Table VI. Isomerization [$\Delta H°_{rxn}$] and Activation [ΔH^*_{rxn}] Enthalpies (kcal/mol)[a]

reaction	ΔH^*_{rxn}-(calcd)	$\Delta H°_{rxn}$-(calcd)	$\Delta H°_{rxn}$(exptl)	ref
H—NC → H—CN	27.2	−15.3	−10.3 ± 1.1 −14.8 ± 2	52
CH_3—NC → CH_3—CN	37.6	−24.2	−23.70 ± 0.14	51
CH_2—NC → CH_2—CN	29.1	−22.0	−14.3 ± 3.7	25
$^-CH_2$—NC → CH_2=CN^-	39.7	−33.1	−25.5 ± 3.7	25
NH_2—NC → H_2N—CN	36.4	−44.9		

[a] The theoretical values are derived from "MP4/6-311++G(d,p)" calculations with scaled HF/-31+G(d) zero-point energies except CH_3CN/CH_3NC which uses scaled HF/6-31G(d) zero-point energies and HCN/HNC which is MP4-3-311++G(d,p) with scaled HF/6-31G(d) zero-point energies.

the trends in these data. There are two different values in the literature for the HNC/HCN energy difference. The first, 10.3 ± 1.1 kcal/mol, derives from an analysis[52] of the intensty of the infrared spectrum of HNC measured in a heated bath of pure HCN. The second, 14.8 ± 2 kcal/mol, derives from an ion cyclotron resonance[53] determination of the threshold for deuteron abstraction from protonated DCN. Several high-level quantum mechanical calculations of this energy difference have been performed and they uniformly favor the higher energy difference; these include values[54-56] of 14.6, 15 ± 2, and 15.0 kcal/mol. For $CH_3NC \rightarrow CH_3CN$ experimental and theoretical determinations of the energy differences agree. For CH_2NC and $^-CH_2NC$, however, the theoretical values are roughly 8 kcal/mol lower than the experimental values. This may be related to the discrepancy in the computed and measured values for the proton affinity of $^-CH_2NC$. If the measured value is too low, as these calculations suggest, then the agreement between theory and experiment for these rearrangement enthalpies would be improved.

Acknowledgment. We have had extensive conversations with Drs. A. K. Rappê, L. B. Harding, and T. H. Dunning about GVB structures for these reactive intermediates. G.B.E. thanks Argonne National Laboratory for their hospitality during a two-month visit to the Theoretical Chemistry Group at ANL. The experimental work in Boulder was supported by the United States Department of Enegy (contract No. DE-AC02-80ER10722). The VAX 11/750 digital computer used to carry out the Franck–Condon factor calculations was acquired with the help of the National Science Foundation (CHE-8407084).

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Cluster-Assisted Formation and Cleavage of C–H and C–C Bonds. $[Fe_3(CO)_9(CCO)]^{2-}$ and Its Acetylide and Alkyne Derivatives

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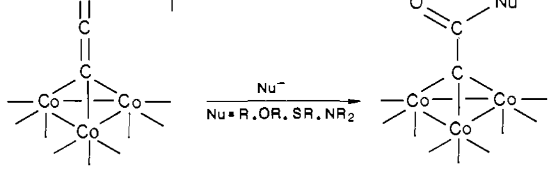
Abstract: The ketenylidene cluster $[Fe_3(CO)_9(CCO)]^{2-}$ (**1**) is ethylated or acylated at the ketenylidene oxygen atom to generate anionic acetylide clusters $[Fe_3(CO)_9(CCOR)]^-$. The reaction of **1** with methyl trifluoromethanesulfonate generates a similar acetylide cluster and also the previously reported alkylidyne species $[Fe_3(CO)_{10}(CCH_3)]^-$. The acetylide clusters are readily protonated at low temperature to generate unstable alkyne clusters of the formula $Fe_3(CO)_9(HCCOR)$. When a solution of the ethoxyalkyne cluster is warmed to room temperature, facile cleavage of the carbon–carbon bond occurs to yield $Fe_3(CO)_9(CH)(COCH_2CH_3)$. Crystal data for $[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]$: triclinic, $P\bar{1}$, $Z = 2$, $a = 10.934$ (5) Å, $b = 13.189$ (7) Å, $c = 17.075$ (6) Å, $\alpha = 84.90$ (4)°, $\beta = 70.14$ (3)°, $\gamma = 85.97$ (4)°, $V = 2305$ Å^3. Refinement of 595 variables on 4425 reflections with $I > 3\sigma(I)$ converged at $R = 4.40$ and $R_w = 4.93$.

The stabilization of reactive ligand intermediates is an important aspect of organometallic chemistry. In metal clusters there exists the added possibility that an ensemble of several metals may interact with a ligand to produce bonding modes and reactivities which are unique to the metal ensemble. The ketenylidene ligand, CCO, is an example of a ligand which is readily formed on trimetallic clusters and displays a wide range of reactivities. The behavior of the CCO moiety is greatly influenced by the identity of the metals and the charge on the cluster.

This is the first of three papers describing the chemistry of anionic ketenylidenes containing metals from the iron triad: $[Fe_3(CO)_9(CCO)]^{2-}$, $[Ru_3(CO)_9(CCO)]^{2-}$, and $[Os_3(CO)_9(CCO)]^{2-}$. These anionic clusters are highly reactive with electrophiles, but the nature of the products varies dramatically in the iron triad.

The first ketenylidene cluster was a cation, $[Co_3(CO)_9(CCO)]^+$, discovered in Seyferths' laboratory, and it was found to react with a variety of nucleophiles (eq 1).[1] In all cases the nucleophile is



(1)

observed to attack at the β-carbon atom (the β-carbon atom is defined as the second carbon atom of the CCO ligand, i.e., $C_\alpha C_\beta O$), in reactions which are analogous to those observed for

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(1) (a) Seyferth, D.; Williams, G. H. *J. Organomet. Chem.* **1972**, *38*, C11. (b) Seyferth, D.; Hallgren, J. E.; Eschbach, C. S. *J. Am. Chem. Soc.* **1974**, *96*, 1730.

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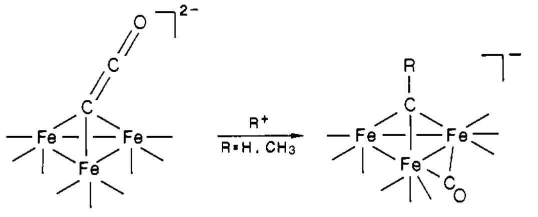
organic ketene molecules.[2] Research by Shapley and co-workers with $H_2M_3(CO)_9(CCO)$ (M = Ru, Os) has demonstrated that nucleophilic attack also occurs at the β-carbon atoms of neutral ketenylidene clusters.[3,4]

The first report of the reaction of electrophiles with the anionic ketenylidene cluster $[Fe_3(CO)_9(CCO)]^{2-}$ (**1**) showed that both acids or methyl iodide attack the α-carbon atom and cleave the C–CO bond to form alkylidyne clusters (eq 2).[5] These reactions



(2)

1

2a, R=H
b, R=CH$_3$

are quite interesting because of the facile cleavage of an apparently strong carbon–carbon bond (C–C = 1.28 Å, $^1J_{CC}$ = 74 Hz).[5] Subsequent work has demonstrated that other first-row metal ketenylidene clusters are protonated in a similar fashion.[6-8]

In this paper we report the reactions of **1** with electrophiles which maintain the ketenylidene carbon–carbon bond. Also reported are reactivity studies of the acetylide and alkyne derivatives of **1**, including another example of the facile cluster-assisted scission of a carbon–carbon bond. Portions of this work were reported in a preliminary communication.[9]

Experimental Section

General Comments. All manipulations were performed under an atmosphere of purified nitrogen using standard Schlenk and needlestock techniques or in a Vacuum/Atmospheres drybox. Solvents were stored under nitrogen after being refluxed with and distilled from appropriate drying agents (THF and Et_2O, Na/benzophenone; CH_2Cl_2, P_2O_5; Me_2CO and pentane, 4A molecular sieves; MeOH and 2-PrOH, Mg/I_2). $Fe_3(CO)_{12}$ (Strem) and [PPN]Cl (Alfa) were used as received. Acetyl chloride was rigorously dried by distilling from PCl_5 followed by vacuum distillation from quinoline. Trifluoromethanesulfonic acid and its esters were distilled before use. Solvents for NMR spectroscopy were vacuum distilled from appropriate drying agents.

IR spectra were recorded with a Perkin-Elmer 283 grating spectrophotometer using 0.1-mm path length CaF_2 solution cells and were calibrated with the 1601 cm^{-1} band of polystyrene. NMR spectra were recorded with a JEOL FX-270 (^{1}H, 269.65 MHz; ^{13}C, 67.8 MHz) or a Varian XL-400 (^{1}H, 399.942 MHz; ^{13}C, 100.577 MHz) spectrometer. All shifts are reported positive if downfield from TMS and were referenced to the solvent resonance ($CHDCl_2$, ^{1}H, 5.32 ppm; CD_2Cl_2, ^{13}C, 53.8 ppm). Mass spectra were recorded by Dr. D. L. Hung of the Northwestern University Analytical Services Laboratory with a Hewlett-Packard HP5905A spectrometer using 70-eV ionization. Elemental analyses were performed by Galbraith Laboratories.

Synthesis of $[PPN]_2[Fe_3(CO)_9(CCO)]$. A Schlenk flash was charged with a 5.0-g (9.9-mmol) sample of $Fe_3(CO)_{12}$ and a magnetic stirbar. A solution of 5.6 g (100 mmol) of KOH in 50 mL of methanol was added with stirring. After 30 min, the dark red-brown solution was filtered through a medium-porosity frit. Treatment of the solution with 12 g (21 mmol) of [PPN]Cl dissolved in 50 mL of methanol produced crystals. These were isolated via filtration and washed with methanol and Et_2O before vacuum drying. The product was dissolved in 40 mL of dichloromethane, the solution was filtered, and a 1.5-mL aliquot of acetyl chloride was added with stirring. After 30 min, the brown solution was evaporated to dryness. The oily solids were extracted with three 20-mL portions of Et_2O and the extracts discarded. After drying, the black solids were treated with a THF solution (200 mL) containing sodium (0.45 g, 20 mmol) and benzophenone (3.6 g, 20 mmol). Continued stirring produced a dark orange precipitate and a light red solution. The product was isolated via filtration and washed with methanol and Et_2O before drying. Recrystallization was accomplished by adding Et_2O (105 mL) to a filtered acetone (70 mL) solution of the cluster. The final product consisted of large dark red crystals. Isolated: 8.7 g, 57% yield. Anal. Calcd for $C_{83}H_{60}N_2Fe_3P_4O_{10}$: C, 64.86; H, 3.94; N, 1.82; Fe, 10.90. Found: C, 65.04; H, 4.10; N, 1.84; Fe, 10.51.

Synthesis of $[PPN]_2[Fe_3(^*CO)_9(^*C^*CO)]$. A 2.5-g (5.0-mmol) sample of $Fe_3(CO)_{12}$ was treated with 25 mL of a methanolic KOH (2.8 g, 50 mmol) solution. After 30 min of stirring, the reaction mixture was transferred via cannula into a 300-mL flask. The flask was attached to a vacuum line and the solution freeze–thaw degassed three times. Then 190 torr of 99% ^{13}CO was introduced at 77 K. The solution was warmed to room temperature and stirred for ca. 12 h. The flask was again cooled to 77 K, the CO removed, and 190 torr of fresh 99% ^{13}CO introduced. The solution was stirred for 12 h at room temperature. After filtration and treatment with [PPN]Cl, the material was converted to $[PPN]_2[Fe_3(^*CO)_9(^*C^*CO)]$ as described in the previous section. This results in enrichment to ca. 35% ^{13}C at all 11 of the carbon atoms.

Synthesis of $[PPN]_2[Fe_3(^*CO)_9(C^*CO)]$. A 300-mL Schlenk flask was charged with 2.0 g (1.3 mmol) of $[PPN]_2[Fe_3(CO)_9(CCO)]$ and 20 mL of dichloromethane. The solution was freeze-thaw degassed three times, and then 165 torr of 99% ^{13}CO was introduced at 77 K. The flask was warmed to room temperature and the solution stirred for 1 day. After filtration, the addition of 20 mL of Et_2O produced crystals. These were collected via filtration and washed with methanol and Et_2O before drying. Isolated: 1.75 g, 88% yield. This material is enriched to ca. 35% ^{13}C at the carbonyl and ketenylidene β-carbon atoms on the basis of ^{13}C NMR spectroscopy.

Synthesis of $[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]$. A solution of 0.957 g (0.623 mmol) of $[PPN]_2[Fe_3(CO)_9(CCO)]$ dissolved in 5 mL of dichloromethane was treated with 70 μL (0.98 mmol) of acetyl chloride. After 20 min of stirring, a 25-mL portion of Et_2O was added. The solution was filtered through a medium-porosity frit and evaporated to dryness. The crude product was redissolved in 5 mL of dichloromethane, and 5 mL of 2-propanol was added. Slow concentration in vacuo produced a dark red microcrystalline solid. It was washed with 2-propanol and Et_2O before drying. Isolated: 0.550 g, 85% yield. Anal. Calcd for $C_{49}H_{33}NFe_3O_{11}P_2$: C, 56.52; H, 3.19; N, 1.34; Fe, 16.09. Found: C, 55.84; H, 3.28; N, 1.35; Fe, 16.12. IR (ν_{CO}, CH_2Cl_2): 2049 w, 1990 s, 1982 s, 1961 m, 1936 sh, 1770 w, br cm^{-1}.

Synthesis of $[PPN][Fe_3(CO)_9(CCOCH_2CH_3)]$. A solution consisting of 1.002 g (0.6520 mmol) of $[PPN]_2[Fe_3(CO)_9(CCO)]$ in 10 mL of dichloromethane was treated with 0.13 mL (1.0 mmol) of $CH_3CH_2SO_3CF_3$. After the solution was stirred for 30 min, a 30-mL portion of Et_2O was added. The solution was filtered through a medium-porosity frit and evaporated to dryness. The solid was redissolved in 10 mL of dichloromethane, and 10 mL of 2-propanol was added. Slow concentration of the solution produced red crystals. These were isolated via filtration and washed with Et_2O before drying. Isolated: 0.466 g, 70% yield. Anal. Calcd for $C_{49}H_{35}NFe_3O_{10}P_2$: C, 57.29; H, 3.43; N, 1.36; Fe, 16.31. Found: C, 56.66; H, 3.78; N, 1.07; Fe, 16.56. IR (ν_{CO}, CH_2Cl_2): 2045 w, 1988 s, 1978 s, 1959 s, 1932 m cm^{-1}.

Synthesis of $Fe_3(CO)_9(COCH_3)(CCH_3)$. A flask was charged with a solution consisting of 0.205 g (0.202 mmol) of $[PPN][Fe_3(CO)_{10}(CCH_3)]$[5] dissolved in 5 mL of dichloromethane. A 150-μL (1.32-mmol) aliquot of $CH_3SO_3CF_3$ was added with stirring. After 4 h, the orange-red solution was evaporated to dryness. The solids were extracted with 20 mL of pentane, and the solution was filtered. Concentration of the solution followed by cooling to ca. −10 °C for several days produced large red crystals. Isolated: 0.031 g, 31% yield. Infrared mass, and ^{1}H NMR spectra matched those reported previously for this compound.[24]

X-ray Crystal Structure of $[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]$. A suitable crystal was obtained via the slow diffusion of pentane into a dichloromethane/diethyl ether (1:2) solution of the compound. A crystal was glued to the end of a glass fiber and quickly transferred into the nitrogen cold stream of an Enraf-Nonius CAD4 diffractometer. A summary of the unit-cell, data-collection, and refinement parameters is listed in Table I. The unit-cell dimensions were determined during a normal alignment procedure by the least-squares refinement of the setting angles of 25 independent reflections (30° < 2θ < 35°) which were collected by using graphite-monochromated molybdenum radiation. Data

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[4] Holmgren, J. S.; Shapley, J. R. *Organometallics* **1984**, *3*, 1322.

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[7] Crespi, A. M.; Shriver, D. F. *Organometallics* **1986**, *5*, 1750.

[8] Ching, S.; Kolis, J. W.; Holt, E. M.; Shriver, D. F., submitted for publication.

[9] Hriljac, J. A.; Shriver, D. F. *Organometallics* **1985**, *4*, 2225.

Table I. X-ray Crystal Structure Data for $[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]$

formula	$C_{49}H_{33}NFe_3O_{11}P_2$
mol wt, amu	1041.25
cryst size, mm	ca. 0.1 × 0.1 × 0.3
cryst color	red
cryst habit	irregular
cryst system	triclinic
space group	$P\bar{1}$
a, Å	10.934 (5)
b, Å	13.189 (7)
c, Å	17.075 (6)
α, deg	84.90 (4)
β, deg	70.14 (3)
γ, deg	85.97 (4)
V, Å^3	2305
Z	2
d_{calcd}, g cm^{-3}	1.500
$F(000)$	1060
λ(Mo Kα), Å	0.71073
μ(Mo Kα), cm^{-1}	10.593
2θ range, deg	3–50
scan mode	$\omega-2\theta$
scan width, deg	$\omega = 0.8 + 0.35 \tan\theta$
scan speed range, deg min^{-1}	0.69–2.06
reflctns measd	$+h,\pm k,\pm l$
total data	8545
unique data	8077
data, $I > 3\sigma(I)$	4425
no. of variables	595
abs correctn	empirical based on psi scan data
transmissn factors	0.91–1.00
R, R_w	4.40, 4.93
weighting scheme	$w = 4F^2/(\sigma(I)^2 + (0.05F^2)^2)$
esd observn of unit wt	1.109
temp, °C	−100

were collected with a variable scan rate with the parameters listed in Table I. The intensities of five reflections were remeasured every 3 h, and the average intensity loss was 4.3%. No decay correction was applied. Backgrounds were measured at the side of each scan for a total time equal to one-half of the scan time. Data were corrected for Lorentz and polarization effects.[10] Anomalous dispersion terms were included for all non-hydrogen atoms.

The positions of the iron and phosphorus atoms were determined by direct methods using MULTAN 11/82.[11] The remaining non-hydrogen atoms were located by using DIRDIF[12] and difference Fourier techniques. Hydrogen atoms were introduced in idealized positions (C–H = 0.95 Å) and were not refined. Refinement of a scale factor, positional parameters, and anisotropic thermal parameters converged with $R = 4.44\%$ and $R_w = 4.93\%$.[13] The largest peak in the final difference electron density map was 0.4 e/Å^3.

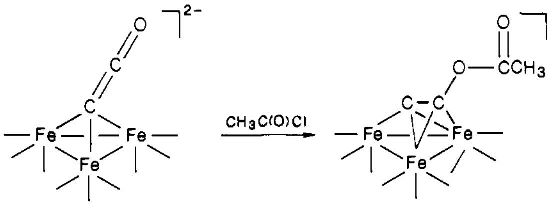
Results and Discussion

Reactions of $[PPN]_2[Fe_3(CO)_9(CCO)]$ (1). When a dichloromethane solution of **1** is treated with acetyl chloride, a new cluster can be isolated in high yield, and analytical and spectroscopic data, Tables II and III, fit the formulation $[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]$ (**3a**). On the basis of a previous study,[5] the expected product was $[PPN][Fe_3(CO)_{10}(CC(O)CH_3)]$. However, the ^{13}C NMR spectrum of a sample of **3a**, which was prepared from **1** enriched at all 11 carbon atoms, contains two resonances which clearly display satellites due to carbon–carbon coupling. This observation indicates that a new ligand has formed which retains the ketenylidene carbon–carbon bond. The value of this coupling constant, 39 Hz, is substantially lower than that of the starting cluster **1**, 74 Hz. The exact nature of **3a** was confirmed by a single-crystal X-ray diffraction study (described below), and the reaction is shown in eq 3. This represents the first example of

Table II. ^1H NMR Data of Selected Trimetallic Clusters[a,b]

compd	conditns	^1H NMR data (ppm)
$[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]$	CD_2Cl_2, +25 °C	2.30
$[PPN][Fe_3(CO)_9(CCOCH_2CH_3)]$	CD_2Cl_2, +25 °C	4.18 (q, $J_{HH} = 7.1$ Hz, CH_2), 1.43 (t, $J_{HH} = 7.1$ Hz, CH_3)
$Fe_3(CO)_9(HCCOC(O)CH_3)$[c]	CD_2Cl_2, −80 °C	2.56 (CH_3), 1.55 (CH)
$Fe_3(CO)_9(HCCOCH_2CH_3)$[c,d]	CD_2Cl_2, −90 °C	4.41 (CH_2), 1.83 (CH), 1.64 (CH_3)

[a] All chemical shifts in parts per million downfield of Me_4Si, signals due to the PPN cation are not reported. [b] All resonances singlets unless noted: t, triplet; q, quartet. [c] Generated in situ. [d] Resonances too broad to resolve J_{HH}.



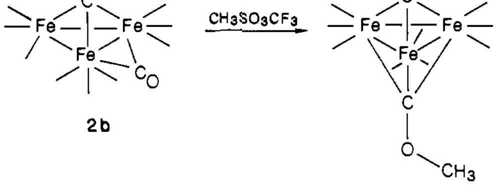
1 **3a**

(3)

reactivity at the oxygen atom of a ketenylidene group and is analogous to the conversion of monometallic ketenyl compounds to alkyne systems.[14]

When a dichloromethane solution of **1** is treated with ethyl trifluoromethanesulfonate (triflate), a product is formed with spectral characteristics which are very similar to those observed for **3a** (Table II and III). This product is formulated as $[PPN][Fe_3(CO)_9(CCOCH_2CH_3)]$ (**3b**). For both **3a** and **3b** the assignments of the α- and β-carbon resonances in the ^{13}C NMR spectra were confirmed by synthesizing the products using **1** which was only ^{13}C enriched at the carbonyl and β-carbon atoms. For both clusters the α-carbon resonance is further downfield than the β-carbon resonance, and this indicates an interaction with three metal atoms in a σ–π bonding mode.[15,16]

When **1** is treated with methyl triflate, two products are observed. One of these is the same product that is formed from **1** and methyl iodide, $[PPN][Fe_3(CO)_{10}(CCH_3)]$ (**2b**) (eq 1).[5] On the basis of the ^{13}C NMR data (Table III), the second product is formulated as $[PPN][Fe_3(CO)_9(CCOCH_3)]$ (**3c**). The ratio of the two products is approximately 2:1. Attempts to separate these two compounds have failed. Reaction of **2b** with excess methyl triflate generates the doubly capped alkylidyne cluster $Fe_3(CO)_9(COCH_3)(CCH_3)$ (**2c**) previously synthesized by an alternate route.[24]



2b **2c**

(4)

X-ray Crystal Structure of $[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]$ (3a). As shown in Figure 1, the cluster anion in **3a** contains an

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(10) Computations were performed on a VAX 11/730 computer using the "Structure Determination Package" by B. A. Frenz and Associates, or local programs.

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(13) Function minimized: $\sum w(|F_o| - |F_c|)^2$; $R = (\sum ||F_o| - |F_c||)/\sum|F_o|$; $R_w = [(\sum w(|F_o| - |F_c|)^2)/\sum w(|F_o|)^2]^{1/2}$.

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Table III. ^{13}C NMR Data for Selected Trimetallic Clusters[a,b]

compound	conditns	^{13}C NMR data (ppm)	$^{1}J_{CC}$,[c] Hz	ref
$[PPN]_2[Fe_3(CO)_9(CCO)]^{d}$	CD_3CN, −40 °C	222.3 (*C*O), 182.2 (ds, C*C*O), 90.1 (ds, *C*CO)	74	5
$[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]^{d}$	CD_2Cl_2, +25 °C	216.1 (*C*O), 172.9 (ds, C*C*O), 168.1 (*C*(O)CH_3), 132.2 (ds, *C*CO), 20.6 (q, J_{CH} = 130 Hz, *C*H_3)	39	*e*
$[PPN][Fe_3(CO)_9(CCOCH_2CH_3)]^{d}$	CD_2Cl_2, +25 °C	217.1 (*C*O), 160.7 (ds, C*C*O), 148.5 (ds, *C*CO), 74.2 (t, J_{CH} = 146 Hz, *C*H_2), *C*H_2), (q, J_{CH} = 128 Hz, *C*H_3)	42	*e*
$[PPN][Fe_3(CO)_9(CCOCH_3)]^{d,f}$	CD_2Cl_2, −90 °C	215.3 (*C*O), 160.4 (ds, C*C*O), 147.6 (ds, *C*CO)	42	*e*
$[Ph_4P][Fe_3(CO)_9(CCCH_3)]$	*g*	217.1 (6*C*O), 216.0 (3*C*O), 184.7 (*C*CCH_3), 99.5 (C*C*CH_3), 17.7 (*C*H_3)	*g*	23
$Fe_3(CO)_9(HCCOC(O)CH_3)^{d,f}$	CD_2Cl_2, −80 °C	225.7 (HC*C*), 210.7 (6*C*O), 207.1 (3*C*O), 70.2 (d, J_{CH} = 186 Hz, H*C*C)	<15	*e*
$Fe_3(CO)_9(HCCOCH_2CH_3)^{d,f}$	CD_2Cl_2, −90 °C	248.9 (HC*C*), 211.4 (6*C*O), 207.7 (3*C*O), 69.7 (d, J_{CH} = 182 Hz, H*C*C)	<15	*e*
$Fe_3(CO)_9(CH_3CH_2CCCH_2CH_3)$	$CDCl_3$, +21 °C	221.9 (*C*C), 212.2 (6*C*O), 207.9 (3*C*O), 106.8 (C*C*), 39.5 (*C*H_2), 21.8 (*C*H_2), 16.5 (*C*H_3), 15.4 (*C*H_3)	*g*	19
$[PPN][Fe_3(CO)_{10}(CH)]$	CD_3CN, −40 °C	262.4 (d, J_{CH} = 165 Hz, *C*H), 220.5 (*C*O)		5
$[PPN][Fe_3(CO)_{10}(CCH_3)]$	CD_3CN, −40 °C	286.2 (*C*CH_3), 221.2 (*C*O), 43.6 (*C*H_3)		5
$Fe_3(CO)_9(CCH_3)(COCH_3)$	C_6D_6, +25 °C	359.8 (*C*OCH_3), 334.6 (*C*CH_3), 209.6 (*C*O), 72.4 (O*C*H_3), 46.9 (C*C*H_3)		24
$Fe_3(CO)_9(CCH_3)(COCH_2CH_3)$	*g*	333 (*C*OCH_2), 292.8 (*C*CH_3)		22d
$Fe_3(CO)_9(CH)(COCH_2CH_3)^{f}$	CD_2Cl_2, −90 °C	360.5 (*C*OCH_2), 293.9 (d, J_{CH} = 171 Hz, *C*H), 208.9 (*C*O)		*e*

[a] All chemical shifts in parts per million downfield of TMS; signals due to the PPN cation are not reported. [b] All resonances singlets unless noted: ds, doublet on singlet; d, doublet; t, triplet; q, quartet. [c] The value for the two carbon atoms derived from the ketenylidene moiety. [d] ^{13}C enriched at C_α and C_β. [e] This work. [f] Generated in situ. [g] Not reported.

Table IV. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations for $[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]$

Bond Distances			
Fe(1)–Fe(2)	2.626 (1)	Fe(2)–C(21)	1.765 (7)
Fe(1)–Fe(3)	2.494 (1)	Fe(2)–C(22)	1.793 (7)
Fe(2)–Fe(3)	2.646 (1)	Fe(2)–C(23)	1.788 (8)
C(1)–Fe(1)	2.033 (5)	Fe(3)–C(31)	1.790 (6)
C(1)–Fe(2)	1.809 (6)	Fe(3)–C(32)	1.794 (7)
C(1)–Fe(3)	2.044 (5)	Fe(3)–C(33)	1.777 (7)
C(2)–Fe(1)	2.047 (5)	C(11)–O(11)	1.133 (7)
C(2)–Fe(3)	2.011 (5)	C(12)–O(12)	1.155 (6)
C(1)–C(2)	1.314 (8)	C(13)–O(13)	1.145 (7)
C(2)–O(2)	1.371 (6)	C(21)–O(21)	1.155 (7)
C(3)–C(4)	1.488 (8)	C(22)–O(22)	1.142 (7)
C(3)–O(2)	1.389 (6)	C(23)–O(23)	1.133 (7)
C(3)–O(3)	1.189 (7)	C(31)–O(31)	1.141 (6)
Fe(1)–C(11)	1.788 (7)	C(32)–O(32)	1.143 (6)
Fe(1)–C(12)	1.777 (6)	C(33)–O(33)	1.140 (7)
Fe(1)–C(13)	1.793 (7)		
Bond Angles			
Fe(2)–Fe(1)–Fe(3)	62.16 (3)	C(11)–Fe(1)–C(13)	99.8 (3)
Fe(1)–Fe(2)–Fe(3)	56.47 (3)	C(12)–Fe(1)–C(13)	100.2 (3)
Fe(1)–Fe(3)–Fe(2)	61.37 (3)	C(1)–Fe(2)–C(21)	105.4 (3)
C(2)–C(1)–Fe(1)	71.8 (3)	C(1)–Fe(2)–C(22)	149.1 (3)
C(2)–C(1)–Fe(2)	150.6 (4)	C(1)–Fe(2)–C(23)	102.3 (3)
C(2)–C(1)–Fe(3)	69.7 (3)	C(21)–Fe(2)–C(23)	100.7 (3)
Fe(1)–C(1)–Fe(2)	86.0 (2)	C(21)–Fe(2)–C(22)	95.0 (3)
Fe(1)–C(1)–Fe(3)	75.4 (2)	C(22)–Fe(2)–C(23)	96.3 (3)
Fe(2)–C(1)–Fe(3)	86.5 (2)	C(1)–Fe(3)–C(2)	37.8 (2)
C(1)–C(2)–O(2)	143.4 (5)	C(1)–Fe(3)–C(31)	128.2 (3)
C(1)–C(2)–Fe(1)	70.6 (3)	C(1)–Fe(3)–C(32)	98.7 (2)
C(1)–C(2)–Fe(3)	72.5 (3)	C(1)–Fe(3)–C(33)	127.2 (2)
O(2)–C(2)–Fe(1)	135.4 (4)	C(2)–Fe(3)–C(31)	153.5 (2)
O(2)–C(2)–Fe(3)	131.1 (4)	C(2)–Fe(3)–C(32)	106.0 (2)
Fe(1)–C(2)–Fe(3)	75.8 (2)	C(2)–Fe(3)–C(33)	89.5 (2)
C(4)–C(3)–O(2)	109.6 (5)	C(31)–Fe(3)–C(32)	98.1 (2)
C(4)–C(3)–O(3)	128.0 (5)	C(31)–Fe(3)–C(33)	96.7 (3)
O(2)–C(3)–O(3)	122.5 (5)	C(32)–Fe(3)–C(33)	100.8 (3)
C(2)–O(2)–C(3)	117.4 (4)	Fe(1)–C(11)–O(11)	177.4 (6)
C(1)–Fe(1)–C(2)	37.6 (2)	Fe(1)–C(12)–O(12)	177.4 (6)
C(1)–Fe(1)–C(11)	126.9 (3)	Fe(1)–C(13)–O(13)	178.8 (6)
C(1)–Fe(1)–C(12)	127.5 (3)	Fe(2)–C(21)–O(21)	178.9 (6)
C(1)–Fe(1)–C(13)	96.5 (3)	Fe(2)–C(22)–O(22)	178.0 (6)
C(2)–Fe(1)–C(11)	89.4 (3)	Fe(2)–C(23)–O(23)	176.8 (6)
C(2)–Fe(1)–C(12)	151.7 (2)	Fe(3)–C(31)–O(31)	175.4 (6)
C(2)–Fe(1)–C(13)	105.2 (2)	Fe(3)–C(32)–O(32)	179.3 (5)
C(11)–Fe(1)–C(12)	98.6 (3)	Fe(3)–C(33)–O(33)	179.1 (5)

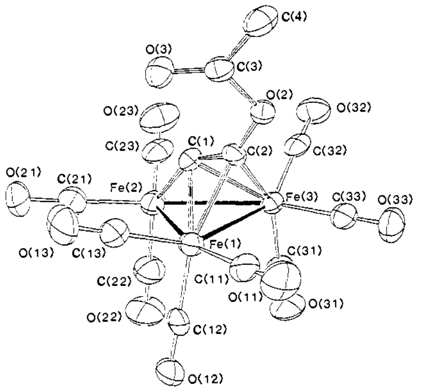
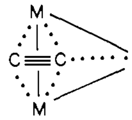
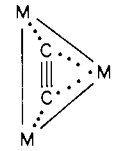


Figure 1. An ORTEP diagram of the cluster unit in $[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]$ (**3a**) with thermal ellipsoids drawn at the 50% probability level.

acetylide ligand, $CCOC(O)CH_3$, which is the product of acetyl attack at the oxygen atom of the ketenylidene group in **1**. The ligand is bonded in a μ_3-(η^2-⊥) configuration[15] to a closed trimetallic framework. In this mode the carbon–carbon bond is oriented perpendicular to a metal–metal bond, A, rather than parallel to a metal–metal bond, B. Selected bond distances and angles are listed in Table IV and atomic positional parameters in Table V.



A. μ_3-(η^2-⊥)



B. μ_3-(η^2-∥)

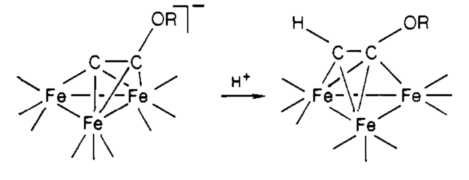
The metrical parameters for **3a** compare well with those in related acetylide clusters.[15] The metal–metal bonding is asymmetric with the bond bridged by the acetylide unit considerably shorter than the other two (2.494 (1) Å vs. 2.626 (1) and 2.646 (1) Å). Each metal atom bears three terminal carbonyl groups with no semibridging interactions. The carbon–carbon bond distance does not lengthen significantly from **1**[5] (1.28 (3) Å) to **3a** (1.314 (8) Å), but the carbon–oxygen distance increases by approximately 0.2 Å (1.18 (3) Å vs. 1.371 (6) Å). There is also a dramatic change in the C–C–O angle from approximately linear in **1** (173 (2)°) to 143.4 (5)° in **3a**. This indicates a rehybridization within the ligand has occurred. The acetylide ligand is formally bonded to the metals by one σ bond from the unique iron atom to the α-carbon atom (Fe(2)–C(1) = 1.809 (6) Å) and two π bonds from the carbon–carbon bond to the other iron atoms (average Fe–C = 2.034 (16) Å).[15] This formalism necessitates viewing the change in bonding from C═C═O to C≡C—O and conversion of the ligand from a 4-electron donor in **1** to a 5-electron donor.

Table V. Positional Parameters and Their Estimated Standard Deviations for $[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]$

atom	*x*	*y*	*z*
C(1)	0.8006 (5)	−0.7489 (4)	0.7507 (3)
C(2)	0.8204 (5)	−0.6778 (4)	0.6892 (3)
C(3)	1.0341 (5)	−0.6675 (4)	0.5933 (3)
C(4)	1.1245 (6)	−0.5915 (5)	0.5379 (4)
O(2)	0.9142 (3)	−0.6195 (3)	0.6327 (2)
O(3)	1.0554 (4)	−0.7562 (3)	0.6050 (2)
Fe(1)	0.68785 (7)	−0.77563 (6)	0.68204 (5)
Fe(2)	0.69189 (7)	−0.82848 (7)	0.83313 (5)
Fe(3)	0.65480 (7)	−0.63823 (6)	0.77952 (5)
C(11)	0.6753 (5)	−0.7012 (5)	0.5922 (4)
C(12)	0.5303 (5)	−0.8261 (4)	0.7186 (4)
C(13)	0.7828 (6)	−0.8834 (5)	0.6330 (4)
C(21)	0.7556 (6)	−0.9543 (5)	0.8150 (4)
C(22)	0.5293 (6)	−0.8649 (5)	0.8913 (4)
C(23)	0.7365 (5)	−0.8059 (5)	0.9214 (4)
C(31)	0.4871 (5)	−0.6518 (5)	0.8411 (3)
C(32)	0.7031 (5)	−0.5753 (5)	0.8526 (3)
C(33)	0.6306 (5)	−0.5326 (5)	0.7134 (4)
O(11)	0.6709 (4)	−0.6518 (4)	0.5353 (3)
O(12)	0.4282 (4)	−0.8591 (3)	0.7394 (3)
O(13)	0.8443 (4)	−0.9524 (4)	0.6027 (3)
O(21)	0.7991 (4)	−1.0360 (3)	0.8024 (4)
O(22)	0.4270 (4)	−0.8910 (4)	0.9285 (3)
O(23)	0.7706 (4)	−0.7930 (4)	0.9753 (3)
O(31)	0.3792 (4)	−0.6534 (4)	0.8801 (3)
O(32)	0.7325 (4)	−0.5348 (3)	0.8995 (2)
O(33)	0.6159 (4)	−0.4656 (3)	0.6701 (3)
P(1)	1.1296 (1)	−0.3380 (1)	0.75416 (8)
P(2)	1.3422 (1)	−0.1990 (1)	0.73164 (8)
N(1)	1.2656 (4)	−0.2888 (3)	0.7170 (3)
C(111)	1.1592 (4)	−0.4729 (4)	0.7458 (3)
C(112)	1.2853 (5)	−0.5117 (4)	0.7079 (3)
C(113)	1.3080 (5)	−0.6152 (5)	0.7001 (3)
C(114)	1.2069 (5)	−0.6797 (4)	0.7288 (3)
C(115)	1.0824 (5)	−0.6417 (4)	0.7662 (3)
C(116)	1.0577 (5)	−0.5390 (4)	0.7743 (3)
C(121)	1.0238 (5)	−0.2947 (4)	0.6968 (3)
C(122)	1.0701 (6)	−0.2378 (5)	0.6212 (3)
C(123)	0.9896 (7)	−0.2039 (6)	0.5782 (4)
C(124)	0.8602 (6)	−0.2249 (6)	0.6086 (4)
C(125)	0.8114 (6)	−0.2814 (5)	0.6828 (4)
C(126)	0.8917 (5)	−0.3157 (5)	0.7276 (4)
C(131)	1.0411 (5)	−0.3150 (4)	0.8614 (3)
C(132)	1.0657 (5)	−0.3770 (4)	0.9248 (3)
C(133)	1.0021 (6)	−0.3550 (5)	1.0071 (4)
C(134)	0.9125 (6)	−0.2745 (5)	1.0253 (3)
C(135)	0.8891 (5)	−0.2125 (5)	0.9631 (4)
C(136)	0.9541 (5)	−0.2326 (4)	0.8806 (3)
C(211)	1.4608 (4)	−0.1644 (4)	0.6319 (3)
C(212)	1.5215 (5)	−0.0725 (4)	0.6167 (3)
C(213)	1.6156 (5)	−0.0497 (5)	0.5399 (4)
C(214)	1.6486 (6)	−0.1196 (5)	0.4797 (4)
C(215)	1.5883 (6)	−0.2092 (5)	0.4938 (4)
C(216)	1.4938 (5)	−0.2328 (4)	0.5701 (3)
C(221)	1.4261 (5)	−0.2391 (4)	0.8047 (3)
C(222)	1.5024 (5)	−0.1732 (5)	0.8250 (3)
C(223)	1.5637 (6)	−0.2049 (5)	0.8815 (4)
C(224)	1.5514 (5)	−0.3032 (5)	0.9177 (3)
C(225)	1.4776 (6)	−0.3680 (5)	0.8967 (4)
C(226)	1.4160 (5)	−0.3369 (4)	0.8404 (3)
C(231)	1.2403 (5)	−0.0885 (4)	0.7695 (3)
C(232)	1.2112 (5)	−0.0628 (4)	0.8508 (3)
C(233)	1.1227 (6)	0.0187 (5)	0.8791 (4)
C(234)	1.0678 (5)	0.0731 (5)	0.8276 (4)
C(235)	1.0967 (5)	0.0481 (4)	0.7463 (4)
C(236)	1.1831 (5)	−0.0331 (4)	0.7173 (3)

Reactivity of $[PPN][Fe_3(CO)_9(CCOR)]$ (R = $C(O)CH_3$, 3a; R = CH_2CH_3, 3b). When a THF solution of **3a** is treated with a strong hydride source ($K(s\text{-}Bu)_3BH$ or $Li(s\text{-}Bu)_3BH$), the parent ketenylidene cluster **1** is quantitatively formed as determined by IR and ^{13}C NMR spectroscopy. No intermediates were observed by ^{13}C NMR spectroscopy at low temperature, ca. −50 °C. Presumably hydride attack occurs at the carbonyl carbon atom of the acetylide ligand to form acetaldehyde and **1**.

In contrast, fluorosulfonic acid reacts with **3a** and **3b** at the α-carbon atoms and generates the new alkyne complexes $Fe_3(CO)_9(HCCOR)$ (R = $C(O)CH_3$, **4a**; R = CH_2CH_3, **4b**) (eq 5).



(5)

3a, R=C(O)CH3
b, R=CH2CH3

4a, **b**

These clusters are unstable above approximately −70 °C and have not been isolated. The formulation is based upon the NMR data (Tables II and III). Selective ^{13}C enrichment studies prove that protonation occurs at the α-carbon atoms. Although $^1J_{CC}$ was not observed, the chemical shifts are more consistent with an alkyne ligand rather than separate methylidyne and alkoxyalkylidyne ligands (Table III).[15,16] As depicted in eq 5, the NMR data suggest the alkyne units have slipped across the metal faces and the protonated acetylide carbon atoms have moved from the μ_3- to the μ_2-positions. This is based on a comparison of the chemical shifts for the carbon atoms.[15,16] The α-carbon atoms of acetylide clusters are usually reactive toward nucleophiles,[17] but under forcing conditions (95% H_2SO_4 or neat HSO_3Cl) protonation has been observed at this site.[18]

The bonding mode of the alkyne ligands in **4a**,**b**, and the related iron clusters $Fe_3(CO)_9(RCCR)$ (R = CH_2CH_3,[19] R = Ph[20]), is rather rare. These systems are coordinatively unsaturated 46-electron species. A more common situation is a saturated 48-electron cluster with the carbon–carbon bond parallel to a metal–metal bond, μ_3-(η^2-$\parallel$), such that two metals are σ-bonded and one is π-bonded.[15] The change of the alkyne orientation when the electron count changes has been the subject of a theoretical study.[21]

Surprisingly, **4a** and **4b** were found to be unstable at room temperature. When an NMR tube containing a solution of **4a** is warmed to room temperature, a complex mixture of products is formed. When a solution of **4b** is warmed, a new species forms in approximately 95% spectroscopic yield (Figure 2) and is formulated as $Fe_3(CO)_9(CH)(COCH_2CH_3)$ (**5**) (Table III). Alkyne-scission reactions have been observed to occur in other cluster systems,[22] but never below ambient temperature. In a theoretical study of the alkyne-scission reaction in a related μ_3-(η^2-$\parallel$)-alkyne complex, it was postulated that the alkyne unit rotates into a μ_3-(η^2-$\perp$) configuration before the carbon–carbon bond cleaves.[22c] Thus the facile bond cleavage in **4a** may occur because the μ_3-(η^2-$\perp$) configuration of **4a** is further along the proposed reaction sequence than the more common μ_3-(η^2-$\parallel$) configuration. A second important factor may be the electron-releasing nature of the ethoxide group.

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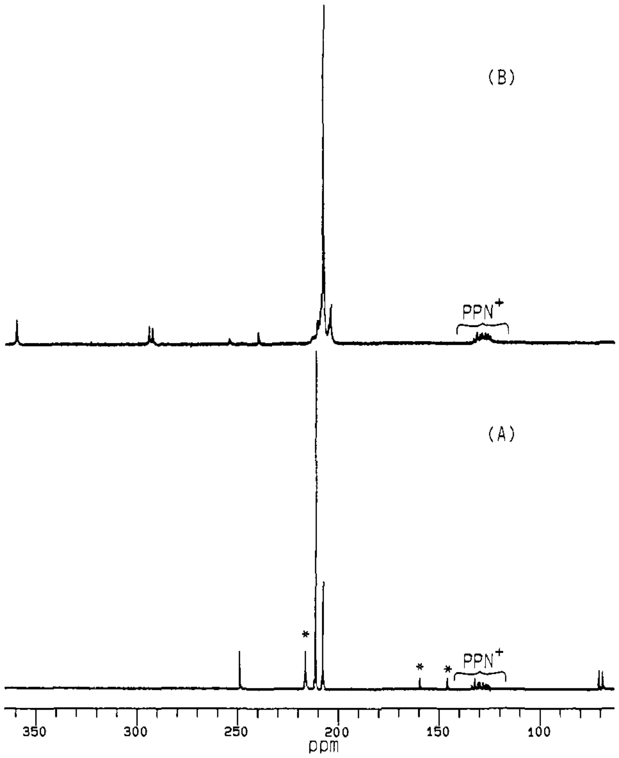

Figure 2. The ^{13}C NMR spectra (proton coupled) of $Fe_3(*CO)_9(H*C*C(O)CH_2CH_3)$ (A) and the same sample after warming to room temperature (B). The spectra were recorded at −90 °C as CD_2Cl_2 solutions. The peaks marked with an asterisk are due to unreacted $[Fe_3(*CO)_9(*C*COCH_2CH_3)]^-$.

Reactions of **3a** and **3b** with methyl triflate were also investigated. Both of these reactions were very slow (>3 days with a fivefold excess of methyl triflate) and yielded complex mixtures of products. Mass spectral analysis of the cluster products from the reaction with **3b** indicated some substitution of methyl groups for ethyl groups on the alkyne ligands. These reactions were not pursued.

Reactivity of Anionic Ketenylidene Clusters. As evidenced by previous work[5] and this study, the cluster anion in **1** can react with electrophiles at either the α-carbon or oxygen atoms of the ketenylidene moiety. The reasons for the site preference are still not clear. The acetylide clusters that are formed by attack at the oxygen atom do not appear to be metastable products since conversion to alkylidyne systems is not observed. No change was detected when a dichloromethane solution of **2b** and **3b** was left standing for 1 day or when a THF solution of **3a** was refluxed for 4 h. Steric effects would appear to play a role, as protonation of **1** occurs exclusively at the α-carbon atom[5] and larger electrophiles are observed to only react at the oxygen atom. However, other factors must also contribute to the complex reactivity since the reaction of **1** with methyl iodide leads to a single product whereas methyl triflate yields a mixture of two products.

In summary, the anionic ketenylidene cluster $[Fe_3(CO)_9(CCO)]^{2-}$ reacts with bulkier carbocation reagents to produce acetylide clusters of the general formula $[Fe_3(CO)_9(CCOR)]^-$. This result contrasts with the formation of an alkylidyne $[Fe_3(CO)_{10}(CR)]^-$ upon reaction with CH_3I.[5] This difference in reactivity is attributed to easier access of the ketenylidene oxygen to bulky electrophiles. The acetylide clusters are very reactive and are protonated to yield unstable alkyne clusters. When the ethyl derivative is warmed, clean scission of the carbon–carbon bond is observed to yield two alkylidyne fragments. This unusual instability may be due to a weakening of the carbon–carbon bond by the orientation of the alkyne ligand and the presence of an electron-withdrawing group bound to the alkyne carbon atom.

Tables of crystal data, positional parameters, bond lengths, bond angles, anisotropic thermal parameters, and observed and calculated structure factors for $[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]$ are available as submitted in ref 9.

Acknowledgment. This research was supported by the National Science Foundation through Grants CHE-8204401 and CHE-8506011.

Alkylation Reactions of the CCO Ligand in Triruthenium Carbonyl Clusters. Synthesis and X-ray Crystal Structure of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}C{=}C(OCH_3)CH_3)$

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Abstract: Alkylation reactions of the series of ruthenium ketenylidenes $[Ru_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}CCO)]^{2-}$ (**1**), $[HRu_3(CO)_9(\mu_3\text{-}CCO)]^-$ (**2**), and $H_2Ru_3(CO)_9(\mu_3\text{-}CCO)$ (**3**) were studied. The dinegative cluster **1** is attacked by the electrophile CH_3I to produce the acetyl cluster $[Ru_3(CO)_{10}(\mu_3\text{-}CC(O)CH_3)]^-$ (**4**). ^{13}C-labeling experiments show that the acyl CO in **4** is derived from a metal-bound carbonyl ligand on **1**, instead of from the CO of the CCO ligand. An alkylation mechanism consistent with the observations is proposed. The product of the reaction of **1** with CH_3I reacts further with the strong alkylating reagent $CH_3OSO_2CF_3$ to produce the vinylidene cluster $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}C{=}C(OCH_3)CH_3)$ (**5**) which has been characterized by a single-crystal X-ray structure determination. Compound **5** readily reacts with H_2 with concomitant CO loss to produce $H_2Ru_3(CO)_9(\mu_3\text{-}C{=}C(OCH_3)CH_3)$ (**6**). In contrast to the nucleophilicity of dianion **1**, the mononegative and neutral clusters $[HRu_3(CO)_9(\mu_3\text{-}CCO)]^-$ (**2**) and $H_2Ru_3(CO)_9(\mu_3\text{-}CCO)$ (**3**) are electrophilic, as demonstrated by their reaction with the nucleophile $LiCH_3$. In either case, attack by $LiCH_3$ occurs at the β-carbon of the CCO ligand. Extended Hückel molecular orbital calculations suggest that the observed reactions of **2** and **3** with nucleophiles are orbital-controlled reactions. The ^{13}C NMR data reported for the compounds include carbon–carbon coupling constants for the capping ligands. Crystals of **5** are monoclinic of space group $P2_1/n$ with $a = 8.3993$ (17) Å, $b = 15.9259$ (16) Å, $c = 14.1140$ (13) Å, $\beta = 90.95$ (1)°, $V = 1887.73$ Å,^{3} and $d_{calcd} = 2.296$ g/cm^3 for $Z = 4$. Refinement of 254 variables on 4067 reflections with $I > 3\sigma(I)$ converged at $R = 0.025$ and $R_w = 0.052$.

In the course of studies on metal cluster ketenylidenes, we discovered that the doubly negative ruthenium ketenylidene $[Ru_3(CO)_9(\mu_3\text{-}CCO)]^{2-}$ (**1**) protonates sequentially on the metal framework to yield the mononegative ketenylidene $[HRu_3\text{-}$

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