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Registry No. 1, 84254-55-7; **2**, 74282-47-6; Na(Me_5C_5), 40585-51-1; YbI_2, 31217-99-9; $EuBr_2$, 13780-48-8; Et_2O, 60-29-7.

Conversion of the Ketenylidene Cluster $[Fe_3(CO)_9(CCO)]^{2-}$ to the Acetylide Cluster $[Fe_3(CO)_9(CCOC(O)CH_3)]^-$ and Reactivity of the Acetylide System

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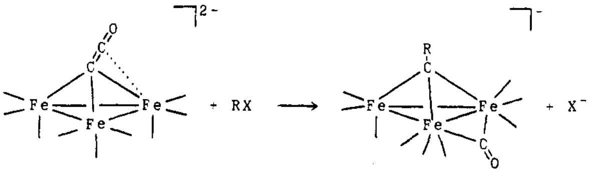
Summary: Acylation occurs at the oxygen atom of the ketenylidene moiety in $[Fe_3(CO)_9(CCO)]^{2-}$ to generate $[Fe_3(CO)_9(CCOC(O)CH_3)]^-$, which has been characterized spectroscopically and by single-crystal X-ray diffraction. The preservation of the C-C bond of the ketenylidene is noteworthy, and the product of this acylation reaction is the first acetylide cluster which contains an atom other than carbon or hydrogen adjacent to the C-C triple bond. Reactions with hydride and proton sources are described.

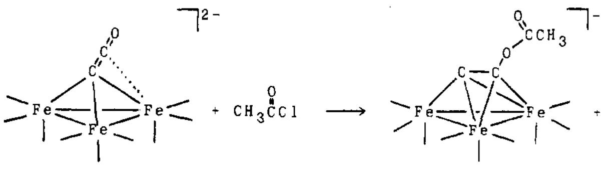
One important aspect of transition-metal cluster chemistry is the possibility of multi-metal bonding of ligands, which may activate bonds within the moiety or stabilize an otherwise unknown ligand.[1] The ketenylidene (C=C=O) ligand in the cluster anion $[Fe_3(CO)_9(CCO)]^{2-}$,[2] I, is an example of multi-metal ligand stabilization since the CCO moiety is unknown either in the free state or in monometal complexes. Earlier work demonstrated that in contrast to organic ketenes[3] or ketenyl ligands bound to a single metal center,[4] I reacts with protons or methylating agents at the α-carbon of the ketenylidene with subsequent C-C bond cleavage. The carbonyl group migrates onto the cluster framework affording II (eq 1).[2]



(1)

I

II a,b (a, R=H, X=CF_3CO_2; b, R=CH_3, X=I)



I

III

(2)

In this communication, we report that I displays a second reaction pathway in which acetyl chloride attacks the ketenylidene oxygen without C–C bond cleavage and forms an acetylide cluster, III (eq 2). This cluster has been fully characterized spectroscopically and by single-crystal X-ray diffraction. We also report the reactivity of III toward hydride and proton sources.

When a CH_2Cl_2 solution of I is treated with acetyl chloride, a new compound, III, can be isolated in high yield.[5] Analytical and spectroscopic data indicate the formula $[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]$.[6] On the basis of earlier work,[2] we expected a compound with structure II (R = $C(O)CH_3$) to be formed. However, there is no resonance in the ^{13}C NMR spectrum in the region associated with capping μ_3-CR groups, ca. 250–350 ppm.

The results of a single-crystal X-ray diffraction study of III show (Figure 1) that the acetyl group is attached to the ketenylidene oxygen.[7] This compound represents the product of the first example of reactivity at the oxygen atom of a cluster-bound ketenylidene moiety. Reaction 2 causes a change in bonding within the ligand from a four-electron donating ketenylidene (C=C=O) to a five-electron donating acetylide (C≡C—O). The analogous conversion of a π-bound ketenyl ligand to an alkyne has been observed in monometallic systems.[4] Clusters containing similar μ_3-(η^2-⊥)[11] bound acetylides are commonly synthesized from a terminal acetylene via C–H or C–X

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(5) In the preparation of III, 0.957 g (0.623 mmol) of I was dissolved in 5 mL of CH_2Cl_2 under an N_2 atmosphere. Acetyl chloride, 70 μL (0.98 mmol), was added and the solution stirred and then 25 mL of Et_2O was added and the solution filtered from [PPN]Cl. Solvent was removed, and the residue was crystallized from CH_2Cl_2/2-propanol; isolated 0.550 g, 85% yield. Pure material was recrystallized by slow diffusion of pentane into a CH_2Cl_2/Et_2O (1:2) solution of III.

(6) Anal. Calcd for $C_{49}H_{33}Fe_3NO_{11}P_2$: C, 56.52; H, 3.19; Fe, 16.09; N, 1.34. Found: C, 55.84; H, 3.28; Fe, 16.12; N, 1.35. IR: ν_{CO} (CH_2Cl_2) 2049 (w), 1990 (s), 1982 (s), 1961 (m), 1936 (m, sh), 1770 (w, br) cm^{-1}. ^1H NMR (CD_2Cl_2, +25 °C): 7.460 (m, 30 H, PPN^+), 2.296 (s, 3 H, $C(O)CH_3$). ^{13}C NMR (CD_2Cl_2, +25 °C): 216.1 (s, Fe–*C*O), 172.9 (s, *C*COC(O)CH$_3$), 168.1 (s, CCO*C*(O)CH$_3$), 132.2 (s, C*C*OC(O)CH$_3$), 20.6 (q, $^1J_{CH}$ = 130 Hz, CH_3) ppm, with ca. 0.03 M $Cr(acac)_3$ added. ^{13}C NMR (CD_2Cl_2, −90 °C) on a sample of III prepared from $[PPN]_2[Fe_3(^*CO)_9(^*C^*CO)]$ (ca. 30% ^{13}C): 215.8 (s, 9 C), 171.6 (d on s, 1 C, $^1J_{CC}$ = 39 Hz), 130.8 (d on s, 1 C, $^1J_{CC}$ = 39 Hz) ppm, with $Cr(acac)_3$ added.

(7) Crystal data for III (−100 °C): triclinic; $P\bar{1}$; a = 10.934 (5) Å, b = 13.189 (7) Å, c = 17.075 (6) Å; α = 84.90 (4)°, β = 70.14 (3)°, γ = 85.97 (4)°; V = 2305 Å^3; D(calcd) = 1.500 g·cm^{-3}; Z = 2; $\mu_{MoK\alpha}$ = 10.593 cm^{-1}. Data collection: Enraf Nonius CAD4 diffractometer, graphite-monochromated Mo radiation, variable speed ω–2θ scans, 3° < 2θ < 50°, $\lambda_{MoK\alpha}$ = 0.71073 Å. Data (4425 with I > 3σ (I)) were corrected for Lorentz, polarization, and background effects.[8] An empirical absorption correction based on psi scans was performed. The structure was solved by direct methods (MULTAN,[9] DIRDIF[10]). Hydrogen atoms were input in idealized positions, C–H = 0.95 Å. Refinement of scale factor, positional parameters, and anisotropic thermal parameters for all non-hydrogen atoms converged to R_F = 4.440% and R_{wF} = 4.926%.

(8) All computations were performed on a VAX 11/730 computer with Enraf-Nonius SDP software and local programs.

(9) MULTAN 11/82 by P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson.

(10) DIRDIF: Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van den Hark, Th., E. M.; Prick, P. A. J. "Computational Crystallography"; Sayre, D., Ed.; Clarendon Press: Oxford, 1982.

(11) The notation μ_3-(η^2-⊥) signifies that the acetylide C–C bond is perpendicular to a metal–metal bond to distinguish from the case where the C–C bond is parallel to a metal–metal bond, μ_3-(η^2-‖). See ref 12.

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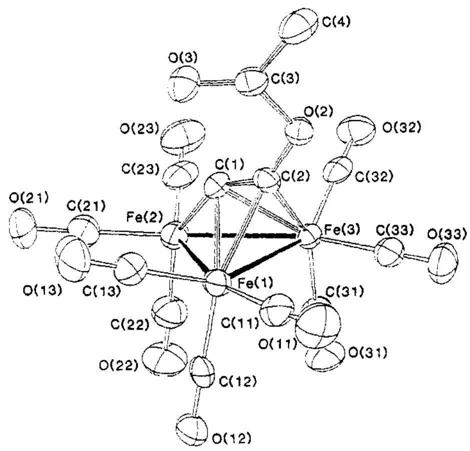


Figure 1. ORTEP diagram of the cluster unit in [PPN][$Fe_3(CO)_9(CCOC(O)CH_3)$], III, with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (deg) with estimated standard deviations in parentheses: Fe(1)–Fe(2), 2.626 (1); Fe(2)–Fe(3), 2.646 (1); Fe(1)–Fe(3), 2.494 (1); Fe(1)–C(1), 2.033 (5); Fe(2)–C(1), 1.809 (6); Fe(3)–C(1), 2.044 (5); Fe(1)–C(2), 2.047 (5); Fe(3)–C(2), 2.011 (5); C(1)–C(2), 1.314 (8); C(2)–O(2), 1.371 (6); O(2)–C(3), 1.389 (6); Fe(1)–Fe(2)–Fe(3), 56.47 (3); Fe(2)–Fe(3)–Fe(1), 61.37 (3); Fe(3)–Fe(1)–Fe(2), 62.16 (3); Fe(2)–C(1)–C(2), 150.6 (4); C(1)–C(2)–O(2), 143.4 (5); C(2)–O(2)–C(3), 117.4 (4).

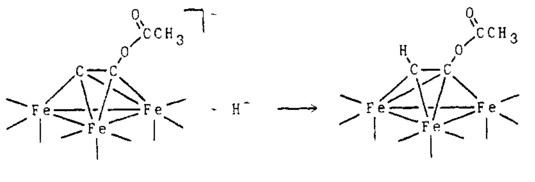
bond cleavage,[12] or via coupling of a carbide and an ethylidyne.[13]

Interestingly, the C–C bond distance does not change significantly from I[2] to III, 1.28 (3) Å vs. 1.314 (8) Å, but the C–O bond lengthens by approximately 0.2 Å, from 1.18 (3) Å in I to 1.371 (6) Å in III. There also is a dramatic change in the C–C–O angle from approximately linear in I, 173 (2)°, to 143.4 (5)° in III. The structural parameters for III are consistent with those of other clusters containing μ_3-(η^2-$\perp$)-CCR ligands.[13] To our knowledge III is the first example of an acetylide cluster with an atom other than a carbon or hydrogen occupying the position adjacent to the triple bond. The bonding in III may be considered as a σ-bond between Fe(2) and C(1) and two π-bonds from the C(1)–C(2) triple bond to Fe(1) and Fe(3). In this manner the acetylide ligand is a five-electron donor and the cluster has the necessary 48 valence electrons.

The change in ligand bonding from I to III is also evident in the ^{13}C NMR spectra. The C_α (*C*CO) and C_β (C*C*O) resonances in I are at 90.1 and 182.2 ppm, respectively, with $^1J_{CC}$ equal to 74 Hz.[2] In III they have shifted to 171.6 and 130.8 ppm, respectively, with $^1J_{CC}$ decreased to 39 Hz.[14] These values for III compare reasonably well with the ^{13}C NMR data available for the related cluster [$Fe_3(CO)_9(\mu_3$-η^2-CCMe)]$^-$.[13] The large downfield shift of the resonance for the α-carbon is indicative of both σ- and π-bonding to the metal framework.[12,15]

When a THF solution of III is treated with K(s-Bu)$_3$BH or Li(s-Bu)$_3$BH, the parent ketenylidene complex I is quantitatively generated as determined by IR and NMR spectroscopy. Even at low temperatures (ca. −50 °C) no intermediate product was detected by ^{13}C NMR spectroscopy. Presumably hydride attack occurs on the acetyl carbon to generate acetaldehyde and I.

In contrast, HSO_3F reacts with III at the α-carbon of the acetylide[14] to generate a new cluster, IV, which is unstable above approximately −70 °C and has not been isolated. The NMR data for IV[16] are more consistent with



III IV (3)

a cluster containing an intact, bound alkyne fragment rather than products arising from C–C bond scission (i.e., HC and COC(O)CH$_3$ fragments), and therefore IV is formulated as shown in eq 3. The C–C coupling within the proposed alkyne ligand was not observed, and therefore $^1J_{CC}$ is estimated to be less than 15 Hz, a plausible result in view of the large decrease of 35 Hz for $^1J_{CC}$ from I to III. As shown by NMR data for III, the resonances for carbon atoms which are both σ- and π-bound to metals are shifted significantly downfield.[12,15] The ^{13}C NMR data for IV suggest a slipping of the alkyne unit across the metal framework so that C_α is only bonded to two metals and C_β is bonded to all three. Further support for this formulation is the similarity of the ^{13}C NMR spectra of IV and the isoelectronic $Fe_3(CO)_9(EtCCEt)$ which shows carbonyl resonances at 212.2 and 207.9 ppm and alkyne resonances at 221.9 and 106.8 ppm.[17]

The ketenylidene ligand in I presumably is derived via the coupling of an exposed carbide carbon and a carbonyl ligand.[2] The present study demonstrates that the acetyl electrophile attacks the ketenylidene oxygen to form an acetylide ligand (eq 2), which is readily converted to an alkyne ligand via protonation (eq 3). In these reactions the C–C bond remains intact through several ligand transformations. Thus the present work provides a link between clusters that contain two important and previously distinct classes of ligands, ketenylidenes and acetylides.

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Registry No. I, 98942-64-4; III, 98942-66-6; IV, 98942-67-7; acetyl chloride, 75-36-5.

Supplementary Material Available: Tables of crystal data, positional parameters, bond lengths, bond angles, anisotropic thermal parameters, and observed and calculated structure factors for [PPN][$Fe_3(CO)_9(CCOC(O)CH_3)$] (56 pages). Ordering information is given on any current masthead page.

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(12) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203 and references therein.

(13) De Montauzon, D.; Mathieu, R. *J. Organomet. Chem.* **1983**, *252*, C83.

(14) The assignment of the C_α and C_β resonances was confirmed by measuring the ^{13}C NMR spectra using samples of III prepared from I ^{13}C enriched only at the carbonyls and C_β.[2]

(15) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135.

(16) ^{1}H NMR (CD_2Cl_2, −80 °C): 2.561 (s, HCCOC(O)C*H*$_3$), 1.548 (s, *H*CCOC(O)CH$_3$) ppm. ^{13}C NMR (CD_2Cl_2, −80 °C): 225.7 (s, HCCOC(O)CH$_3$), 210.7 (s, Fe–CO), 207.1 (s, Fe–CO), 70.2 (d, $^1J_{CH}$ = 186 Hz, HCCOC(O)CH$_3$) ppm. This data was obtained on a sample of IV synthesized by the in situ reaction at −80 °C of a stoichiometric amount of HSO_3F and III ^{13}C enriched at the carbonyls, C_α and C_β.

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