THF was treated as described above to give an inseparable diastereomeric mixture of products as a red oil (0.075 g, 69.4%, ratio 50:50): IR (thin film) 2993, 1649, 1545, 1449, 1242, 1083, 850 cm^{-1}; MS, *m/z* (relative intensity) 470 (M^+, 12), 455 (7), 412 (100), 395 (21), 384 (15), 339 (53), 311 (21); ^1H NMR (300 MHz, C_6D_6) δ 4.44 (br s, 2 H), 4.25 (m, 1 H), 4.22 (m, 1 H), 4.00 (br s, 1 H), 3.81 (br s, 1 H), 3.50 (br s, 2 H), 3.45 (m, 2 H), 3.16 (dd, J = 14.5, 5.0 Hz, 1 H), 2.98 (dd, J = 14.0, 13.0 Hz, 1 H), 2.63 (dd, J = 14.5, 5.0 Hz, 1 H), 2.47 (m, 3 H), 2.29 (dd, J = 14.5, 12.0 Hz, 1 H), 2.12 (m, 5 H), 1.85 (m, 8 H), 1.74 (s, 3 H), 1.68 (s, 3 H), 1.61 (m, 4 H), 1.51 (br s, 6 H), 1.38 (s, 3 H), 1.34 (s, 3 H), 0.42 (s, 9 H), 0.38 (s, 3 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 111.2, 111.1, 104.3, 96.5, 95.5, 95.3, 94.9, 94.2, 81.8, 81.6, 79.3, 78.7, 78.6, 78.4, 78.2, 78.1, 76.9, 76.8, 30.1, 27.6, 27.5, 27.3, 27.0, 26.5, 25.1, 24.8, 24.7, 24.6, 23.4, 23.3, 22.8, 22.6, 22.5, 22.2, 15.8, 7.6, 6.9, 0.3, 0.2.

Diene Complexes 35. A solution of **23** (0.153 g, 0.62 mmol) in toluene (5 mL) was degassed by three freeze–pump–thaw cycles and then added under nitrogen to **34** (0.215 g, 0.56 mmol) in a 15-mL round-bottom flask equipped with a reflux condenser. The mixture was heated at reflux and irradiated by a projector lamp (GE-ENH 250 W) for 10 h. The solvent was removed under vacuum and the residue filtered through activity 3 alumina with pentane to provide an inseparable mixture of two isomers of **35** (0.285 g, 87.3%, ratio 58:42) as a red oil (0.143 g, 69.4%): IR (thin film) 2961, 1604, 1501, 1452, 1253, 838, 707 cm^{-1}; MS, *m/z* (relative intensity) 584 (M^+, 9), 511 (6), 369 (17), 338 (29), 280 (8), 229 (13), 214 (3), 169 (8), 119 (25), 105 (10), 97 (17), 83 (20), 71 (30), 57 (100); HRMS calcd for $C_{37}H_{53}CoSi$, 584.3248, found, 584.3266; ^1H NMR (300 MHz, C_6D_6) for major isomer, δ 7.05–7.23 (m, 5 H), 4.87 (br s, 1 H), 3.86 (br s, 1 H), 3.61 (br s, 2 H), 2.78 (m, 1 H), 2.40–2.52 (m, 2 H), 2.33 (m, 3 H), 1.87–2.18 (m, 4 H), 1.40–1.85 (m, 12 H), 1.31 (s, 3 H), 1.11 (d, J = 6.1 Hz, 3 H), 1.10 (s, 3 H), 0.85–1.0 (m, 2 H), 0.40–0.55 (m, 2 H), 0.29 (s, 9 H), for minor isomer, δ 7.05–7.23 (m, 5 H), 4.29 (br s, 1 H), 4.27 (br s, 1 H), 4.08 (br s, 1 H), 3.97 (br s, 1 H), 2.97 (m, 1 H), 2.40–2.52 (m, 2 H), 2.33 (m, 3 H), 1.87–2.18 (m, 4 H), 1.40–1.85 (m, 12 H), 1.28 (s, 3 H), 1.07 (d, J = 6.0 Hz, 3 H), 1.03 (s, 3 H), 0.85–1.0 (m, 2 H), 0.40–0.55 (m, 2 H), 0.30 (s, 9 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 152.6, 128.2, 125.9, 125.1, 125.0, 111.9, 108.7, 93.9, 87.4, 83.0, 81.2, 80.1, 79.4, 78.7, 78.6, 56.0, 55.7, 49.1, 48.1, 41.4, 40.8, 40.6, 40.0, 39.9, 36.3, 36.1, 36.0, 35.9, 34.8, 34.1, 34.0, 33.8, 33.7, 32.9, 30.5, 30.4, 29.9, 29.4, 29.3, 29.1, 28.0, 27.6, 24.9, 24.4, 24.2, 24.1, 24.0, 23.6, 23.2, 22.9, 22.5, 22.3, 0.8, 0.7.

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Registry No. **3**, 112505-23-4; **4**, 59581-87-2; **5**, 106509-11-9; **7**, 97371-54-5; **8**, 104870-75-9; **10**, 112505-24-5; **11**, 65253-04-5; **12**, 112505-25-6; **13**, 112505-26-7; **14**, 112505-27-8; **15**, 464-49-3; **16**, 106509-10-8; **17**, 106566-51-2; **18**, 112505-28-9; **19**, 112505-29-0; **20**, 112505-30-3; **21**, 37002-45-2; **22**, 112572-77-7; **23**, 112505-34-7; **24**, 112505-35-8; **25a**, 106564-05-0; **26a**, 106564-06-1; **27**, 112505-33-6; **28**, 106563-88-6; **30**, 2039-93-2; **31**, 135-98-8; **32** (R^1 = $Si(CH_3)_3$, R^2 = H), 83182-85-8; **32** (R^1 = $Si(CH_3)_3$, R^2 = CH_3), 112505-31-4; **32** (R = $Si(CH_3)_3$, R^2 = CH_2CH_3), 112505-32-5; **32** (R^1 = Me, R^2 = H), 4116-92-1; **33** (R^1 = $Si(CH_3)_3$, R^2 = H, from **23**), 112505-38-1; **33** (R^1 = H, R^2 = $Si(CH_3)_3$, from **23**), 112572-79-9; **33** (R^1 = $Si(CH_3)_3$, R^2 = CH_3, from **23**), 112505-39-2; **33** (R^1 = CH_3, R^2 = $Si(CH_3)_3$, from **23**), 112572-80-2; **33** (R^1 = $Si(CH_3)_3$, R^2 = Et, from **23**), 112505-40-5; **33** (R = Et, R^2 = $Si(CH_3)_3$, from **23**), 112572-81-3; **33** (R^1 = H, R^2 = Me, from **23**), 112505-41-6; **33** (R^1 = Me, R^2 = H, from **23**), 112572-82-4; **33** (R^1 = H, R^2 = Et, from **23**), 112505-42-7; **33** (R^1 = Et, R^2 = H, from **23**), 112572-83-5; **33** (R^1 = $Si(CH_3)_3$, R^2 = Et, from **28**), 112572-85-7; **33** (R^1 = Et, R^2 = $Si(CH_3)_3$, from **28**), 112505-44-9; **34**, 74585-57-2; **35** (isomer 1), 112505-43-8; **35** (isomer 2), 112572-84-6; 1,7-decadiyne, 63815-29-2; $TiCl_3$, 7705-07-9; $Co_2(CO)_8$, 10210-68-1; $ICo(CO)_4$, 15976-97-3; cyclopentadiene, 542-92-7; (2*R*,4*R*)-4-methyl-2-(2-phenyl-2-propyl)cyclohexanone, 104870-79-3; (1*R*,2*R*,5*R*)-5-methyl-2-(2-phenyl-2-propyl)cyclohexanol, 104870-80-6; cyclopentadienylsodium–dimethoxyethane, 62228-16-4.

Synthesis, Reactivity, and X-ray Crystal Structure of an Anionic, Mixed-Metal Ketenylidene Cluster: $[PPN][Fe_2Co(CO)_9(CCO)]$

Stanton Ching,[1a] Elizabeth M. Holt,[1b] Joseph W. Kolis,[1a,c] and Duward F. Shriver*[1a]

Departments of Chemistry, Northwestern University, Evanston, Illinois 60201, and Oklahoma State University, Stillwater, Oklahoma 74078

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The anionic mixed-metal ketenylidene cluster $[PPN][Fe_2Co(CO)_9(CCO)]$ (1) can be prepared in high yield by a facile metal substitution reaction between $[PPN]_2[Fe_3(CO)_9(CCO)]$ and $Co_2(CO)_8$ under a CO atmosphere. This cluster is structurally similar to $[Fe_3(CO)_9(CCO)]^{2-}$, but its reactivity more closely resembles that of the cationic cluster $[Co_3(CO)_9(CCO)]^+$. Compound 1 undergoes protonation at the α-carbon atom to give $Fe_2Co(CO)_{10}(CH)$ but is inert to electrophilic attack by carbocationic reagents. Nucleophilic reagents such as $LiCH_3$, $NaOCH_3$, and $KBEt_3H$ attack at the β-carbon atom to afford dinegatively charged species $[Fe_2Co(CO)_9(CC(O)R)]^{2-}$ (R = CH_3, OCH_3, H). Compound 1 crystallizes in the space group $C2/c$ with a = 27.231 (7) Å, b = 17.670 (6) Å, c = 23.072 (10) Å, β = 126.54 (3)°, V = 8919.9 (70) Å^3, and Z = 8.

Introduction

Ketenylidene (CCO) ligands on trinuclear metal clusters are known to undergo diverse chemistry with respect to C–C bond cleavage, C–O activation, C–C and C–O bond formation, and cluster building.[2-13] An important factor in determining the reactivity of the CCO ligand is the charge on the cluster. Ketenylidene ligands on cationic[2-4]

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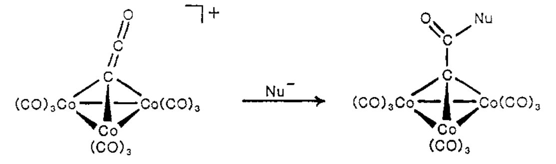
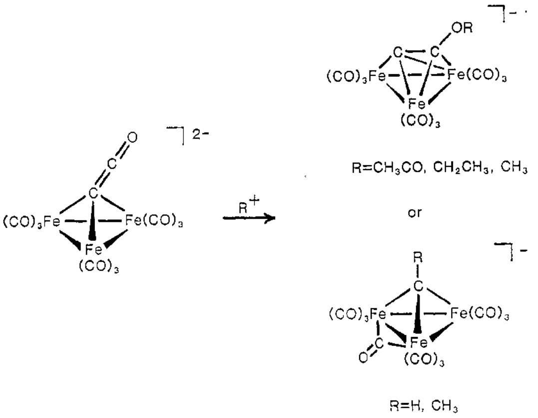
and neutral clusters[5-7] show electrophilic character while those on dinegatively charged clusters[8-11] behave as nucleophiles. Of the numerous ketenylidene clusters now known, $[Co_3(CO)_9(CCO)]^+$ and $[Fe_3(CO)_9(CCO)]^{2-}$ are among the most thoroughly studied.[2,3,8,9,12] The difference in reactivity between these two clusters can be rationalized in terms of their significant difference in charge. Cationic $[Co_3(CO)_9(CCO)]^+$ readily reacts with nucleophiles at the β-carbon atom of the CCO ligand to give neutral products with the general formula $Co_3(CO)_9(CC(O)Nu)^{2,3}$ (eq 1).[14]



(1)

Nu=R, OR, SR, NR₂
are examples

In contrast, the dinegatively charged ketenylidene cluster $[Fe_3(CO)_9(CCO)]^{2-}$ reacts with electrophiles at either the α-carbon[8] or the CCO oxygen atom[9] to afford clusters with capping alkylidyne and acetylide ligands (eq 2). In the present research, the reactivity of $[Fe_2Co(CO)_9(CCO)]^-$ was investigated to clarify the influence of charge on the reactions of the CCO ligand. The synthesis of $[PPN][Fe_2Co(CO)_9(CCO)]$ (1) has been previously communicated,[13] but an improved procedure is reported here.



(2)

Experimental Section

General Procedures. All manipulations were carried out under a purified N_2 atmosphere by using standard Schlenk and syringe techniques[15] or in a Vacuum Atmospheres drybox. CH_2Cl_2 was dried over P_2O_5. THF and Et_2O were dried over Na/benzophenone ketyl. Pentane was dried over Na. MeOH and *i*-PrOH were dried over Mg/I_2. All solvents were distilled prior to use and deaerated with N_2.

HSO_3CF_3 (Aldrich) was distilled before use. $LiCH_3$ (1.2 M in Et_2O, Aldrich) and $KBEt_3H$ (1.0 M solution in THF, Aldrich) were deaerated before use. $NaOCH_3$ (anhydrous powder, Aldrich) was used as received as was [PPN]Cl (Alfa Products). $Co_2(CO)_8$ (Strem) was freshly sublimed before use.

NMR spectra were obtained on a JEOL FX-270 spectrometer (^{1}H, 269.65 MHz; ^{13}C, 67.80 MHz). CD_2Cl_2 and THF-d_8 were vacuum distilled from P_2O_5 and Na, respectively. All chemical shifts are reported positive if downfield from Me_4Si and are obtained indirectly by using residual solvent protons (^{1}H) or solvent (^{13}C) as the internal references. IR spectra were recorded on either a Model 283 or 399 Perkin-Elmer spectrometer using solution cells with 0.1-mm path lengths and CaF_2 windows or Nujol mulls pressed between KBr plates. The mass spectrum on $Fe_2Co(CO)_{10}(CH)$ was obtained by Dr. D. Hung of the Northwestern University Analytical Services Laboratory on a HP5985A spectrometer using 70-eV ionization. Elemental analyses were performed by Elbach Laboratories (Germany).

$[PPN][Fe_2Co(CO)_9(CCO)]$ (1). A 2.50-g (1.63-mmol) sample of $[PPN]_2[Fe_3(CO)_9(CCO)]^8$ and 0.60 g (1.75 mmol) of $Co_2(CO)_8$ were slurried in 15 mL of THF under a CO atmosphere. The sparingly soluble $[PPN]_2[Fe_3(CO)_9(CCO)]$ rapidly dissolved as the THF-soluble $[PPN][Fe_2Co(CO)_9(CCO)]$ was produced. After 20 min, the solvent and volatile $Fe(CO)_5$ were removed by vacuum, and the resulting oil was dissolved in 20 mL of Et_2O. The orange/brown solution was filtered to remove $[PPN][Co(CO)_4]$, and 20 mL of 2-propanol was added. The solvents were removed by vacuum yielding the black/purple, microcrystalline product which was then washed thoroughly with three 20-mL portions of pentane and dried by vacuum. Yield: 1.37 g (84.1%). IR: ν_{CO} (Et_2O) 2068 (w), 2001 (s), 1990 (s, sh), 1966 (m, sh), 1930 (w) cm^{-1}. Anal. Calcd for $C_{47}H_{30}NO_{10}Fe_2Co$: C, 56.38; H, 3.02; N, 1.40; Fe, 11.15; Co, 5.89. Found: C, 56.24; H, 3.12; N, 1.37; Fe, 11.80; Co, 6.24. $[Fe_2Co(CO)_9(CCO)]^-$ can be obtained with ^{13}C enrichment at all carbon atoms by using enriched $Fe_3(CO)_9(CCO)]^{2-\,8}$ as starting material. It is also possible to obtain compound 1 which is selectively enriched at all carbon atoms except for the α-carbon atom by stirring a sample of 1 in CH_2Cl_2 under 1 atm of ^{13}CO for 4 days.

$Fe_2Co(CO)_{10}(CH)$ (2). A 0.20-g (0.20-mmol) sample of $[PPN][Fe_2Co(CO)_9(CCO)]$ was dissolved in 10 mL of CH_2Cl_2, and 0.020 mL (0.23 mmol) of HSO_3CF_3 was added with stirring. The solution turned purple/red, and after 10 min the solvent was removed by vacuum. The resulting oil was extracted with 25 mL of pentane and filtered. Removal of the solvent left a gummy, black/purple solid which, despite many attempts, could not be crystallized. IR: ν_{CO} (pentane) 2108 (w), 2051 (vs), 2035 (s), 2013 (m), 1853 (m) cm^{-1}. Anal. Calcd for $C_{11}HO_{10}Fe_2Co$: C, 28.47; H, 0.22. Found: C, 27.73; H, 0.64. Mass spectrum: parent ion at m/e 464 with successive loss of 10 carbonyl units down to the Fe_2CoCH^+ core. The isotope pattern for the parent ion was analyzed by using MASPAN.[16] Calculated and observed intensities for the two most intense peaks associated with the parent ion and the Fe_2CoCH ion core: parent (m/e 465, 464) calcd 12.73, 72.85; obsd 13.19, 75.82; core (m/e 184, 183) calcd 69.04, 15.27; obsd 67.02, 14.01. The isotopic fit of the parent and core ions gave agreement factors of 10.9% and 8.4%, respectively.

$[PPN]_2[Fe_2Co(CO)_9(CC(O)CH_3)]$ (3a). A 0.10-g (0.10-mmol) sample of $[PPN][Fe_2Co(CO)_9(CCO)]$ was dissolved in 10 mL of Et_2O and the solution cooled to 0 °C. A 0.10-mL (0.12-mmol) sample of $LiCH_3$ (1.2 M) in Et_2O was then added, leading to the immediate formation of a black precipitate and leaving a light orange solution. The solvent was removed by filtration and the solid washed with two 10-mL portions of Et_2O before being redissolved in 10 mL of CH_2Cl_2 containing 0.060 g (0.10 mmol) of [PPN]Cl. The orange/brown solution was filtered, concentrated to 2 mL, and layered with 4 mL of Et_2O. After 4 h, the product crystallized as black needles that were isolated by filtration and washed with 10 mL of MeOH followed by two 10-mL washings with Et_2O. Yield: 0.10 g (64%). IR: ν_{CO} (CH_2Cl_2) 2000 (w), 1944 (s, sh), 1930 (vs), 1868 (m) cm^{-1}; ν_{CO} (Nujol) 2002 (w), 1926 (vs), 1902 (s), 1860 (m), 1565 (w) cm^{-1}. Anal. Calcd for $C_{84}H_{63}N_2O_{10}P_4Fe_2Co$: C, 64.88; H, 4.05; N, 1.80; Fe, 7.18; Co, 3.79. Found: C, 64.01; H, 4.01; N, 1.80; Fe, 7.63; Co, 3.75.

$[PPN]_2[Fe_2Co(CO)_9(CCO_2CH_3)]$ (3b). A 0.10-g (0.10-mmol) sample of $[PPN][Fe_2Co(CO)_9(CCO)]$, 0.10 g (1.9 mmol) of NaO-

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Table I. Crystal Data for [PPN][$Fe_2Co(CO)_9(CCO)$]

formula	$Fe_2CoP_2C_{47}O_{10}H_{30}N$
mol wt	1001.1
a, Å	27.231 (7)
b, Å	17.670 (6)
c, Å	23.072 (10)
β, deg	126.54 (3)
V, Å^3	8919.9 (70)
$F(000)$	4064
μ(Mo K_α), cm^{-1}	11.36
λ(Mo K_α), Å	0.71069
D_{calcd}, g cm^{-3}	1.491
Z	8
measd reflctn	5872
obsd reflctn	2761
R/R_w, %	8.6/12.6
space group	$C2/c$
largest residual in diff Fourier, e/Å^3	0.4

Table II. Positional Parameters for the Cluster Anion of [PPN][$Fe_2Co(CO)_9(CCO)$][a]

atom	x	y	z
Co1	0.2859 (1)	0.0334 (2)	0.7834 (2)
Fe1	0.2830 (1)	0.1776 (2)	0.7725 (2)
Fe2	0.2114 (1)	0.0953 (2)	0.6611 (2)
O1	0.3283 (8)	0.0974 (10)	0.6451 (8)
C1	0.3011 (12)	0.0991 (11)	0.7304 (13)
C2	0.3118 (11)	0.0972 (11)	0.6831 (11)
O11	0.1082 (7)	0.0960 (8)	0.6710 (8)
O12	0.1752 (6)	−0.0413 (8)	0.5734 (7)
O13	0.1659 (7)	0.2104 (8)	0.5481 (8)
O21	0.2020 (8)	0.2068 (9)	0.8128 (9)
O22	0.3969 (8)	0.2097 (9)	0.9130 (9)
O23	0.2664 (8)	0.3177 (8)	0.6931 (9)
O31	0.2915 (8)	−0.1164 (8)	0.7328 (8)
O32	0.1992 (7)	0.0020 (8)	0.8176 (8)
O33	0.3984 (9)	0.0260 (10)	0.9259 (9)
C11	0.1503 (10)	0.0951 (11)	0.6681 (12)
C12	0.1894 (10)	0.0135 (11)	0.6064 (12)
C13	0.1833 (10)	0.1651 (11)	0.5929 (11)
C21	0.2339 (9)	0.1959 (11)	0.7968 (13)
C22	0.3536 (10)	0.1980 (13)	0.8577 (13)
C23	0.2714 (11)	0.2620 (13)	0.7223 (11)
C31	0.2881 (10)	−0.0582 (11)	0.7520 (12)
C32	0.2357 (12)	0.0162 (10)	0.8053 (13)
C33	0.3516 (13)	0.0275 (15)	0.8683 (12)

[a] Estimated standard deviations given in parentheses.

CH_3, and 0.070 g (0.13 mmol) of [PPN]Cl were dissolved in 10 mL of MeOH to give an orange/brown solution. After 2 h, the solvent was removed by vacuum and the resulting solid was dissolved in 10 mL of CH_2Cl_2. The solution was then filtered, concentrated to 2 mL, and layered with 4 mL of Et_2O. After 4 h, the product crystallized as black plates which were isolated by filtration and washed with 10 mL of MeOH followed by two 10-mL washings with Et_2O. Yield: 0.12 g (76%). IR: ν_{CO} (CH_2Cl_2) 2001 (w), 1944 (s), 1836 (m) cm^{-1}; ν_{CO} (Nujol) 2003 (w), 1935 (vs), 1904 (s), 1877 (m), 1858 (m), 1634 (w) cm^{-1}. Anal. Calcd for $C_{84}H_{63}N_2O_{11}P_4Fe_2Co$: C, 64.22; H, 4.01; N, 1.78; Fe, 7.11; Co, 3.75. Found: C, 63.83; H, 4.01; N, 1.75; Fe, 7.68; Co, 3.85.

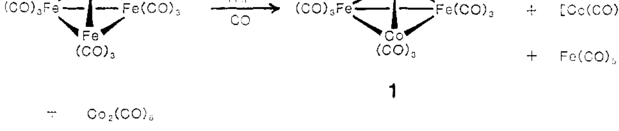
[PPN]$_2$[$Fe_2Co(CO)_9(CC(O)H)$] (3c). A 0.10-g (0.10-mmol) sample of [PPN][$Fe_2Co(CO)_9(CCO)$] was dissolved in 12 mL of THF and the solution cooled to −23 °C. A 0.15-mL (0.15-mmol) sample of $KBEt_3H$ (1.0 M) in THF was then added to the orange/brown solution. After 1 h, the solution had become red/brown. The solvent was removed by vacuum and the resulting oil dissolved in 15 mL of CH_2Cl_2 containing 0.060 g (0.10 mmol) of [PPN]Cl. The solution was filtered, concentrated to 2 mL, and layered with 6 mL of Et_2O. When the solution was left sitting overnight, an oily solid could be isolated by filtration and washed twice with 10 mL of MeOH followed by two 10-mL washings with Et_2O. No elemental analysis was performed since the compound could not be isolated in a pure state. IR: ν_{CO} (THF) 2002 (w), 1946 (s), 1888 (m) cm^{-1}; ν_{CO} (Nujol) 2002 (w) 1928 (vs), 1901 (s), 1864 (m), 1577 (w) cm^{-1}.

Low-Temperature ^1H and ^{13}C NMR Spectra of 3c. A 0.20-g (0.20-mmol) sample of ^{13}C-enriched 1 was placed in a 10-mm NMR tube under N_2 and capped with a rubber septum. The sample was dissolved in 1.8 mL of THF-d_8 and cooled to −63 °C. A 0.30-mL (0.30-mmol) sample of $KBEt_3H$ (1.0 M) in THF was then added via syringe, and the solution was allowed to sit for 8 h at −63 °C. The NMR tube was then transferred to the NMR probe that was precooled to −65 °C. The spectroscopic yield of 3c was approximately 50% based on comparison of the CC(O)H resonance with those of PPN^+ in the ^1H NMR spectrum. Strong resonances resulting from the $KBEt_3H$ and undeuteriated THF were present, but these signals were upfield of 4 ppm and did not interfere with the integration of the PPN^+ (7.5 ppm) and CC(O)H (8.9 ppm) resonances.

X-ray Crystallography of [PPN][$Fe_2Co(CO)_9(CCO)$] (1). Crystals of 1 suitable for X-ray analysis were grown by slow diffusion of pentane into an Et_2O solution containing the cluster. A purple/black, rhombohedral crystal of 1, in a stream of N_2 gas and at ambient temperature, was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$). A total of 5872 data points ($\pm h,k,l$) were collected by using a variable scan rate, a θ–2θ scan mode, and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum value of 45°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were measured after every 97 reflections, and since the intensities of these reflections showed less than 8% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects. After removal of redundant and space group forbidden data, 2761 reflections were considered observed [$I > 3.0\sigma(I)$]. The structure was solved by direct methods using MULTAN 80.[17] The MULTAN solution showed three peaks of high intensity of which the highest was assigned as Co. Refinement of scale factors and positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence.[18] The refinement did not permit differentiation between Co and Fe. The metal–metal distances show only minor differences [range 2.540 (4)–2.557 (4) Å] and metal–carbonyl carbon distances are all within experimental error. Metal–CCO distances were not informative. Thus, the crystallographic refinement does not establish the specific positioning of the metals; indeed the possibilities of disorder cannot be discounted. The final cycle of refinement (function minimized, $\sum(|F_o| - |F_c|)^2$) led to a final agreement factor, R = 8.6% ($R = \sum||F_o| - |F_c||/\sum|F_o| \times 100$). Anomalous dispersion corrections were made for Fe and Co. Scattering factors were taken from Cromer and Mann.[19] Unit weights were used throughout. An absorption correction was not considered necessary and, therefore, not applied since the crystal was block-shaped (0.3 × 0.2 × 0.2 mm) and the linear absorption coefficient was quite small (μ = 11.36 cm^{-1}). Positional parameters are listed in Table II.

Results and Discussion

Synthesis and Properties of [PPN][$Fe_2Co(CO)_9(CCO)$]. A metal substitution reaction occurs between [PPN]$_2$[$Fe_3(CO)_9(CCO)$] and $Co_2(CO)_8$ in THF under a CO atmosphere (eq 3) to produce the anionic, mixed-metal



1

(3)

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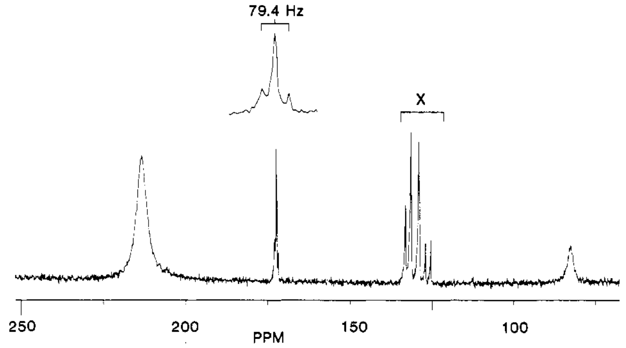

Figure 1. ^{13}C NMR spectrum of [PPN][$Fe_2Co(CO)_9(CCO)$] (1) at -90 °C in CD_2Cl_2. Peaks marked with an X are due to the PPN cation.

ketenylidene [PPN][$Fe_2Co(CO)_9(CCO)$] (1), which can be isolated with a yield of 84%. The side products [PPN][$Co(CO)_4$] and $Fe(CO)_5$ are produced in equimolar amounts. The yield of 1 is considerably lower (35%) when the reaction is run under N_2. This result agrees with the requirement of gaseous CO in eq 3. Good yields of 1 are also obtained by using acetone, CH_3CN, and CH_2Cl_2 as solvents. Metal substitution reactions have been studied in several laboratories and are now fairly well-known among clusters with a capping ligand, especially those containing Fe and Co.[20,21] Reaction 3 goes to completion upon mixing at room temperature, whereas other reactions of this type require heating and longer reaction times.[20]

The IR and NMR spectra of 1 are analogous to those of $[Fe_3(CO)_9(CCO)]^{2-}$, with the expected shifts to higher ν_{CO} in the IR and upfield shifts in the ^{13}C NMR spectra relative to $[Fe_3(CO)_9(CCO)]^{2-}$. The ^{13}C NMR spectrum of 1 at -90 °C (Figure 1; Table IV) contains only three resonances originating from the cluster. The terminal carbonyl groups are highly fluxional and exhibit only one signal at 213.5 ppm. This signal is broadened by partial coupling to the quadrupolar ^{59}Co nucleus. The resonance due to the α-carbon atom of the ketenylidene ligand is found at 82.8 ppm and is also broadened by Co. At room temperature, this signal broadens into the base line. However, the β-carbon is one atom removed from Co and displays a relatively sharp resonance at 172.5 ppm, so that ^{13}C coupling satellites can be easily seen. Selective irradiation of the broad resonance at 82.8 ppm results in the collapse of the satellites at 172.5 ppm, confirming the C–C coupling.[22] The assignments of the α- and β-carbon atoms were also confirmed by obtaining a ^{13}C NMR spectrum of 1 which had been selectively enriched at all carbon atoms of the cluster except for the α-carbon atom. Selectively ^{13}C-enriched 1 could easily be obtained by stirring 1 under a ^{13}CO atmosphere in CH_2Cl_2 for 4 days. The fact that the β-carbon atom is enriched indicates that it participates in CO exchange with the terminal carbonyl groups, but this exchange is slower than the NMR time scale. This same phenomenon is seen for $[Fe_3(CO)_9(CCO)]^{2-}$.[8]

X-ray Structure of [PPN][$Fe_2Co(CO)_9(CCO)$] (1). The compound [PPN][$Fe_2Co(CO)_9(CCO)$] (1) (PPN = bis(triphenylphosphine)nitrogen(1+) cation) crystallizes in a centrosymmetric unit cell.[13,23] This assignment was confirmed by the satisfactory refinement of the structure in *C*2/*c*. The structure of the cluster anion shows a ketenylidene ligand bound to the face of a metal triangle with each metal atom of the triangle further bonded to three terminal carbonyl groups (Figure 2). Bond distances and angles for the anionic cluster are listed in Table III. The

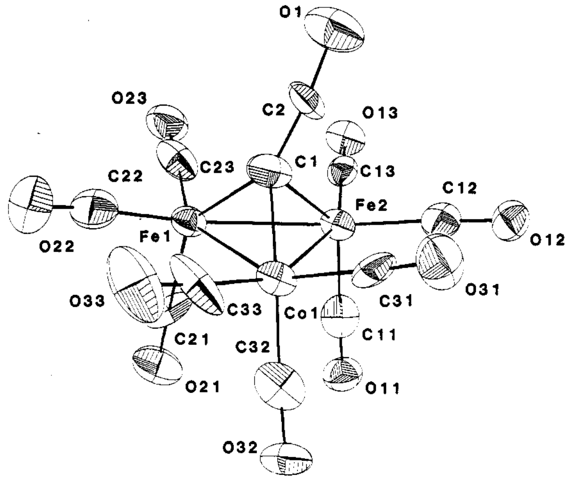

Figure 2. An ORTEP drawing of the cluster anion in [PPN]-[$Fe_2Co(CO)_9(CCO)$] (1).

Table III. Bond Distances (Å) and Bond Angles (deg) for the Cluster Anion of [PPN][$Fe_2Co(CO)_9(CCO)$]

Fe1–Fe2	2.557 (4)	Fe2–C11	1.76 (3)
Fe1–Co1	2.555 (4)	Fe2–C12	1.77 (2)
Fe2–Co1	2.540 (4)	Fe2–C13	1.77 (2)
Fe1–C1	1.92 (3)	Co1–C31	1.79 (2)
Fe2–C1	1.97 (2)	Co1–C32	1.74 (4)
Co1–C1	1.90 (3)	Co1–C33	1.69 (2)
C1–C2	1.29 (5)	C11–O11	1.18 (4)
C2–O1	1.20 (4)	C12–O12	1.15 (2)
Fe1–C2	2.97 (3)	C13–O13	1.16 (2)
Fe2–C2	2.46 (3)	C21–O21	1.14 (4)
Co1–C2	3.01 (3)	C22–O22	1.12 (2)
Fe1–C21	1.76 (3)	C23–O23	1.15 (3)
Fe1–C22	1.78 (1)	C31–O31	1.14 (3)
Fe1–C23	1.79 (2)	C32–O32	1.21 (4)
		C33–O33	1.17 (2)
Fe2–Fe1–Co1	59.6 (1)	Fe2–Co1–C33	154.8 (11)
Fe1–Co1–Fe2	60.2 (1)	C31–Co1–C32	100.4 (12)
Fe1–Fe2–Co1	60.2 (1)	C31–Co1–C33	98.4 (11)
Fe1–C1–Fe2	82 (1)	C32–Co1–C33	97.2 (15)
Fe2–C1–Co1	82 (1)	Fe1–C21–O21	179 (2)
Co1–C1–Fe1	84 (2)	Fe1–C22–O22	177 (3)
C1–C2–O1	173 (2)	Fe1–C23–O23	177 (2)
C2–C1–Fe1	134.8 (17)	Fe2–C11–O11	178 (2)
C2–C1–Fe2	96.2 (15)	Fe2–C12–O12	177 (2)
C2–C1–Co1	140.8 (16)	Fe2–C13–O13	179 (2)
Fe2–Fe1–C21	98.9 (6)	Co1–C31–O31	178 (2)
Fe2–Fe1–C22	153.8 (8)	Co1–C32–O32	177 (2)
Fe2–Fe1–C23	95.1 (6)	Co1–C33–O33	176 (3)
Fe2–Fe1–C1	49.6 (7)	C1–Co1–C32	143.2 (10)
Co1–Fe1–C1	47.7 (9)	C1–Co1–C33	107.2 (14)
C1–Fe1–C21	140.0 (11)		
C1–Fe1–C22	105.7 (12)	C1–Fe2–C11	135.0 (13)
C1–Fe1–C23	105.9 (13)	C1–Fe2–C12	109.6 (10)
Co1–Fe1–C21	97.8 (7)	C1–Fe2–C13	111.6 (11)
Co1–Fe1–C22	98.2 (7)	Co1–Fe2–C11	94.0 (7)
Co1–Fe1–C23	150.9 (9)	Co1–Fe2–C12	98.5 (6)
C21–Fe1–C22	97.8 (13)	Co1–Fe2–C13	157.2 (6)
C21–Fe1–C23	100.2 (13)	C11–Fe2–C12	97.2 (12)
C22–Fe1–C23	101.7 (10)	C11–Fe2–C13	98.7 (11)
Fe1–Fe2–C11	96.1 (7)	C12–Fe2–C13	98.6 (10)
Fe1–Fe2–C12	155.6 (6)	Fe1–Co1–C31	150.2 (10)
Fe1–Fe2–C13	99.5 (6)	Fe1–Co1–C32	102.6 (7)
Fe1–Fe2–C1	48.0 (8)	Fe1–Co1–C33	97.2 (9)
Co1–Fe2–C1	47.8 (9)	Fe2–Co1–C1	50.1 (7)
Fe2–Co1–C31	97.9 (6)	Fe1–Co1–C1	48.2 (8)
Fe2–Co1–C32	98.7 (7)	C1–Co1–C31	102.7 (13)

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(22) This work was performed at the University of Illinois NSF Regional Instrumentation Facility.

(23) The X-ray crystal structure of 1 was previously determined incorrectly in the space group $P\bar{1}$. In this redetermination of the structure reported here, we found that the correct space group is *C*2/*c*.

metal-metal distances [range 2.540 (4)–2.557 (4) Å] are consistent with those observed in other iron-containing trimeric clusters: $[Fe_3(CO)_9(CCO)]^{2-}$, average 2.569 (4) Å, and $[Fe_3(CO)_{10}(CH)]^-$, average 2.548 (4) Å.[8] In 1 the ketenylidene ligand is bound asymmetrically to the face of the trimetallic cluster with some degree of tilt of the CCO ligand toward one of the metal atoms [Co1–C1, 1.90 (3) Å; Fe1–C1, 1.92 (3) Å; Fe2–C1, 1.97 (3) Å; metal–C1–C2 angles Co1, 140.8 (16)°, Fe1, 134.8 (17)°, Fe2, 96.2 (15)°] and shorter nonbonded interactions of the *β*-carbon atom with one metal atom of the cluster [Fe2–C2, 2.46 (3) Å; Fe1–C2, 2.97 (3) Å; Co1–C2, 3.01 (3) Å]. The CCO ligand is slightly nonlinear (173 (2)°), and the least-squares line through the ligand (std. dev. 0.04) shows it to be tilted 29.8° from the perpendicular. Although the Fe and Co atoms could not be distinguished in the refinement of the X-ray data, a Mössbauer spectroscopy study of 1 showed that the cluster contains two distinct Fe sites, which agrees with the formulation of 1 in which the CCO ligand tilts toward one of the Fe atoms.[24]

The arrangement of ligands around the trinuclear metal framework of 1 resembles that of its dinegatively charged parent cluster, $[Fe_3(CO)_9(CCO)]^{2-}$, which also has a ketenylidene ligand asymmetrically bonded to the face of a metal triangle (33° angle between the least-squares line through the CCO ligand and the perpendicular to the metal plane). The CCO angle is 172.8 (23)° for $[Fe_3(CO)_9(CCO)]^{2-}$, which is similar to that of 1. By contrast, the ketenylidene ligand of the uncharged cluster $H_2Os_3(CO)_9(CCO)$ is perpendicular to the plane of the three Os atoms with approximately equal Os–C distances, and the CCO is linear.[6] Comparison of the corresponding C–C and C–O bond lengths for these three structures reveals them to be the same within error. The only other mixed-metal ketenylidene that has been structurally characterized is $[MnCo_2(CO)_9(CCO)]^-$, which, like 1, also has a 1– charge.[25] The structure of the $MnCo_2$ cluster shows the CCO to be almost linear (177.7 (3)°) and tilted toward a Co atom by 14°.

Reactions with Electrophiles. Upon treatment of 1 with acid, the *α*-carbon atom is protonated and the carbonyl fragment of the CCO ligand migrates to the metal framework, giving $Fe_2Co(CO)_{10}(CH)$ (2) (eq 4). The resulting CO disposition includes a bridging CO across the Fe–Fe bond. Similar reactivity has been observed for anionic ketenylidene clusters with first-row transition metals. Both $[Fe_3(CO)_9(CCO)]^{2-}$ and $[Co_2Mn(CO)_9(CCO)]^-$ form methylidyne clusters upon protonation.[8,25] The ^1H NMR spectrum of 2 (Table IV) shows a low-field proton signal typical of μ_3-methylidynes.[8,20,25] The ^{13}C NMR spectrum at −90 °C displays a downfield doublet (J_{CH} = 170.5 Hz) which becomes a singlet upon selective ^1H decoupling of the methylidyne resonance, thus confirming the attachment of the hydrogen. The terminal CO region shows two signals of relative intensity 2:1. This spectrum agrees with C_s symmetry for 2 if it is assumed that on the NMR time scale, the terminal carbonyl groups on each metal undergo a fast turnstile rotation but no metal-to-metal CO exchange occurs. The IR spectrum of 2 contains a bridging CO band at 1853 cm⁻¹ and closely resembles that of an analogous mixed-metal ethylidyne cluster, $Fe_2Co(CO)_{10}(CCH_3)$, which is proposed to have the same type of structure.[26]

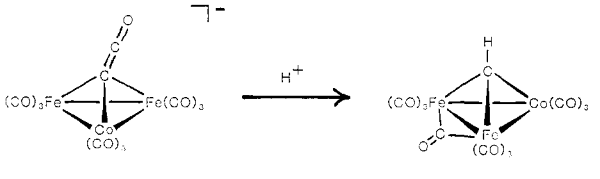

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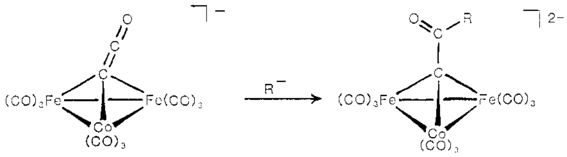
Table IV. NMR Spectroscopic Data

compound	^1H NMR, ppm	^{13}C NMR, ppm
$[Fe_2Co(CO)_9(CCO)]^-$ (**1**)[a]		213.5, 172.5 (C*C*O), 82.8 (*C*CO); J_{CC} = 79.4 Hz
$Fe_2Co(CO)_{10}(CH)$ (**2**)[a]	12.72	269.8 (CH), 250.3 (μ-CO), 207.3 $[Fe(CO)_3]$, 200.0 $[Co(CO)_3]$; J_{CH} = 170.5 Hz
$[Fe_2Co(CO)_9(CC(O)CH_3)]^{2-}$ (**3a**)[a]	2.30	255.4 (*C*C(O)CH_3), 218.3, 214.7 (C*C*(O)CH_3), 30.8 (CH_3); J_{CC} = 44.0 Hz
$[Fe_2Co(CO)_9(CCO_2CH_3)]^{2-}$ (**3b**)[a]	3.52	235.0 (*C*CO_2CH_3), 218.7, 186.8 (C*C*O_2CH_3), 50.3 (OCH_3); J_{CC} = 66.0 Hz
$[Fe_2Co(CO)_9(CC(O)H)]^{2-}$ (**3c**)[b]	8.93	243.2 (*C*C(O)H), 217.6, 164.7 (C*C*(O)H); J_{CC} = 51.4 Hz, J_{CH} = 174.4 Hz

[a] CD_2Cl_2, −90 °C. [b] THF-d_8, −65 °C.

Unlike dinegatively charged ketenylidene clusters, 1 does not react with electrophiles other than H⁺. Exposure of solutions of 1 to tenfold excesses of strong carbocation reagents such as $CH_3OSO_2CF_3$, $(CH_3)_3OBF_4$, CH_3I, and $CH_3C(O)Cl$ for periods of up to 2 days gives no signs of reaction. The inertness of 1 toward methylation at the *α*-carbon atom is somewhat surprising given that $[Fe_3(CO)_{10}(CCH_3)]^-$ can be prepared by methylation of $[Fe_3(CO)_9(CCO)]^{2-}$ and that $[Fe_2Co(CO)_{10}(CCH_3)$ is a known compound.[8,26] Cluster 1 does not react further with $Co_2(CO)_8$ nor has it shown the propensity to undergo cluster-building reactions that are characteristic of $[Fe_3(CO)_9(CCO)]^{2-}$.[12,13] Metal-containing electrophiles such as $Fe_2(CO)_9$, $[Mn(CO)_3(CH_3CN)_3][PF_6]$, and $Cr(CO)_3(CH_3CN)_3$ do not react with 1 while $[Rh(CO)_2Cl]_2$ reacts to give an insoluble, uncharacterizable red solid. The preceding experiments thus demonstrate that 1 is considerably less nucleophilic than the dinegatively charged ketenylidenes.

Reactions with Nucleophiles. Nucleophilic reagents such as $LiCH_3$, $NaOCH_3$, and $KBEt_3H$ attack 1 at the *β*-carbon atom of the ketenylidene ligand to afford the dinegatively charged products $[Fe_2Co(CO)_9(CC(O)R)]^{2-}$ (R = CH_3, OCH_3, H; **3a–c**) (eq 5). This reactivity pattern



(5)

3a–c (a, CH_3
b, OCH_3
c, H)

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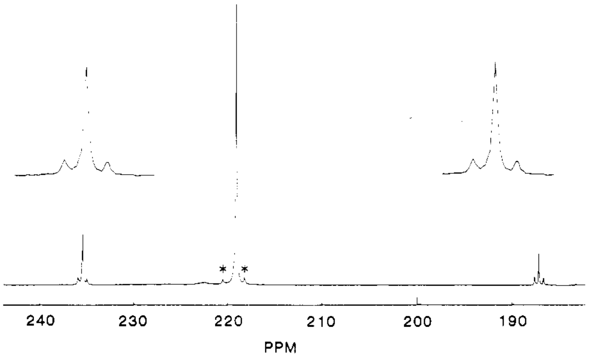

Figure 3. ^{13}C NMR spectrum of $[PPN]_2[Fe_2Co(CO)_9(CCO_2CH_3)]$ (**3b**) at −90 °C in CD_2Cl_2. Peaks due to minor impurities are denoted by an asterisk.

is well-known for cationic and neutral ketenylidene clusters, but the reactions shown in eq 5 demonstrate that the CCO ligand can maintain electrophilicity in an anionic cluster as well. Compounds **3a–c** are the anionic analogues of the large number of $Co_3(CO)_9(CC(O)R)$ neutral clusters that can be synthesized by the reaction of $[Co_3(CO)_9(CCO)]^+$ with nucleophiles.[2,3]

Compounds **3a** and **3b** can both be crystallized and isolated in yields of 64% and 76%, respectively. The NMR spectra of these clusters are in full agreement with the proposed structures (Table IV). The ^1H NMR spectra of **3a** and **3b** contain singlets at 2.30 and 3.52 ppm, respectively, which are in the expected regions for methyl ketones and esters. These values also compare favorably with their counterparts in the $Co_3(CO)_9(CC(O)R)$ series of compounds.[27] Resonances in the ^{13}C NMR spectra of **3a** and **3b** (Figure 3) at −90 °C are sharp in comparison to **1**. Apparently, the effect of quadrupolar line broadening by Co is diminished for these dinegatively charged clusters. In both **3a** and **3b**, the terminal carbonyl groups are highly fluxional as indicated by the observation of a single ^{13}C resonance in the terminal CO region down to the lowest temperature investigated at −90 °C. The resonances due to the α-carbon atoms of the CC(O)R ligands are shifted substantially downfield relative to **1**, 255.4 ppm for **3a** and 235.0 ppm for **3b**, while the β-carbon atoms give signals at 214.7 and 186.8 ppm. The location of the α- and β-carbon resonances are reasonable for clusters of this sort,[28] and the assignments are further verified by spectra of **3a** and **3b** obtained from selectively ^{13}C-enriched $[Fe_2Co(C^*O)_9(CC^*O)]^-$. The decrease in the C–C coupling between the α- and β-carbon atoms (44.0 Hz for **3a** and 66.0 Hz for **3b**) relative to **1** suggests a lowering of the C_α–C_β bond order. The IR spectra of **3a** and **3b** are of interest because of their low stretching frequencies for the μ_3-CC(O)R carbonyl groups (1565 and 1634 cm^{-1}, respectively). Presumably these ν_{CO} values are low compared to those of the $Co_3(CO)_9(CC(O)R)$ analogues[27] because the negative charge is delocalized onto the capping ligand. These low CO stretching frequencies suggest that the oxygen atom of the μ_3-CC(O)R ligands might be very basic.

Compound **3c** could not be isolated in pure form but gave IR and ^1H and ^{13}C NMR spectroscopies analogous to those of **3a** and **3b**. The spectroscopic yield for **3c** is in the range of 50%. The ^1H NMR spectrum of **3c** shows a downfield resonance at 8.93 ppm, which is similar to that reported for $Co_3(CO)_9(CC(O)H)$.[3] The ^{13}C NMR spectrum of **3c** at −65 °C exhibits a resonance at 243.2 ppm showing C–C coupling satellites of 51.4 Hz, which is assigned to the α-carbon, and a doublet at 164.7 ppm assigned to the β-carbon atom ($^1J_{CH}$ = 174.4 Hz). Upon ^1H decoupling, the β-carbon doublet becomes a pseudotriplet, with C–C coupling satellites of 51.4 Hz which were not resolved in the ^1H-coupled ^{13}C NMR spectrum.

A few attempts were made to utilize **1** in cluster-building reactions with metal-containing nucleophiles. The IR spectra of products obtained by the interaction of **1** with $Na[Fe(\eta\text{-}C_5H_5)(CO)_2]$ or $Na_2[Fe(CO)_4]$ in THF showed predominantly starting material and lower frequency ν_{CO} absorptions due to some new species. These compounds could only be isolated in small quantities as black, impure solids so these reactions were not pursued further.

Although **1** reacts with nucleophiles to give products that are analogous to those obtained from cationic and neutral ketenylidenes, its reactions are much less facile, as might be expected for an anionic electrophile. Alkylation reactions of $[Co_3(CO)_9(CCO)]^+$ with organolithium reagents lead mostly to decomposition, and the milder reagents such as organozinc halides and organotin compounds are required for smooth alkylation.[2] In contrast, the reaction of **1** with $LiCH_3$ proceeds rapidly and smoothly to give **3a**. Likewise, $[Co_3(CO)_9(CCO)]^+$,[2] $[H_3M_3(CO)_9(CCO)]^+$ (M = Os, Ru),[5-7] and $H_2Os_3(CO)_9(CCO)$[5] react with CH_3OH to give neutral organometallic esters while **1** is stable in CH_3OH and requires a large excess of $NaOCH_3$ in CH_3OH to achieve optimum yields of $[Fe_2Co(CO)_9(CCO_2CH_3)]^{2-}$.

On the basis of its negative charge and structural similarity to $[Fe_3(CO)_9(CCO)]^{2-}$, one would predict that **1** might show nucleophilic behavior and react analogously to $[Fe_3(CO)_9(CCO)]^{2-}$. However, the results presented here along with those previously reported for cationic and neutral ketenylidene clusters suggest that there is a strong preference for the CCO ligand to undergo attack by nucleophiles at the β-carbon site. Such reactivity is consistent with the behavior shown by organic ketenes toward nucleophilic attack.[29] The reaction of **1** with H^+ demonstrates that the cluster maintains some nucleophilicity at the α-carbon atom, but this nucleophilicity is clearly very weak. The small size and high charge density of the proton are probably important factors in its reaction with **1**. In the case of dinegatively charged ketenylidene clusters, the increased negative charge appears to be sufficient to make the CCO ligand a more effective nucleophile. Extended Hückel molecular orbital calculations were performed on **1** and $[Fe_3(CO)_9(CCO)]^{2-}$ to determine if the charge distribution along the CCO ligand of these clusters might rationalize their differences in reactivity.[30] However, the calculations reveal only slight differences in the net charges of the α- and β-carbon atoms between **1** (C_α, −0.334; C_β, +0.933) and $[Fe_3(CO)_9(CCO)]^{2-}$ (C_α, −0.330; C_β, +0.916). Firm conclusions cannot be drawn from these results, and thus the calculated charge distribution on the ketenylidene ligand cannot explain the different reactivity of these two clusters.

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Registry No. 1, 88657-64-1; 1 (^{13}C labeled), 112682-04-9; 2,

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88657-66-3; **3a**, 112682-00-5; **3b**, 112682-02-7; **3c**, 112712-03-5; $[PPn]_2[Fe_3(CO)_9(CCO)]$, 87710-96-1; $Co_2(CO)_8$, 15226-74-1; Fe, 7439-89-6; Co, 7440-48-4.

Supplementary Material Available: Listings of positional parameters and bond angles and distances for the PPN cation of 1 and a complete listing of anisotropic thermal parameters for 1 and a numbering scheme for PPN (8 pages); a listing of observed and calculated structure factors for 1 (44 pages). Ordering information is given on any current masthead page.

Activation of C–H and C–C Bonds of 4-Octyne in the Gas Phase by Bare Transition-Metal Ions, M^+ (M = Cr, Mn, Fe)[†]

Christian Schulze, Thomas Weiske, and Helmut Schwarz*

Institut für Organische Chemie, Technische Universität Berlin, D-1000 Berlin 12, F.R.G.

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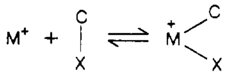
Organometallic complexes of 4-octyne with bare Cr^+ were generated in the gas phase and the unimolecular dissociations studied by means of tandem mass spectrometry. A detailed comparison is made with the previously reported M^+/4-octyne systems (M = Mn, Fe). All transition-metal ions (presumably in excited states) were found to activate C–H and C–C bonds, though the nature and amounts of neutrals eliminated differ for the various metal ions. While Fe^+ nearly exclusively generates C_2H_4, both Cr^+ and Mn^+ form, in addition to C_2H_4, molecular hydrogen, and methane. Moreover, Mn^+ causes loss of C_3H_6. The study of labeled isotopomers provides a relatively detailed insight into the mechanistic variants of the various activation steps, and it is demonstrated that all metal ions behave distinctly, with the chemistry of the Fe^+/4-octyne complex as the least complicated one. An unprecedented 1,6-elimination process across the C–C triple bond is reported for the Mn^+-induced demethanation of 4-octyne. This mechanism is not operative for the analogous elimination of CH_4 from the Cr^+/4-octyne complex; the latter reaction follows a straightforward 1,2-elimination mode, which is associated with some remarkable kinetic isotope effects. Distinct mechanisms are also operative for the metal ion induced dehydrogenation of 4-octyne, which for M = Mn^+ follows a formal 1,2-elimination (involving the terminal methyl and the adjacent CH_2 group). In contrast, for M = Cr^+ this process contributes to only a minor extent (ca. 22%); the major part (ca. 78%) of H_2 originates from C(2)/C(3). The kinetic isotope effects associated with $H_{2-x}D_x$ (x = 0, 1) losses are practically identical for the two routes (i.e. C(1)/C(2) versus C(2)/C(3)); this may indicate that the reductive elimination step is rate-determining. The analysis further suggests that Cr^+-induced reductive elimination of hydrogen proceeds through a symmetric transition structure with respect to the metal–hydrogen bonds to be cleaved. Ethylene loss from M^+/4-octyne, while being similar for M = Cr^+ or Fe^+, must have some metal-specific features that are also reflected in the isotope effects associated with the elimination of C_2H_4.

Introduction

Gas-phase experiments with bare transition-metal ions offer an unique possibility to probe, in the absence of any solvation and ion-pairing effects, the inherent properties of reactive organometallic species and to evaluate the potential role these remarkable transients may well play in the initial stages of the activation of C–H and C–C bonds. This topic is, not surprisingly, of fundamental interest in catalysis and has attracted considerable attention in the last decade.[1,2] While many transition-metal ions M^+ readily undergo oxidative insertion (eq 1) in C–X bonds (X = hydrogen, carbon, halogen, nitrogen, oxygen, etc.[1]), some metals like Mn^+ and Cr^+ show a distinctly lower reactivity toward these substrates.[3,4]



$$M^+ + \overset{C}{\underset{X}{|}} \rightleftharpoons \overset{+}{M}\langle{}^{C}_{X} \qquad (1)$$

The decreased reactivity[5] has been explained by the particular ground-state electronic configurations of Cr^+ ($3d^5$) and Mn^+ ($3d^54s^1$), which are not favorable for the formation of M–X bonds. It has been suggested that in those cases in which reactions of Cr^+ and Mn^+ with organic substrates are observed, the insertion processes may be

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[†] Dedicated to Professor Emanuel Vogel, Köln, on the occasion of the 60th birthday.

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