equiv) in THF for 26 h at 35 °C, the μ-(3-p-tolylprop-2-enylidyne)diiron complex 3[6]
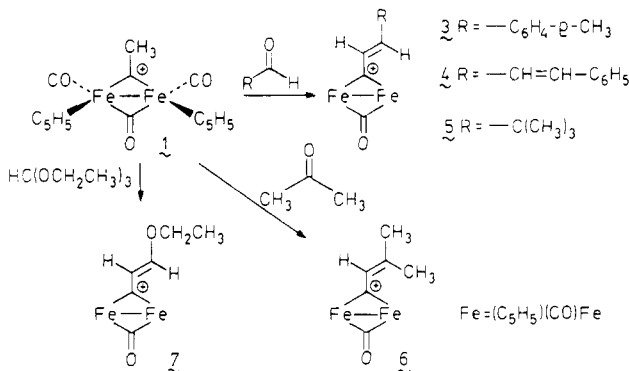
was formed in 93% yield as analytically pure purple microcrystals. The key ^{1}H NMR spectral features of 3 are the low-field chemical shifts of the vinylcarbyne protons at δ 10.26 (μ-CCH=CHR) and
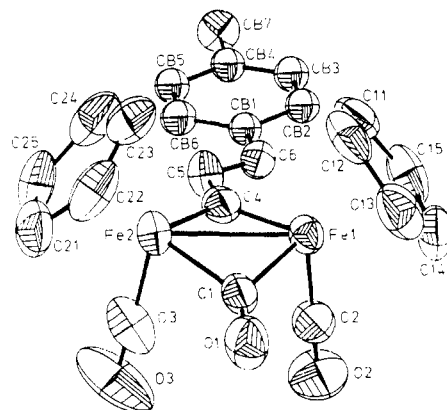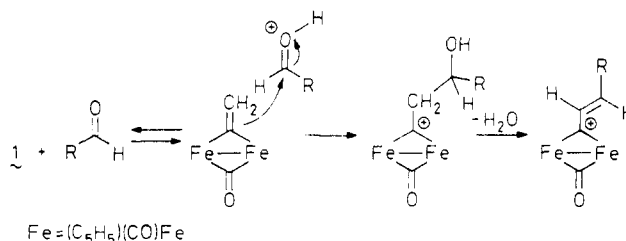
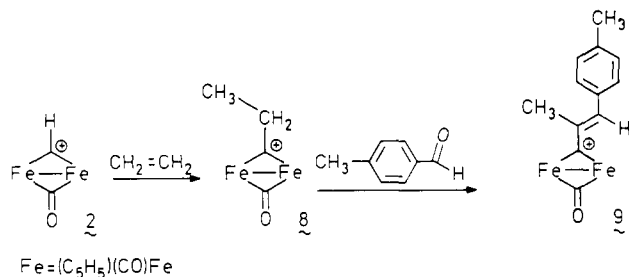(1) Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620.
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(6) **3**: ^{1}H NMR (270 MHz, acetone-d_6) δ 10.26 (d, *J* = 14.9 Hz, 1 H, CCH=CH), 8.20 (d, *J* = 8.2 Hz, 2 H, C$_6$H$_4$), 8.09 (d, *J* = 14.9, Hz, 1 H, CCH=CH), 7.48 (d, *J* = 8.1 Hz, 2 H, C$_6$H$_4$), 5.67 (s, 10 H, C$_5$H$_5$'s), 2.45 (s, 3 H, CH$_3$); ^{13}C{^{1}H} NMR (50.10 MHz, acetone-d_6, 0.07 M Cr(acac)$_3$) δ 439.9 (μ-CCH), 254.3 (μ-C=O), 208.9 (terminal CO), 153.4, 152.4 (CC-H=CH), 146.8 (CH=CHC), 133.5, 131.6 (ortho, meta), 132.8 (CCH$_3$), 93.1 (C$_5$H$_5$), 22.2 (CH$_3$); IR (CH$_2$Cl$_2$) ν(CO) 2033 (s), 2000 (m), 1848 (m) cm^{-1}. Anal. Calcd for C$_{23}$H$_{19}$BF$_4$Fe$_2$O$_3$: C, 50.98; H, 3.53. Found: C, 51.06; H, 3.76.

Figure 1. Structure of 3, BF$_4^-$ omitted for clarity.

8.09 (μ-CCH=CHR). In the X-ray structure of 3 (Figure 1),[7] the two iron centers and the entire vinylcarbyne ligand lie approximately in the same plane. The dihedral angles between the vinyl group and p-tolyl ring and between the vinyl group and the μ-CFe$_2$ unit are 11.0° and 1.5°, respectively. The vinylcarbyne ligand is best described as having a single bond between the μ-alkylidyne carbon and the vinyl group (1.422 (8) Å) and a localized double bond in the vinyl unit (1.335 (8) Å).

Similar condensation reactions of μ-ethylidyne complex 1 with other aldehydes, ketones, and ortho esters have been observed. Reaction of 3 equiv of cinnamaldehyde with a suspension of 1 in THF occurred over 10 h at 35 °C to give vinylcarbyne complex 4[7] in 98% yield. Condensation of a large excess of pivalaldehyde with a suspension of 1 in THF occurred over 20 h at 50 °C to produce vinylcarbyne complex 5[7] in 74% yield. When an acetone solution of 1 was stirred for 20 h at 35 °C, condensation occurred to produce the known vinylcarbyne cation 6[8] in 83% yield. Reaction of a large excess of triethyl orthoformate with a suspension of 1 in THF led to the isolation of the vinyl ether carbyne complex 7[7] in 90% yield.

μ-Propylidyne complex 8 was prepared from μ-methylidyne complex 2 and ethylene in a hydrocarbation reaction.[3,4] When a suspension of 8 was stirred in neat p-tolualdehyde at ambient temperature, 8 slowly dissolved and a more highly substituted vinylcarbyne complex 9[7] was isolated in 83% yield after 20 h.

We believe that the formation of vinylcarbyne complexes can best be explained by the mechanism shown above. μ-Alkylidyne complexes and aldehydes are proposed to be in equilibrium with μ-alkenylidene complexes and protonated aldehydes. The μ-alkenylidene complex can act as a carbon nucleophile to attack the protonated aldehyde in the key carbon–carbon bond-forming step. The driving force for this reaction is the formation of a carbon–carbon bond and of a cationic carbon center stabilized by two strongly electron donating iron atoms. Subsequent acid-catalyzed dehydration produces the vinylcarbyne complex.

Diiron vinylcarbyne complexes are now readily available either by the new condensation reaction reported here or by hydride abstraction from μ-alkenylidene complexes.[8] These crystalline materials are easily handled at room temperature in air. We are currently studying reactions of these new vinylcarbyne complexes with carbon nucleophiles to exploit their potential for synthesis.

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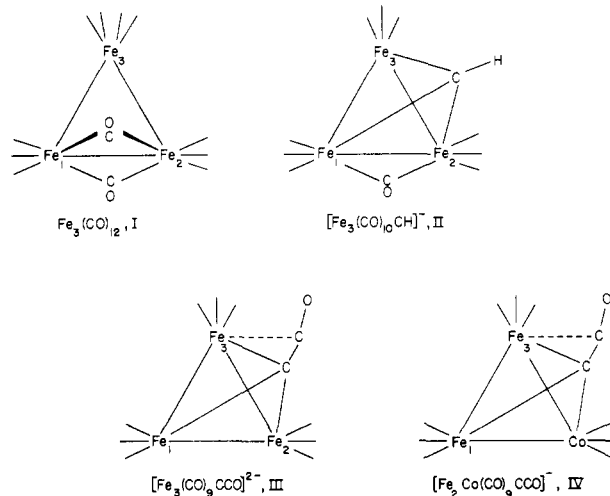
$Fe = (C_5H_5)(CO)Fe$

Supplementary Material Available: Elemental analysis and spectral characterization of **4**, **5**, **7**, and **9** and tables of crystal structure data for **3** (21 pages). Ordering information is given on any current masthead page.

Mössbauer Effect Study of $Fe_3(CO)_{12}$ and the Reduced Carbide Clusters $(PPN)[Fe_3(CO)_{10}CH]$, $(PPN)_2[Fe_3(CO)_9CCO]$, and $(PPN)[Fe_2Co(CO)_9CCO]$

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Metal carbide cluster compounds are expected to play a key role in understanding the cleavage of carbon monoxide on a metal surface. With the exception of the isoelectronic four-iron butterfly clusters[1,2] $Fe_4(CO)_{13}C$ and $[Fe_4(CO)_{12}C]^{2-}$ no metal carbide clusters with four or more metal atoms have shown reactivity at the carbide.[3,4] In contrast the three-iron cluster $[Fe_3(CO)_9CCO]^{2-}$ containing the ketenylidene ligand, CCO, has recently been shown to exhibit carbide reactivity and may indicate a role for ketenylidenes in the reduction of carbon monoxide at a surface. The importance of these clusters and the electronic properties at the metal and ligand sites has led us to undertake a detailed Mössbauer effect study of $Fe_3(CO)_{12}$ (I) and the closely related reduced carbide clusters $(PPN)[Fe_3(CO)_{10}CH]$ (II), $(PPN)_2[Fe_3(CO)_9$-CCO] (III), and $(PPN)[Fe_2Co(CO)_9CCO]$ (IV). Mössbauer spectroscopy proved very useful[5] in the structural elucidation of $Fe_3(CO)_{12}$, where it indicates the presence of two distinct iron sites in a two to one ratio,[6,7] and some related heteronuclear trimers.[8-10] Although the X-ray structures of $Fe_3(CO)_{12}$ and of both reduced compounds are known,[11,12] few details of the internal

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electronic environment are known. The Mössbauer effect isomer shifts have proven useful in elucidating the localization of the electronic density on the iron sites and in understanding the activation of the ketenylidene carbon toward nucleophilic attack.

$Fe_3(CO)_{12}$ was obtained from Alpha Inorganics and recrystallized from 50:50 acetone water. The reduced clusters were the same samples as studied earlier.[12] Mössbauer effect spectra were obtained on a conventional Ranger Scientific constant acceleration spectrometer which utilized a room temperature rhodium matrix cobalt-57 source. The spectra were fit to Lorentzian line shapes by using standard least squares computer minimization techniques[13] and standard error propagation techniques. The resulting Mössbauer spectra which were fit to symmetric doublets of either independent or constrained areas are illustrated in Figure 1. The resulting Mössbauer spectral parameters are listed in Table I where $\sum \delta$ is the sum of the isomer shifts for the three sites and $\Delta\delta$ is the change in isomer shift for each iron site upon reduction from $Fe_3(CO)_{12}$ to the carbides.

The results obtained for $Fe_3(CO)_{12}$ are typical of those found in earlier investigations[6,7] and indicate at 78 K the expected two structurally distinct iron sites[11] in the approximate ratio of two to one where the unique iron site Fe(3) has a virtually symmetric site symmetry and shows little or no quadrupole splitting at 78 K.[14,15] The isomer shift results obtained for $Fe_3(CO)_{12}$ are important because they form the basis of our understanding of the spectra obtained upon reduction. The values of $\sum \delta$ which decrease in going from the neutral to the monocation and dication clusters indicate the expected increase in the s electronic density at the nucleus upon reduction. Perhaps more useful is $\Delta\delta$ the change in δ for each site upon reduction. Upon reduction the value of $\Delta\delta$ is much larger for the Fe(1,2) sites than for the Fe(3) site. This indicates that upon reduction the added electron or electrons are *predominately* localized on the Fe(1,2) sites, the reduction having a much smaller influence on the electronic density on the Fe(3) site.

The quadrupole interaction values reveal details of the structural changes in the "parent" $Fe_3(CO)_{12}$ upon the formation of II. The replacement of a bridging CO group in I by the μ-CH methyne group in II has little influence upon the electronic symmetry at the Fe(1,2) sites, but the displacement of a terminal CO group from Fe(3) causes a dramatic reduction in the symmetry at Fe(3) in II. The further reduction of II to form the ketenylidene containing cluster, III, results in a large decrease in the quadrupole interaction on both the Fe(1,2) and the Fe(3) sites. For the Fe(1,2) site the

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