[PPN][$Fe_3(CO)_9(C{\equiv}CH)$] and [$Fe_3(CO)_9(C{\equiv}COTi(THF)_4Cl)$] from the Reaction of Low-Valent Titanium with [$Fe_3(CO)_9(CCO)]^{2-}$

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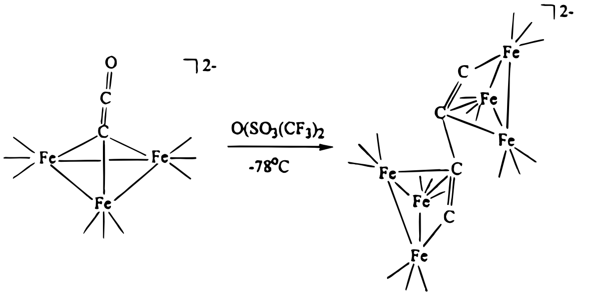
$TiCl_3(DME)_{1.5}$ (DME = 1,2-dimethoxyethane) and a Zn−Cu couple react with $[PPN]_2[Fe_3(CO)_9(CCO)]$ to give the new compound [PPN][$Fe_3(CO)_9(C{\equiv}CH)$] (**I**) (70% yield), a known compound [$Fe_3(CO)_{10}(CCH_2)$] (**II**) (9% yield), and another new compound [$Fe_3(CO)_9(CCOTi(THF)_4Cl)$] (**III**). Compound **I** was characterized by ^1H and ^{13}C NMR, IR, mass spectrometry, and X-ray crystallography. Compound **III** was characterized by IR, mass spectrometry, ^{13}C NMR, and X-ray crystallography.

In earlier research we found that reaction at the oxygen of a carbonyl with an electrophile followed by chemical reduction leads to carbon−carbon bond formation, as in the formation of $[Fe_3(CO)_9(CCO)]^{2-}$ from $[Fe_3(CO)_{11}]^{2-}$.[1] Further reaction of $[Fe_3(CO)_9(CCO)]^{2-}$ with a strong electrophile, triflic anhydride ($O(SO_2CF_3)_2$), results in formation of the C_4-containing cluster $[Fe_6(CO)_{18}C_4]^{2-}$, where the C_4 unit arises from two ketenylidene ligands (CCO) as shown in eq 1.[2]



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In the present research we explored the possibility that a single reagent, an oxophilic reducing agent, might effect concerted CCO formation followed by C−O cleavage and reduction to yield a polycarbon metal cluster compound. Electrophiles interact with carbonyl ligands and ketenylidene ligands in several ways. In the reaction of $[Fe_3(CO)_9(CCO)]^{2-}$ with the labile organometallic species $M(CO)_3(NCCH_3)_3$ (M = W, Cr), tetrahedral metal carbide clusters are formed: $[MFe_3(CO)_{12}C]^{2-}$.[3,4] Similarly, the reaction of $[Fe_3(CO)_9(CCO)]^{2-}$ with $[Re(CO)_5]^-$ and $[CpFe(CO)_2]^-$ produces $[Fe_3(CO)_9CCRe(CO)_5]^-$ and $[Fe_3(CO)_9CCFeCp(CO)_2]^-$, respectively.[5,6]

The present research was designed to explore the reactions of metal cluster carbonyls with the McMurry reagent, a low oxidation state titanium species.[7,8] The active titanium species in the McMurry reagent is thought to be Ti(0) or Ti(II), which serves to abstract oxygen atoms and form a carbon−carbon bond from an aldehyde and starting material.[9−11] In our research, we explored the possibility that the McMurry reagent might reduce CO and CCO concomitant with oxygen abstraction to produce cluster polycarbon compounds.

Experimental Section

General Procedures and Materials. Manipulation of air-sensitive solutions and volatile materials was carried out with standard Schlenk techniques under a prepurified N_2 atmosphere. Solids were handled in a drybox with a N_2 atmosphere. Solvents were distilled under nitrogen from appropriate drying agents. Infrared spectra were recorded on a Bomem MB-Series FTIR spectrometer at 2 cm^{-1} resolution. Solution IR spectra were obtained in matched air-free cells with CaF_2 windows, and solid samples were prepared as Nujol mulls between KBr plates. The ^1H and ^{13}C NMR spectra were acquired on a Varian Unity 400+ spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C. CD_2Cl_2 was used as an internal standard and before use was vacuum distilled from P_4O_{10}. Magnetic measurements were determined with a Quantum Design MPMS SQUID operating at either 500 or 1000 G. Mass spectra were determined on a VG 70-SE unit. Elemental analyses were determined by Elbach Analytical Laboratories, Engelskirchen, Germany. Published procedures were employed for the synthesis of $[PPN]_2[Fe_3(CO)_9(CCO)]$,[12] $Ru_3(CO)_{12}$,[13] $[PPN]_2[Ru_3(CO)_9(CCO)]$,[14] $[PPN]_2[Os_3(CO)_9(CCO)]$,[15] $[PPN]_2[Ru_6(CO)_{16}C]$,[16]

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and $TiCl_3(DME)_{1.5}$[17] (DME = 1,2-dimethoxyethane), where $[PPN]^+ = [(PPh_3)_2N]^+$.

Reaction of $[PPN]_2[Fe_3(CO)_9(CCO)]$ with a Ti(0)/Ti(II) Reducing Solution. A reducing solution was prepared by refluxing 0.822 g (2.84 mmol) of $TiCl_3(DME)_{1.5}$ and 0.738 g (11.36 mmol) Zn−Cu couple in 20 mL of DME at 90 °C for 3 h.[8] The solution was cooled to room temperature, and 40 mL of THF was added followed by 1.454 g (0.946 mmol) of solid $[PPN]_2[Fe_3(CO)_9(CCO)]$. $[PPN]_2[Fe_3(CO)_9(CCO)]$ is only slightly soluble in THF, so the mixture was stirred overnight, followed by filtration through Celite, and solvent was then removed under vacuum. A 50 mL aliquot of CH_2Cl_2 was added to the solids, and after 2 h the solution was filtered to remove white solids. Solvent was removed from the filtrate under vacuum, and the resulting dark solids were redissolved in 10 mL of THF. Pentane (50 mL) was added to this solution, and vigorous shaking gave a red-black oil of $[PPN][Fe_3(CO)_9(CCH)]$ (**I**) and a brown-red solution of $[Fe_3(CO)_{10}(CCH_2)]$ (**II**), which were separated by filtration. This separation process was repeated three times. The oil was dissolved in 10 mL of THF and layered with 50 mL of pentane to give light red crystals and a colorless solution. The crystals were isolated by filtration, washed twice with 5 mL of pentane, and dried to yield 0.652 g of $[PPN][Fe_3(CO)_9(CCH)]$(**I**) (70% yield based on iron). The filtrates were combined, and solvent was removed under vacuum. The resulting solid was dissolved in pentane and filtered, and the solvent was removed under vacuum, leaving 0.0410 g of $[Fe_3(CO)_{10}(CCH_2)]$ (**II**) (9% yield based on iron).

The infrared spectrum of $[PPN][Fe_3(CO)_9(CCH)]$ (**I**) in THF displayed ν_{CO} at 2044(w), 1986(vs), 1978(vs), 1959(s), 1933(m) cm^{-1}; (Nujol) 2044, 2016, 1977, 1951, 1928 cm^{-1}. Anal. Calcd. for $Fe_3C_{47}O_9P_2NH_{31}$ (Found) C, 57.41 (57.06); H, 3.18 (3.35); N, 1.42 (1.55). ^1H NMR (CD_2Cl_2, 25 °C): 7.64 (PPN^+), 7.46 (PPN^+), 1.15 (CC*H*) ppm. ^{13}C NMR (CD_2Cl_2, −30 °C): δ 226.32, 222.44, 216.73, 215.81, 215.47, 211.29, 209.78 (terminal carbonyls), 154.46 (C*C*H), 81.02 (*C*CH) ppm. Electrospray mass spectra contain a parent peak at 446 *m*/*z* corresponding to **I** + H, plus peaks for the sequential loss of two CO ligands.

The CO stretching frequencies for $[Fe_3(CO)_{10}(CCH_2)]$ (**II**) in pentane matched known values, at 2094(w), 2053(vs), 2035(vs), 2028(s), 2010(w), 1984(m), 1877(m, br) cm^{-1}. The ^1H NMR spectrum of **II** in CD_2Cl_2 displayed a feature at 5.30 ppm.[18] The X-ray powder diffraction pattern of this compound matches the *d*-values calculated from X-ray single-crystal data previously reported for **II**.[18]

Reaction of $[PPN]_2[Fe_3(CO)_9(CCO)]$ with $TiCl_3(DME)_{1.5}$. A 15 mL aliquot of THF was added to a Schlenk flask containing 0.0463 g (0.160 mmol) of $TiCl_3(DME)_{1.5}$ and 0.2004 g (0.130 mmol) of $[PPN]_2[Fe_3(CO)_9(CCO)]$. After the mixture was stirred under N_2 for 30 min, solvent was removed under vacuum. A 20 mL portion of Et_2O was added to the solids, and white [PPN]Cl solid was removed by filtration. Diethyl ether was removed under vacuum to yield 0.0571 g (0.0687 mmol) of red, microcrystalline $[Fe_3(CO)_9(CCOTi(THF)_4Cl)]$ (**III**) (53% yield based on iron).

A similar procedure was used with 0.0764 g (0.264 mmol) of $TiCl_3(DME)_{1.5}$ and 0.2019 g (0.131 mmol) of $[PPN]_2[Fe_3(CO)_9(CCO)]$. The initial THF solution was filtered, reduced under vacuum to 5 mL, and layered with 20 mL of pentane. The resulting red solid **III** (0.0286 g, 26% yield based on iron) was collected by filtration. A green solution of $Fe_3(CO)_{10}(CCH_2)$ (**II**) was collected, and solvent was removed (0.0854 g, 68% yield based on iron).

An infrared spectrum of $[Fe_3(CO)_9(CCOTi(THF)_4Cl)]$ (**III**) in THF shows ν_{CO} at 2048(w), 1993(vs), 1960(s), 1930(sh), 1914(m), 1779(w) cm^{-1}. The electrospray mass spectrum of the compound in methanol contains the parent peak for **III** at 836 *m*/*z*, calculated 836 *m*/*z*.

Reaction of $[PPN][Fe_3(CO)_9(CCH)]$ with Triflic Acid. A 2.9 μL (0.0327 mmol) aliquot of HSO_3CF_3 was added to 0.0316 g (0.0321 mmol) of $[PPN][Fe_3(CO)_9(CCH)]$ in 5 mL of THF and stirred for 5 min. The mixture was filtered to remove white, insoluble [PPN](OTf) and dried under vacuum to give $[HFe_3(CO)_9(CCH)]$: IR ν_{CO} (THF) 2062(sh), 2042(s), 2025(vs), 2005(s), 1997(s) cm^{-1}; ^1H NMR 1.266 and −20.0 ppm. ^{13}C NMR at −30 °C shows terminal carbonyls in a 2:2:1:2:1:2 ratio at 212.8, 212.2, 211.1, 210.6, 206.9, and 205.9 ppm and peaks for *C*CH at 182.3 and C*C*H at 39.2 ppm. Electrospray mass spectra of a methanol solution of the compound show a parent peak at 446 *m*/*z* (calcd = 446 *m*/*z*).

X-ray Crystal Structure Determination of $[PPN][Fe_3(CO)_9(CCH)]$ (I). A THF solution of **I** was layered with pentane, and one of the resulting crystals was mounted on a glass fiber with silicon grease. A complete hemisphere of data was collected at 163 K on a Siemens SMART-CCD. The intensity data were collected with 30 s frame times and interpreted with SAINT.[19] The initial unit cell parameters were determined from several frames of data, but were redetermined using all of the data. The structure was solved and refined using SHELXTL on 28 216 reflections and corrected for absorption using SADABS.[20,21] Hydrogen atoms were placed in idealized positions and refined with a riding model. Because of the method used by SADABS, no transmission factors are reported for the corrected data.

X-ray Crystal Structure Determination of $[Fe_3(CO)_9(CCOTi(THF)_4Cl)]$ (III). A crystal of **III** was mounted on a glass fiber with paratone oil, and a complete hemisphere of data was collected at 153 K on a Bruker SMART 1000-CCD. The intensity data were collected as described above. Cell parameters were determined using all of the unique data, and the structure was solved and refined using SHELXTL and corrected for absorption using SADABS.[20,21] Hydrogen atoms were placed in idealized positions and refined with a riding model. Because of the method used by SADABS, no transmission factors are reported for the corrected data.

Results and Discussion

Reaction of Iron Ketenylidene with McMurry Reagent. $[Fe_3(CO)_9(CCH)]^-$ (**I**) is produced in good yield from the reaction of $[Fe_3(CO)_9(CCO)]^{2-}$ with a low-valent titanium solution. This ethynyl cluster was previously synthesized by Mathieu et al. from the reaction of ethoxyacetylene with $[Fe_3(CO)_{11}]^{2-}$,[18] but it was not completely characterized, and an X-ray structure was not reported. In the present research the CCH moiety is generated by reduction of metal carbonyl ligands (Scheme 1).

Another C_2-containing cluster, $[Fe_3(CO)_{10}(CCH_2)]$ (**II**), is formed in 9% yield. This compound was previously synthesized in 2% yield[23] from the reaction of $Fe_3(CO)_{12}$ with BuLi, Me_3OBF_4, and H_2O, respectively. In our research, it may result from CO bond scission of the ketenylidene ligand followed by proton attack. This is consistent with the change from nine CO ligands in starting material and in **I** to 10 CO ligands in **III**.

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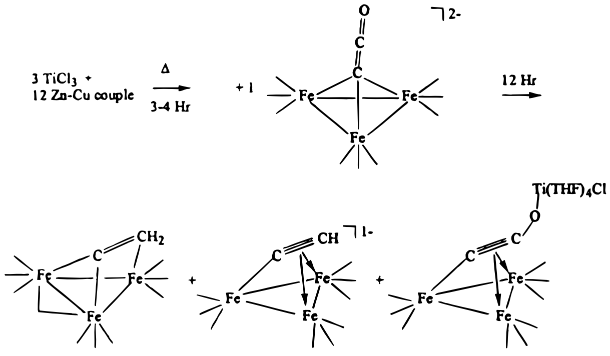
Scheme 1. Reaction of $[PPN]_2[Fe_3(CO)_9(CCO)]$ with Low-Valent Titanium



In typical McMurry reactions, the active species is considered to be Ti(0) particles in a heterogeneous reaction media, and it is believed that C−C coupling occurs on the metal surface via ketyl radical intermediates.[8,9,11] Recent results indicate that $TiCl_2$ in DME may serve as a nucleophile toward the carbonyl oxygen, rather than a radical to effect the coupling reaction.[10,24−26] By analogy with the proposed route for the conversion of CCO to polycarbon ligands, the Ti(II) species may attack the terminal oxygen of the ketenylidene ligand of $[Fe_3(CO)_9(CCO)]^{2-}$ followed by reductive cleavage of the C−O bond. The source of the proton in **I** and **II** may be residual water, even though water was not observed spectroscopically in any of the starting materials.

Structure and Characterization of $[PPN][Fe_3(CO)_9(CCH)]$ (I). The compound was characterized in the solid state as a well separated bis(triphenylphosphonium)iminium, PPN, cation and metal cluster anion. The cation is well ordered, and all bonds and angles are reasonable. Crystal data are shown in Tables 1, 2, and 3. The Fe−Fe distances for **I** are Fe1−Fe2, 2.6569(4) Å, and Fe1−Fe3, 2.6769(4) Å. The iron edge which is bridged by the ethynyl ligand is shorter, Fe2−Fe3 (2.4958(4) Å). The CCH moiety bonds to the trimetallic core through one σ and two π bonds ($\sigma + 2\pi$, μ_3-(η^2-$\perp$)) and is nearly perpendicular to one edge of the metal cluster. All three metal atoms are bound to C10, with bond lengths of 1.814(2), 2.049(2), and 2.055(2) Å for C10−Fe1, C10−Fe2, and C10−Fe3, respectively. Longer Fe−C bonds were found for C11 interactions with Fe2 (2.079(2) Å) and Fe3 (2.099(2) Å). The C10−C11 bond length is 1.293(2) Å, slightly longer than expected for a triple bond, but well within the range for similar alkyne clusters, as reviewed by Sappa.[22] The comparisons in Table 6 show that the bond lengths quoted above are typical of ethynyl clusters. A Fourier difference map indicates electron density assignable to the ethynyl proton; however, the structure was refined with the proton in an idealized position.

Table 1. Summary of Crystal Data and Intensity Collection

	I	III
formula	$C_{47}H_{31}NO_9P_2Fe_3$	$C_{27}H_{32}O_{14}ClTiFe_3$
fw	983.22	831.4
a (Å)	9.2601(1)	10.517(1)
b (Å)	29.7878(1)	17.903(2)
c (Å)	15.7931(2)	18.463(2)
α (deg)	90	90
β (deg)	101.313(1)	102.915(2)
γ (deg)	90	90
V (Å^3)	4271.69(7)	3388.7(6)
space group, Z	$P2_1/c$, 4	$P2_1/n$, 4
T (°C)	−110	−120
λ (Å)	0.710 73	0.710 73
ρ_{calc} (g cm^{-3})	1.529	1.630
μ (mm^{-1})	1.139	1.628
R1[a]	0.0466	0.0447
wR2[b]	0.0756	0.0837

[a] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [(\sum w(F_o{}^2 - F_c2)^2)/\sum w(F_o{}^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o{}^2) + (z_1,P)^2 + z_2P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$, z_1, z_2 = weighting and extra extinction.

Table 2. Selected Atomic Coordinates (Å × 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $[PPN][Fe_3(CO)_9(CCH)]$, I

atom	x	y	z	U_{eq}[a]
Fe(1)	4209(1)	1463(1)	2145(1)	25(1)
Fe(2)	5076(1)	620(1)	2469(1)	23(1)
Fe(3)	7015(1)	1213(1)	2686(1)	24(1)
C(1)	4094(2)	1489(1)	993(1)	30(1)
O(1)	3999(2)	1510(1)	260(1)	41(1)
C(2)	4316(3)	2047(1)	2347(2)	40(1)
O(2)	4359(3)	2426(1)	2500(1)	68(1)
C(3)	2282(2)	1396(1)	2092(2)	39(1)
O(3)	1039(2)	1358(1)	2067(1)	67(1)
O(4)	5074(2)	486(1)	625(1)	35(1)
C(4)	5060(2)	548(1)	1341(1)	26(1)
C(5)	3261(2)	403(1)	2464(1)	30(1)
O(5)	2095(2)	259(1)	2409(1)	42(1)
O(6)	6835(2)	−165(1)	3153(1)	43(1)
C(6)	6136(2)	139(1)	2869(1)	30(1)
C(7)	7266(2)	1253(1)	1597(1)	30(1)
O(7)	7502(2)	1271(1)	907(1)	43(1)
O(8)	9535(2)	627(1)	3295(1)	50(1)
C(8)	8560(2)	860(1)	3051(1)	32(1)
C(9)	7851(2)	1740(1)	3058(1)	33(1)
O(9)	8430(2)	2076(1)	3257(1)	50(1)
C(10)	5095(2)	1205(1)	3154(1)	27(1)
C(11)	5984(2)	930(1)	3631(1)	30(1)

[a] U_{eq} is defined as 1/3 the trace of the U_{ij} tensor.

The infrared spectrum of compound **I** contains five bands in the ν_{CO} region. The ethynyl C−H stretch is not observed. The ^{13}C NMR of **I** indicates fluctional behavior of the carbonyl ligands from −80 to 60 °C in CD_2Cl_2 solution. The terminal carbonyl resonances range from δ 200 to 230 ppm, and the α and β carbon of the ethynyl ligand are located at δ 81 and 154 ppm in the ^1H decoupled NMR spectrum. The β carbon is not observed above −30 °C. For comparison, positions of α and β carbons for other ethynyl clusters are provided in Table 7. In the ^1H coupled ^{13}C NMR spectrum collected at −80 °C, the peaks for the α and β carbons are split with $^1J_{C-H} = 188$ Hz and $^2J_{C-H} = 22.9$ Hz. The ^1H NMR of **I** has a peak of 1.15 ppm for the acetylide proton. This value is lower than reported by Mathieu,[18] but it is in the range expected for a metal-bound acetylide.[27]

Structure and Characterization of $[PPN][Fe_3(CO)_9(CCOTi(THF)_4Cl)]$ (III). The structure of **III** is shown in Figure 2, and crystal data are shown in Tables 1, 4, and 5. The Fe1−Fe2 (2.6490(7) Å) and Fe1−Fe3 (2.6360(7) Å) bond lengths are longer than the Fe2−Fe3 (2.4963(7) Å) which is bridged by the C−C moiety.

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Table 3. Bond Lengths (Å) and Angles (deg) for the Anion in [PPN][$Fe_3(CO)_9(CCH)$], I

C(10)−C(11)	1.293(3)	Fe(2)−C(10)	2.049(2)
Fe(1)−C(10)	1.814(2)	Fe(3)−C(10)	2.055(2)
Fe(2)−C(11)	2.079(2)	Fe(3)−C(11)	2.099(2)
Fe(1)−Fe(2)	2.6569(4)	Fe(1)−Fe(3)	2.6769(4)
Fe(2)−Fe(3)	2.4958(4)	C(1)−O(1)	1.146(2)
Fe(1)−C(1)	1.803(2)	C(2)−O(2)	1.153(3)
Fe(1)−C(2)	1.769(2)	C(3)−O(3)	1.149(3)
Fe(1)−C(3)	1.781(2)	O(4)−C(4)	1.149(2)
Fe(2)−C(4)	1.791(2)	C(5)−O(5)	1.150(2)
Fe(2)−C(5)	1.799(2)	O(6)−C(6)	1.151(3)
Fe(2)−C(6)	1.781(2)	C(7)−O(7)	1.154(2)
Fe(3)−C(7)	1.784(2)	O(8)−C(8)	1.145(3)
Fe(3)−C(8)	1.778(2)	C(9)−O(9)	1.150(3)
Fe(3)−C(9)	1.797(2)		

Fe(1)−C(10)−C(11)	155.1(2)	Fe(3)−C(7)−O(7)	176.5(2)
Fe(1)−C(1)−O(1)	178.8(2)	Fe(3)−C(8)−O(8)	178.4(2)
Fe(1)−C(2)−O(2)	177.8(2)	Fe(3)−C(9)−O(9)	176.0(2)
Fe(1)−C(3)−O(3)	178.9(2)	Fe(2)−Fe(1)−Fe(3)	55.80(1)
Fe(2)−C(4)−O(4)	177.2(2)	Fe(3)−Fe(2)−Fe(1)	62.51(1)
Fe(2)−C(5)−O(5)	175.8(2)	Fe(2)−Fe(3)−Fe(1)	61.70(1)
Fe(2)−C(6)−O(6)	177.8(2)		

Table 4. Atomic Coordinates (Å × 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for [$Fe_3(CO)_9(CCOTi(THF)_4Cl)$] (III)

atom	x	y	z	U_{eq}[a]
Fe(1)	2862(1)	4266(1)	719(1)	29(1)
Fe(2)	4321(1)	4888(1)	1923(1)	28(1)
Fe(3)	3774(1)	3534(1)	1966(1)	26(1)
C(1)	3991(4)	4063(2)	142(2)	41(1)
O(1)	4698(3)	3920(2)	-223(2)	62(1)
C(2)	1652(4)	3607(2)	342(2)	35(1)
O(2)	838(3)	3180(2)	124(2)	53(1)
C(3)	2139(4)	5080(2)	241(2)	42(1)
O(3)	1625(3)	5596(2)	-58(2)	65(1)
C(4)	5664(4)	4737(2)	1493(2)	34(1)
O(4)	6539(3)	4648(2)	1236(2)	48(1)
C(5)	3916(4)	5831(2)	1653(2)	38(1)
O(5)	3669(3)	6441(2)	1490(2)	61(1)
C(6)	5170(3)	5100(2)	2842(2)	38(1)
O(6)	5646(3)	5246(2)	3448(2)	62(1)
C(7)	4710(3)	3076(2)	1406(2)	32(1)
O(7)	5342(2)	2736(1)	1089(2)	44(1)
C(8)	4891(4)	3421(2)	2831(2)	36(1)
O(8)	5618(3)	3343(2)	3397(2)	54(1)
C(9)	2635(4)	2806(2)	1988(2)	32(1)
O(9)	1916(3)	2328(1)	2016(2)	48(1)
C(10)	2546(3)	4408(2)	1637(2)	24(1)
C(11)	2821(3)	4432(2)	2361(2)	25(1)
O(10)	2356(2)	4554(1)	2952(1)	26(1)
Ti(1)	895(1)	4612(1)	3374(1)	24(1)
Cl(1)	−965(1)	4703(1)	3871(1)	39(1)
O(20)	−38(2)	3768(1)	2651(1)	33(1)
O(30)	1876(2)	5424(1)	4112(1)	29(1)
O(40)	1677(2)	3783(1)	4149(1)	29(1)
O(50)	90(2)	5482(1)	2600(1)	29(1)

[a] U_{eq} is defined as 1/3 the trace of the U_{ij} tensor.

The interactions of the −CCO ligand with the metal cluster may be regarded as a σ bond to Fe1 and two π bonds to the Fe2−Fe3 edge. The three iron atoms interact with C10, with bond distances of 1.818(3), 2.015(3), and 2.034(3) Å for Fe1, Fe2, and Fe3. The C−C bond length, 1.304(4) Å, is within the range for ketenylidene ligands. The C11−O10 bond (1.310(4) Å) is indicative of a single bond. The Ti−O bonds for the four Ti−THF interactions are all similar, with an average bond length of 2.11 Å; however, the Ti−OCC bond is much shorter, 1.875(2) Å.

Table 5. Bond Lengths (Å) and Angles (deg) for [$Fe_3(CO)_9(CCOTi(THF)_4Cl)$] (III)

C(10)−C(11)	1.304(4)	C(11)−O(10)	1.310(4)
Fe(1)−C(10)	1.818(3)	O(10)−Ti(1)	1.875(2)
Fe(2)−C(10)	2.015(3)	Fe(2)−C(11)	2.094(3)
Fe(3)−C(10)	2.034(3)	Fe(3)−C(11)	2.109(3)
Fe(1)−Fe(2)	2.6490(7)	Fe(2)−Fe(3)	2.4963(7)
Fe(1)−Fe(3)	2.6360(7)	C(1)−O(1)	1.139(4)
Fe(1)−C(1)	1.800(4)	C(2)−O(2)	1.152(4)
Fe(1)−C(2)	1.760(4)	C(3)−O(3)	1.147(4)
Fe(1)−C(3)	1.784(4)	C(4)−O(4)	1.137(4)
Fe(2)−C(4)	1.789(4)	C(5)−O(5)	1.146(4)
Fe(2)−C(5)	1.785(4)	C(6)−O(6)	1.150(4)
Fe(2)−C(6)	1.773(4)	C(7)−O(7)	1.153(4)
Fe(3)−C(7)	1.779(4)	C(8)−O(8)	1.157(4)
Fe(3)−C(8)	1.770(4)	C(9)−O(9)	1.151(4)
Fe(3)−C(9)	1.777(4)	Ti(1)−Cl(1)	2.344(1)
Ti(1)−O(20)	2.107(2)	Ti(1)−O(40)	2.096(2)
Ti(1)−O(30)	2.099(2)	Ti(1)−O(50)	2.155(2)

C(10)−C(11)−O(10)	145.2(3)	C(11)−O(10)−Ti(1)	148.0(2)
C(11)−C(10)−Fe(1)	156.4(3)	Fe(3)−C(7)−O(7)	174.3(3)
Fe(1)−C(1)−O(1)	178.7(4)	Fe(3)−C(8)−O(8)	179.7(4)
Fe(1)−C(2)−O(2)	176.9(4)	Fe(3)−C(9)−O(9)	178.4(3)
Fe(1)−C(3)−O(3)	177.1(4)	Fe(1)−Fe(2)−Fe(3)	61.55(2)
Fe(2)−C(4)−O(4)	178.2(3)	Fe(1)−Fe(3)−Fe(2)	62.08(2)
Fe(2)−C(5)−O(5)	178.9(4)	Fe(2)−Fe(1)−Fe(3)	56.37(2)
Fe(2)−C(6)−O(6)	175.7(4)		

Table 6. Bond Lengths (Å) and Angles (deg) in Clusters Containing Ethynes

	C−C	Fe−C−C	ref
I	1.293(3)	155.1(2)	*a*
III	1.304(4)	156.4(3)	*a*
[PPN][$Fe_3(CO)_9CCRe(CO)_5$]	1.28(1)	159.9(7)	4
[PPN][$Fe_3(CO)_9(CCFeCp(CO)_2)$]	1.288(5)	161.6(3)	4
[PPN][$Fe_3(CO)_9(CCOC(O)CH_3)$]	1.314(8)	150.6(4)	24

[a] This work.

Table 7. ^{13}C NMR Data for Clusters Containing Ethynes

	C_α	C_β	ref
I	81.0	154.5	*a*
III		279	*a*
$[PPN]_2[Fe_3(CO)_9(CCO)]$	90.1	182.2	4
[PPN][$Fe_3(CO)_9(CCOEt)$]	160.7	148.5	10
[PPN][$Fe_3(CO)_9(CCOAc)$]	172.9	132.2	10

[a] This work.

[$Fe_3(CO)_9(CCOTi(THF)_4Cl)$] (**III**) was also isolated in less than 1% yield from the reaction of low-valent titanium with $[Fe_3(CO)_9(CCO)]^{2-}$ from the resulting oily mass of **I** when the reaction to produce **I** was run on very large, 20 g scale of $[PPN]_2[Fe_3(CO)_9(CCO)]$ starting material. Spectroscopic evidence, ν_{CO} at 1779 cm^{-1}, suggests its presence in earlier preparations. To determine if **III** is an intermediate in the formation of **I**, the reaction of $[Fe_3(CO)_9(CCO)]^{2-}$ with $TiCl_3(DME)_{1.5}$ was explored. This reaction formed **III** rapidly and in good yield (53% yield, based on iron). The infrared spectrum of the neutral cluster, **III**, is very similar to that of the monoanionic cluster **I**. The R substituents of the CCR ligand in $[Fe_3(CO)_9(CCR)]^n$ (n = 0 or −1) do not cause large changes in the electron density as judged by infrared stretching frequencies of the terminal carbonyls for similar types of clusters, whether the CC moiety is ethynyl (R = H, $OTi(THF)_4Cl$, $OC(O)CH_3$,[28] or $OCH_2CH_3$28) or ethenyl (CCR = CH_3CCCH_3, CH_3CCH_2Ph, or CH_3CCCH_2-t-Bu);[18,29,30] compounds

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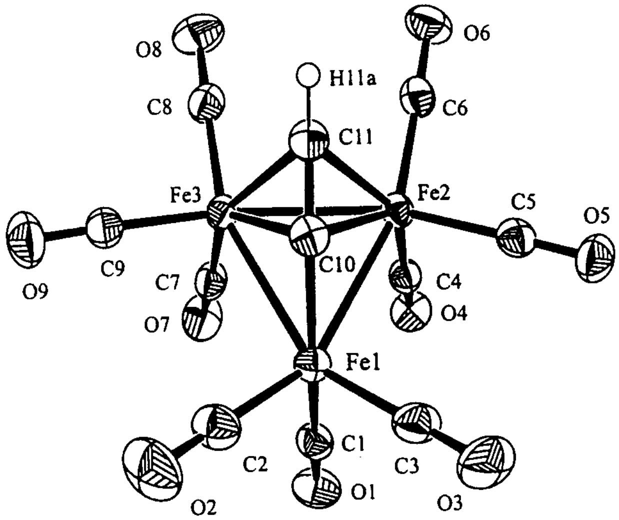

Figure 1. Thermal ellipsoid plot of [PPN][$Fe_3(CO)_9(C\equiv CH)$] (**I**) at 50% probability.

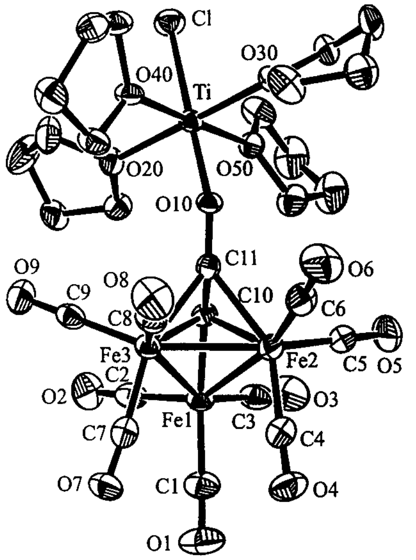

Figure 2. Thermal ellipsoid plot of [$Fe_3(CO)_9$(CCOTi-$(THF)_4$Cl)] (**III**) at 50% probability.

that have similar R groups will have similar ranges of CO stretching frequencies.

At 20 °C, the spectrum for a ^{13}C-enriched sample of **III** shows a broad feature from δ 210 to 230 ppm, with peaks at 228.3, 223.8, 220.7, 217.8, 214.0, and 210.5 ppm, and the peaks for the α and β carbon are not observed. At −80 °C, four broad peaks (~4 ppm) are observed at δ 226.8, 219.2, 214.4, and 209.6 ppm, and another broad feature (~11 ppm) is seen at 279 ppm, which we assign to the β carbon of the ketenylidene. A weak peak for the α carbon is observed in similar compounds, but is not observed in the present case. The position of the β carbon is shifted to a higher field relative to those observed in similar structures (Table 7).[4,10] The observed NMR line widths and shifts are in line with the paramagnetism of the sample.

Magnetic Properties. Assuming that no redox chemistry occurs upon formation of **III**, electron counting indicates that the titanium should be Ti(III). Several methods were used to infer the oxidation state of titanium in [$Fe_3(CO)_9$(CCOTi$(THF)_4$Cl)]. One of these involved the examination of the titanium−atom bond lengths, to determine the effective charge by the "sum of valence bonds" method.[30] This calculation gave a value of 3.1, indicating paramagnetic Ti(III). The broadening of the ^{13}C NMR spectrum for **III** also provides qualitative confirmation of a Ti(III) species. Furthermore, an EPR spectrum of **III** indicates a paramagnetic species, with splitting values for g_x, g_y, and g_z of 2.05, 2.02, and 1.96 for a solid-state sample. These values are within the expected range for Ti(III).[32,33] Magnetic susceptibility was determined by the Evans method,[34] and this measurement (2.01 μ_B for **III**) indicates the presence of Ti(III). A variable-temperature magnetic susceptibility (SQUID) measurement of **III** over the temperature range 5 to 300 K reveals a magnetic moment of 2.64 μ_B, indicating a Ti(II) species. It appears that paramagnetic Ti species are present. A variable-temperature magnetic susceptibility measurement, over the same temperature range, for [PPN]$_2$[$Fe_3(CO)_9$(CCO)] indicated paramagnetic behavior, with a much lower magnetic moment of 0.091 μ_B. The paramagnetic behavior for **III** and that for [PPN]$_2$[$Fe_3(CO)_9$(CCO)] in the SQUID measurements may arise from an adventitious impurity.

Further Reactions of [PPN][$Fe_3(CO)_9$(CCH)] (I). The reaction of **I** with the strong proton source, triflic acid, does not yield **II**; instead protonation occurs at the metal core yielding [$HFe_3(CO)_9$(CCH)] (**IV**) in a quantitative yield. This cluster has been previously reported.[18] The ^{1}H NMR of **IV** contains a large, sharp upfield feature at −20.0 ppm assigned to the metal-bridging hydride. This value is higher than the reported value of −27.8 ppm.[18] Repetition of our NMR experiment gave the same result, and the previously reported peak was not observed. The observed protonation at the metal core is contrary to our expectation that protonation should occur at the β carbon of **I**, by analogy with the structure of **II**. Under an atmosphere of CO, a solution of **I** in THF converts to **II** after several days. This reaction is accompanied by some decomposition of **I**. The solvent was freshly distilled and all solids were stored in a drybox, so the hydrogen needed to form **II** may originate by H abstraction from the solvent.

Reaction of the McMurry Reagent. Reaction of the low-valent titanium compound with $Ru_3(CO)_{12}$, [PPN]$_2$-[$Ru_3(CO)_9$(CCO)], [PPN]$_2$[$Os_3(CO)_9$(CCO)], and [PPN]$_2$-[$Ru_6(CO)_{16}$C] leads to the formation of the known hydride compounds [$H_4Ru_4(CO)_{12}$],[35] [$H_2Ru_3(CO)_9$-(CCO)],[36] [$H_2Os_3(CO)_9$(CCO)],[37] and [$H_2Ru_6(CO)_{16}$C],[38] respectively, presumably through H abstraction from the solvent or from adventitious water. Apparently, the basic nature of these clusters leads to the formation of hydrides. We obtained evidence for the formation of compounds similar to **III** in the reaction of the titanium reagent with [$Ru_3(CO)_9$(CCO)]$^{2-}$ or [$Os_3(CO)_9$(CCO)]$^{2-}$.

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Thus, for the reaction with ruthenium ketenylidene, a peak in the infrared spectrum was observed at 1650 cm^{-1}. This evidence for Ti coordination to the oxygen of the CCO ligand plus a parent peak at 966.5 *m*/*z* in the mass spectrum indicates the presence of $[Ru_3(CO)_9(CCOTi(THF)_4Cl)]$. Similarly, reaction of the titanium reagent with the osmium ketenylidene produces a product with an infrared stretching frequency peak at 1728 cm^{-1}, which is attributed to the CO stretch of CCO in $[Os_3(CO)_9(CCOTi(THF)_4Cl)]$.

Conclusions

Reaction of $[Fe_3(CO)_9(CCO)]^{2-}$ with a low-valent titanium source converts the CCO to an ethynyl ligand. Apparently, a low-oxidation-state Ti species serves as both an oxophile and reducing agent, to afford a new approach for the generation of the C_2 ligand in a metal cluster. Previously ethynyl ligands were introduced into metal clusters by alkyne starting materials. The ^{13}C NMR spectra of the ethynyl cluster and a related mixed metal iron−titanium cluster containing the ketenylidene ligand are reported.

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Supporting Information Available: Crystallographic data for **Ia**, **Ib**, and **III**. This material is available free of charge via the Internet at http://pubs.acs.org.

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