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Substituent Heteroatom Effects on the Chemistry of Triiron Alkyne Clusters Derived from $[Fe_3(CO)_9CCER]^-$: E = O versus E = S

Michael P. Jensen and Duward F. Shriver*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113

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The sulfonic acetylides $[PPN][Fe_3(CO)_9CCOSO_2R]$ (R = p-C_6H_4Me, CF_3) [PPN = bis(triphenylphosphine)nitrogen(1+) cation], prepared from the action of sulfonic anhydrides on the iron ketenylidene $[PPN]_2[Fe_3(CO)_9(CCO)]$, react with thiolate salts to afford the thiolate-substituted acetylide compounds $[PPN][Fe_3(CO)_9CCSR]$ (Ia-d) (R = a, Me; b, Et; c, n-Pr; d, i-Pr). The formation of alkyne ligands from Ia,b was accomplished by addition of PMe_3 to give 48-electron phosphonium alkyne compounds, II, or by protonation to yield 46-electron complexes of terminal alkynes, III. The alkynes undergo further isomerization; the phosphonium alkyne loses thiolate, forming a neutral phosphonium acetylide, and the terminal alkynes rearrange, yielding vinylidene ligands. Both of these reactions are completely different from those of the ethoxide analogues previously prepared from $[PPN][Fe_3(CO)_9CCOEt]$. The divergent behaviors and reactivity between the oxygen and sulfur heteroatom systems are attributed to diminished π donation from sulfur which prevents the rapid alkyne cleavage observed for the 46-electron alkyne $Fe_3(CO)_9HC{\equiv}COEt$. Additionally, the weaker C—SR bond is thought to be responsible for the thiolate displacement from the 48-electron compound $[Fe_3(CO)_9Me_3PC{\equiv}CSMe]$.

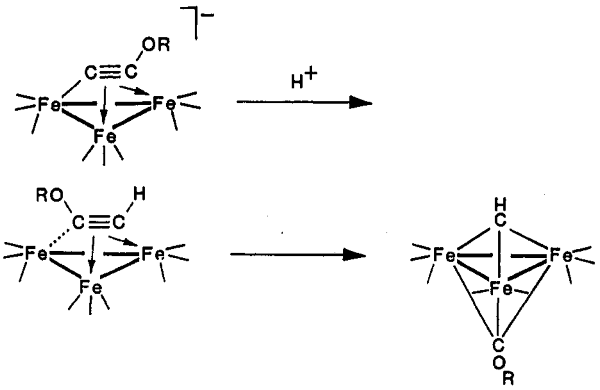
Introduction

Spontaneous bond cleavage is perhaps the most interesting reaction of alkyne ligands coordinated to transition-metal cluster compounds.[1] Reported cases of scission of normally strong C≡C bonds to yield alkylidyne ligands continue to increase in number.[2-6]

Detailed mechanistic understanding of alkyne scission continues to develop, especially for trimetallic compounds;[4,5] several undergo well-defined intramolecular cleavage processes, which are often reversible.[5-7] A key feature of proposed C≡C dissociation mechanisms for trinuclear clusters containing alkyne ligands is induction of electronic unsaturation, usually by loss of a spectator ligand, which results in a shift of alkyne coordination to an edge-bridging position. Subsequent cleavage acts to restore the electron count of the cluster by converting the four-electron donor alkyne into two three-electron alkylidyne ligands. Despite this electron-counting formalism, the driving force for scission is proposed to be an increased negative charge transfer from the electron-rich metals to the resulting carbyne fragments.[8] The cleavage transformation therefore is essentially an oxidative addition of the C≡C bond induced by coordinatively unsaturated, low-valent metal ensembles.

Not all alkyne-containing cluster compounds undergo facile C≡C cleavage. For example, a number of triiron compounds $Fe_3(CO)_9RC{\equiv}CR'$ are stable despite electronic unsaturation;[9] indicated by their 46 valence electron count which falls short of the 48 electrons considered normal for trimetallic clusters. Therefore, electronic unsaturation appears necessary, but not sufficient, to prompt alkyne dissociation.

Alkyne cleavage on other triiron nonacarbonyl compounds nonetheless is extremely facile. For example, the alkyne complex $Fe_3(CO)_9HCCOEt$ rapidly converts to the bis(alkylidyne) cluster $Fe_3(CO)_9(\mu_3\text{-}CH)(\mu_3\text{-}COEt)$ at −70 °C, eq 1.[10] The alkyne can be observed spectroscopically by NMR only when prepared by in situ low-temperature protonation of the acetylide compound $[Fe_3(CO)_9CCOEt]^-$. The very similar compound $Fe_3(CO)_{10}MeCCOEt$ loses a carbonyl ligand and undergoes C–C cleavage even in the solid state;[6] this scission can be reversed by CO replacement[6] or by chemical reduction.[7]



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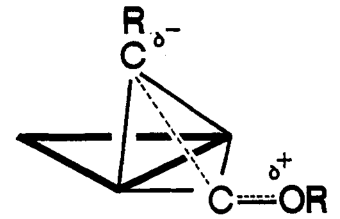

Figure 1. Stabilization of the alkyne cleavage transition state by π donation from the oxygen heteroatom proposed to account for the facile scission of $Fe_3(CO)_9RC{\equiv}COR'$ compounds.

These two instances of facile C$\equiv$C cleavage contrast with the stability of other triiron alkyne clusters and indicate that the alkoxide substituent favors C$\equiv$C cleavage. The influence of π donation from the nitrogen lone pair of aminoalkynes (i.e., $R_2N{-}C{\equiv}C{-}R'$) on resonance structures and coordination has been discussed.[3,11] Significantly, these alkynes also form cleavage products on di- and trinuclear frameworks.[3] The alkoxy substituent therefore likely acts to stabilize a heterolytic transition state for cleavage on the postulated edge-bridging alkyne (Figure 1). This proposal was advanced previously to explain substituent effects on cleavage of $(CpCo)_3RC{\equiv}CR'$ compounds.[4d]

In the present report we examine the role of π-donor substituents in the chemistry of triiron nonacarbonyl clusters by observing the effects of substituting a sulfur heteroatom for oxygen. The thiolate acetylide compounds $[PPN][Fe_3(CO)_9CCSR]$ (R = Me, Et, *n*-Pr, *i*-Pr) were prepared; the chemistry of derivative alkyne clusters was then studied for comparison with C$\equiv$C cleavage and other reactivity previously investigated for $[PPN][Fe_3(CO)_9CCOEt]$.[10,12]

Experimental Section

All manipulations were performed under an atmosphere of purified nitrogen using standard Schlenk techniques or in a Vacuum Atmospheres drybox.[13] Solvents were distilled under nitrogen from appropriate drying agents (CH_2Cl_2 from P_2O_5; Et_2O and THF from sodium/benzophenone ketyl; *i*-PrOH from Mg/I_2; pentane from 4-Å sieves after predrying over H_2SO_4). CD_2Cl_2 (99.6% D, Aldrich) was freeze–pump–thaw degassed and distilled under vacuum from P_2O_5.

Solution IR spectra were recorded on a Bomem MB series benchtop FTIR spectrometer at 2-cm^{-1} resolution using 0.1-mm-path-length cells equipped with CaF_2 windows. Spectra of solids were recorded from Fluorolube mulls between KBr plates. NMR spectra were recorded on a Varian XLA-400 spectrometer operating at 399.942 and 100.577 MHz, respectively, for ^1H and ^{13}C nuclei. Spectra were referenced internally to solvent with positive chemical shifts lying downfield from TMS. ^{13}C NMR spectra were recorded using samples enriched to 30% ^{13}C at all cluster carbonyl and acetylene carbons.[10] Resonances of the PPN^+ counterion were observed in the normal range for the PPN salts but are not reported here. Liquid secondary ion mass spectra were obtained by Dr. D. L. Hung of the Northwestern University Analytical Services Laboratory on a VG70/250SE spectrometer. Elemental analyses were performed by Analytische Laboratorien Elbach (Engleskirchen, Germany) or Oneida Research Services (Whitesboro, NY).

$[PPN]_2[Fe_3(CO)_9(CCO)]$ and its ^{13}C enriched isotopomers were prepared by literature syntheses.[10] Triflic acid (Aldrich) was freeze–pump–thaw degassed and vacuum-distilled prior to use. Triflic anhydride (Aldrich) was freeze–pump–thaw degassed and distilled from P_2O_5. (PPN)Cl (Alfa) and *p*-toluenesulfonic anhydride (Aldrich) were used as received. Some sodium salts of alkane- and benzenethiolates were used as received (Aldrich). Others were prepared by titration of sodium naphthalide in THF with the corresponding thiol (Aldrich), recovered by filtration, washed with Et_2O, and dried under vacuum.

Caution! All preparations involving thiols (RSH) and thiolate (RS^-) salts were performed in an efficient fume hood to avoid exposure to toxic and foul-smelling thiol vapors.

Synthesis of $[PPN][Fe_3(CO)_9CCOTs]$. A 30-mL Schlenk flask was charged with solid samples of $[PPN]_2[Fe_3(CO)_9(CCO)]$ (400 mg, 0.26 mmol) and *p*-toluenesulfonic anhydride (85 mg, 0.26 mmol) in a drybox. The solids were dissolved in 20 mL of CH_2Cl_2 and stirred for 30 min. The solution was evaporated to dryness in vacuo. The red-brown solids were extracted into THF, and the resulting acetylide solution was used in situ with 1 equiv of (PPN)(OTs) also present. IR, ν(C$\equiv$O) (THF, cm^{-1}): 2050 (m), 1994 (vs), 1987 (vs), 1967 (s), 1944 (m).

Synthesis of $[PPN][Fe_3(CO)_9CCOTf]$. A 425-mg (0.28-mmol) sample of $[PPN]_2[Fe_3(CO)_9(CCO)]$ was dissolved in 25 mL of CH_2Cl_2 and cooled in a dry ice/alcohol slush bath. A solution of 200 μL of triflic anhydride in 10.0 mL of CH_2Cl_2 was prepared, and 2.36 mL (0.27 mmol) of this dilute anhydride solution was slowly added to the cooled cluster solution. No reaction was evident until the bath warmed above −60 °C, when the solution slowly turned brown. The bath was allowed to slowly rise to 10 °C and was then removed. The solution was evaporated to dryness. The solids were extracted with THF to afford a red-brown solution of the acetylide complex and off-white solid (PPN)(OTf). No effort was made to remove the triflate salt prior to in situ utilization of the cluster. IR, ν(C$\equiv$O): (CH_2Cl_2, cm^{-1}) 2053 (w), 2039 (m, br), 2000 (vs, br), 1974 (m); (THF, cm^{-1}) 2056 (w), 2040 (vw), 2028 (vw), 2001 (vs), 1993 (vs), 1974 (s), 1951 (m).

Synthesis of $[PPN][Fe_3(CO)_9CCSMe]$ (Ia). Samples of solid $[PPN]_2[Fe_3(CO)_9(CCO)]$ (1.000 g, 0.65 mmol) and *p*-toluenesulfonic anhydride (210 mg, 0.65 mmol) were dissolved in 20 mL of CH_2Cl_2 and stirred for 45 min. The solution was then evaporated to dryness. The solids were extracted with 35 mL of THF, and the resulting slurry was transferred onto Na(MeS) (50 mg, 0.71 mmol). The slurry was stirred for 72 h. Then Et_2O (20 mL) was added. The suspension was filtered through a fine porosity frit. The filtrate was evaporated to dryness. The oils were redissolved in 20 mL of CH_2Cl_2 and 20 mL of *i*-PrOH. Slow concentration of the solution under vacuum precipitated red-brown microcrystals of Ia. The product was recovered by filtration and washed with aliquots of *i*-PrOH and pentane prior to drying under vacuum. Yield: 0.450 g (0.44 mmol, 67%). Anal. Calc (found) for $Fe_3P_2SO_9C_{49}H_{33}N$: Fe, 16.28 (16.05); S, 3.11 (3.13); C, 56.01 (55.90); H, 3.23 (3.20). IR, ν(C$\equiv$O) (THF, cm^{-1}): 2043 (m), 1987 (vs), 1979 (vs), 1961 (s), 1934 (m). ^1H NMR (CD_2Cl_2, ppm): δ 2.57 (s, 3 H). ^{13}C NMR (CD_2Cl_2, ppm): δ 216.7 (9 CO), 196.8 (C_α, $^1J_{C-C}$ = 37 Hz), 103.4 (C_β, q, $^3J_{C-H}$ = 6 Hz), 21.3 (SCH_3). MS (mass): *m/z* 491 (parent), successive loss of seven CO.

Synthesis of $[PPN][Fe_3(CO)_9CCSEt]$ (Ib). The synthesis described for Ia was used to prepare Ib from $[PPN]_2[Fe_3(CO)_9(CCO)]$ (600 mg, 0.39 mmol), *p*-toluenesulfonic anhydride (125 mg, 0.38 mmol), and Na(EtS) (40 mg, 0.48 mmol). The product was obtained as red crystals from slow concentration of a solution of the cluster in 4 mL of CH_2Cl_2 and 4 mL of *i*-PrOH. Yield: 280 mg (0.27 mmol, 69%). Anal. Calc (found) for $Fe_3P_2SO_9C_{49}H_{35}N$: S, 3.07 (2.86); C, 56.41 (55.28); H, 3.38 (3.29); N, 1.34 (0.86). IR: ν(C$\equiv$O) (THF, cm^{-1}) 2043 (m), 1987 (vs), 1979 (vs), 1960 (s), 1935 (m); ν(C$\equiv$C) (mull, cm^{-1}) 1618 (vw). ^1H NMR (CD_2Cl_2, ppm): δ 3.03 (q, 2 H, J_{H-H} = 8.0 Hz), 1.46 (t, 3 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ppm): δ 216.7 (9 CO), 195.3 (C_α, $^1J_{C-C}$ = 38 Hz), 99.9 (C_β). MS (mass): *m/z* 505 (parent), successive loss of four CO, 445 (parent − SEt + 1).

Synthesis of $[PPN][Fe_3(CO)_9CCS\text{-}n\text{-}Pr]$ (Ic). The general procedure described above for Ia was used to prepare Ic from $[PPN]_2[Fe_3(CO)_9(CCO)]$ (200 mg, 0.13 mmol), *p*-toluenesulfonic anhydride (45 mg, 0.14 mmol), and Na(*n*-PrS) (50 mg, 0.51 mmol). Red-brown crystals were grown by evaporation of a cluster solution in 4 mL of CH_2Cl_2 and 5 mL of *i*-PrOH. Yield: 60 mg (0.06 mmol, 44%). IR, ν(C$\equiv$O) (THF, cm^{-1}): 2043 (m), 1987 (vs), 1960 (s),

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1935 (m). ^{1}H NMR (CD_2Cl_2, ppm): δ 2.97 (t, 2 H, J_{H-H} = 7.6 Hz), 1.85 (virtual sextet, 2 H, J_{H-H} = 7.2, 7.6 Hz), 1.04 (t, 3 H, J_{H-H} = 7.2 Hz).

Synthesis of [PPN][$Fe_3(CO)_9$CCS-*i*-Pr] (Id). The procedure described for the synthesis of Ia was modified slightly for the preparation of Id. The THF slurry of (PPN)(OTs) and [PPN][$Fe_3(CO)_9$CCOTs], prepared from $[PPN]_2[Fe_3(CO)_9(CCO)]$ (600 mg, 0.39 mmol) and *p*-toluenesulfonic anhydride (125 mg, 0.38 mmol) was added to Na(*i*-PrS) (40 mg, 0.41 mmol) and stirred 10 days. Subsequent isolation of Id was accomplished as for Ib. Yield: 205 mg (0.19 mmol, 50%). IR, ν(C≡O) (THF, cm^{-1}): 2043 (m), 1987 (vs), 1978 (vs), 1960 (s), 1935 (m). ^{1}H NMR (CD_2Cl_2, ppm): δ 3.37 (m, 5 lines resolved, 1 H, J_{H-H} = 6.4 Hz), 1.47 (d, 6 H). ^{13}C NMR (CD_2Cl_2, ppm): δ 216.8 (9 CO), 194.3 (C_α, $^1J_{C-C}$ = 37 Hz), 97.8 (C_β).

Reaction of [PPN][$Fe_3(CO)_9$CCSMe] (Ia) with PMe_3. A sample of [PPN][$Fe_3(CO)_9$CCSMe] (Ia) (45 mg, 0.04 mmol) was dissolved in 5 mL of CH_2Cl_2 and stirred at room temperature. PMe_3 (10 μL, 0.10 mmol) was added by syringe. The red-brown solution immediately turned bright red. Infrared spectra revealed the formation of a phosphine adduct II, formulated as $[Fe_3(CO)_9Me_3PCCSMe]^-$. This product was observed by IR spectroscopy to convert to $Fe_3(CO)_9CCPMe_3$ with a half-life in excess of 1 h at room temperature. No attempt was made to recover and quantify the compounds or displaced thiolate salts. IR spectral data for the two cluster compounds are discussed below.

Reaction of [PPN][$Fe_3(CO)_9$CCSEt] (Ib) with Triflic Acid. In a typical experiment, 85 mg (82 μmol) of [PPN][$Fe_3(CO)_9$CCSEt] (Ib), enriched to ca. 30% ^{13}C at all cluster carbonyl and acetylide carbons, was loaded into a 30-mL Schlenk flask prepared for filtration with a medium-porosity frit and 30-mL receiving flask. The sample was dissolved in 5 mL of CH_2Cl_2. Addition of 7.2 μL (81 μmol) of triflic acid immediately turned the red-brown solution green. After 5 min, the solvent was rapidly removed under vacuum, and the oils were extracted with 5 mL of Et_2O. The extracts were filtered from solid off-white (PPN)(OTf). The filtrate was quickly evaporated to dryness. The oils were dissolved in 850 μL of CD_2Cl_2 and transferred by syringe into a purged 5-mm NMR tube capped with a rubber septum. Spectroscopic investigation of the solution followed immediately. In situ protonation of acetylide in an NMR sample tube produced concordant but inferior spectroscopic results due to suspension of fine particles of precipitated (PPN)(OTf) throughout the sample.

Complete room-temperature NMR data for ^{13}C-enriched derivatives (a) $Fe_3(CO)_9$HCCSEt (alkyne), (b) $Fe_3(CO)_9$CC(H)SEt (vinylidene), and (c) (EtS)$Fe_3(CO)_9$CCH (acetylide decomposition product) in CD_2Cl_2 solution: (a) ^{1}H NMR (ppm) δ 6.38 (1 H, br, t?, $^1J_{CH}$ = 198 Hz), 2.75–2.68 (2 H, d of q?), 1.47 (3 H, t); (a) ^{13}C NMR (ppm) δ 271.4 (C_α), 212.0 (CO, br), 209.8 (CO), 75.5 (C_β, $^1J_{CH}$ = 197 Hz); (b) ^{1}H NMR (ppm) δ 6.88 (1 H, $^1J_{CH} \simeq$ 183 Hz), 3.10 (2 H, q), 1.53 (3 H, t); (b) ^{13}C NMR (ppm) δ 274.4 (C_α), 210.8 (9 CO, br), 101.4 (C_β, $^1J_{CH}$ = 175 Hz); (c) ^{1}H NMR (ppm) δ 4.94 (1 H, $^1J_{CH}$ = 232 Hz), 2.20 (br), 1.15 (br); (c) ^{13}C NMR (ppm) δ 217 (3 CO ?, v br), 213.4 (1 CO), 212.7 (2 CO), 210.9 (1 CO), 210.2 (1 CO), 200.5 (1 CO), 163.1 (C_α, $^2J_{CH}$ = 16 Hz), 38.5 (C_β, $^1J_{CH}$ = 231 Hz).

Results and Discussion

Synthesis of Sulfonic Acetylides, [PPN][$Fe_3(CO)_9CCOSO_2R$]. Tosylate and triflate acetylide compounds were prepared from reaction of sulfonic anhydrides and iron ketenylidene. The compounds were synthesized and characterized in situ. IR spectra of both compounds reveal the typical ν(C≡O) pattern of triiron acetylides (Table I). These absorptions lie at higher energy than in [PPN][$Fe_3(CO)_9$CCOAc],[10] especially those of $[Fe_3(CO)_9CCOTf]^-$, which are above even $[Fe_3(CO)_9CCOC(O)CF_3]^-$.[12b] Therefore, these compounds should display synthetically useful electrophilicity. The spectrum of the triflate acetylide also contains additional weak, solvent-dependent bands at 2040 and 2028 cm^{-1}. These extra bands may originate from reversible binding of $SO_3CF_3^-$ to the highly electrophilic cluster. Unfortunately, solvents mask the $\nu(SO_3)$ absorptions that would clarify this situation. In situ ^{13}C NMR experiments confirmed the formulation of the tosylate acetylide (Table II), but precipitation of triflate salts prevented investigation of $[Fe_3(CO)_9CCOTf]^-$.

Table I. Carbonyl Stretching Frequencies[a] for Cluster Anions $[Fe_3(CO)_9CCR]^-$

R	ν(C≡O), cm^{-1}				
Me[b]	2044	1982	1976	1955	1930
SMe, Ia	2043	1987	1979	1961	1934
OEt	2044	1986	1976	1958	1931
OAc	2048	1990	1983	1963	1939
OTs	2050	1994	1987	1967	1944
$OC(O)CF_3$	2054	1997	1991	1970	1951
OTf	2056	2001	1993	1974	1951

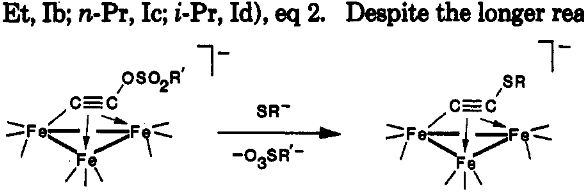
[a] THF solutions except as noted. [b] CH_2Cl_2 solution, ref 7a.

Table II. ^{13}C NMR Data[a] for Acetylide Complexes $[Fe_3(CO)_9CCR]^{n-}$

R	CO	C_α	C_β	$^1J_{CC}$
OEt[b]	217.1	160.7	148.5	42
OAc[b]	216.1	172.9	132.2	39
$OC(O)CF_3$[c]	215.8 (6), 215.5 (3)	178.6	138.2	38
SMe, Ia	216.7	196.8	103.4	37
OTs	215.6	173.6	138.2	35
$PMePh_2$[d]	214.0 (6), 213.3 (3)	226.5	68.2	30
PPh_3[e,f]	213.8 (6), 213.3 (3)	229.5	67.2	28
$AsPh_3$[f]	214.0 (6), 213.4 (3)	229.6	81.6	26
$Fe(CO)_4$[g]	219.9 (9), 219.0 (4)	201.6	114.8	23
$Fe(CO)_2Cp$[f,h]	218.8 (9), 217.0 (2)	206.3	99.0	22

[a] CD_2Cl_2 solutions, 20 °C. δ in ppm and $^1J_{CC}$ in Hz. [b] Reference 10. [c] Jensen, M. P.; Shriver, D. F. Unpublished results. [d] Reference 12a, $^1J_{C_\beta-P}$ = 108 Hz, $^2J_{C_\alpha-P}$ = 4 Hz. [e] $^1J_{C_\beta-P}$ = 104 Hz, $^2J_{C_\alpha-P}$ = 4 Hz. [f] Reference 12b. [g] Jensen M. P.; Phillips, D. A.; Sabat, M.; Shriver, D. F. *Organometallics* **1992**, *11*, 1859. [h] Plus Cp carbons at 87.2 ppm.

Synthesis and Characterization of Acetylides [PPN][$Fe_3(CO)_9$CCSR] (Ia–d). The triiron ketenylidene compound $[PPN]_2[Fe_3(CO)_9(CCO)]$ reacts with bulky electrophiles to produce acetylide clusters [PPN][$Fe_3(CO)_9$CCOR], which in turn react with nucleophiles to give a variety of acetylides $[Fe_3(CO)_9CCR']^{n-}$. The nucleophile is incorporated as the new substituent.[12] Because thiolates attack the acyl carbons of $[Fe_3(CO)_9CCOAc]^-$ and $[Fe_3(CO)_9CCOC(O)CF_3]^-$,[12b] the sulfonic acetylides $[Fe_3(CO)_9CCOSO_2R]^-$ (R = *p*-C_6H_4Me, CF_3) were employed in the syntheses of [PPN][$Fe_3(CO)_9$CCSR] (R = Me, Ia; Et, Ib; *n*-Pr, Ic; *i*-Pr, Id), eq 2. Despite the longer reaction times of the tosylate acetylide, this intermediate was generally utilized in the preparations, rather than $[Fe_3(CO)_9CCOTf]^-$, to facilitate separation of product from displaced sulfonate salts.



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Reactions of the tosylate acetylide with unhindered primary thiolate salts in THF at room temperature require 3 days to reach completion. Addition of crown ether failed to noticeably accelerate the reaction, which suggests that steric congestion about the acetylide ligand from the metal framework has a more pronounced influence on the rate than thiolate solubility or ion pairing. Accordingly, reaction of secondary thiolate Na(*i*-PrS) requires 10 days to reach completion at ambient temperature. The electronically deactivated nucleophile SPh^- fails to react with $[Fe_3(CO)_9CCOTs]^-$ at all.

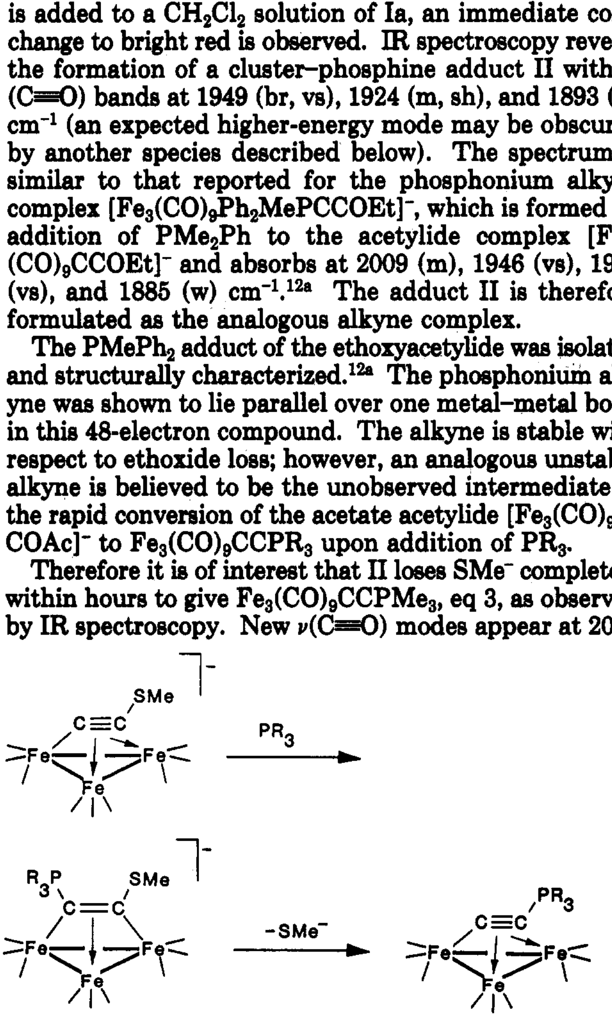
Thiolates react with triflate acetylide $[Fe_3(CO)_9CCOTf]^-$ at a considerably more rapid rate, generally requiring less than 2 h for complete displacement to occur, even for PhS^- and $t\text{-}BuS^-$. The product acetylides bearing these last two thiolates were identified by IR spectroscopy but were not isolated for further study.

The four thiolate acetylides Ia–d have very similar spectroscopic features. The ^{13}C NMR resonances and C_α—C_β spin couplings compare well with those of other triiron nonacarbonyl acetylide compounds (Table II). Predictable ^1H NMR spectra were observed for each different added thiolate. The IR spectrum of each cluster contains virtually identical $\nu(C{\equiv}O)$ bands, with each displaying the five-line pattern characteristic of $[Fe_3(CO)_9CCR]^-$ acetylide complexes; the spectra of $[Fe_3(CO)_9CCOEt]^-$ and $[Fe_3(CO)_9CCSEt]^-$ are indistinguishable in this region. The methane and ethane thiolate clusters Ia,b were additionally characterized by mass spectrometry and elemental analysis.

Reaction of Ia with PMe_3. When an excess of PMe_3 is added to a CH_2Cl_2 solution of Ia, an immediate color change to bright red is observed. IR spectroscopy reveals the formation of a cluster–phosphine adduct II with $\nu(C{\equiv}O)$ bands at 1949 (br, vs), 1924 (m, sh), and 1893 (w) cm^{-1} (an expected higher-energy mode may be obscured by another species described below). The spectrum is similar to that reported for the phosphonium alkyne complex $[Fe_3(CO)_9Ph_2MePCCOEt]^-$, which is formed by addition of PMe_2Ph to the acetylide complex $[Fe_3(CO)_9CCOEt]^-$ and absorbs at 2009 (m), 1946 (vs), 1935 (vs), and 1885 (w) cm^{-1}.[12a] The adduct II is therefore formulated as the analogous alkyne complex.

The $PMePh_2$ adduct of the ethoxyacetylide was isolated and structurally characterized.[12a] The phosphonium alkyne was shown to lie parallel over one metal–metal bond in this 48-electron compound. The alkyne is stable with respect to ethoxide loss; however, an analogous unstable alkyne is believed to be the unobserved intermediate in the rapid conversion of the acetate acetylide $[Fe_3(CO)_9CCOAc]^-$ to $Fe_3(CO)_9CCPR_3$ upon addition of PR_3.

Therefore it is of interest that II loses SMe^- completely within hours to give $Fe_3(CO)_9CCPMe_3$, eq 3, as observed by IR spectroscopy. New $\nu(C{\equiv}O)$ modes appear at 2064 (w), 2008 (vs), 1999 (vs), and 1987 (s) cm^{-1}; these are comparable to absorptions of other $Fe_3(CO)_9CCPR_3$ complexes.[12] For example, the spectrum of $Fe_3(CO)_9CCPMePh_2$ contains $\nu(C{\equiv}O)$ bands at 2063 (m), 2010 (vs), 2001 (vs), and 1988 (s) cm^{-1} and a $\nu(C{\equiv}C)$ mode at 1573 (w, br) cm^{-1}. The acetylide stretch of $Fe_3(CO)_9CCPMe_3$ is observed at 1575 cm^{-1} in the present work.



(3)

Notwithstanding the increased basicity of PMe_3, thiolates are better leaving groups than alkoxides, and the less polarizable C_β–SR bond is more readily broken than a C–OR linkage. Nevertheless this displacement occurs slowly, which, unlike C–OAc scission, permits direct observation of the intermediate nucleophile adduct II as it converts to product (Figure 2).

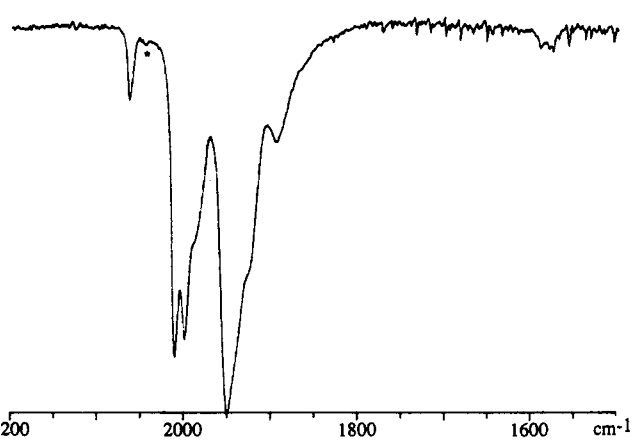


Figure 2. IR spectrum of $\nu(C{\equiv}O)$ and $\nu(C{\equiv}C)$ regions, 1 h after addition of PMe_3 to a CH_2Cl_2 solution of Ia as described in the Experimental Section, illustrating conversion of adduct II (lower energy bands) to $Fe_3(CO)_9CCPMe_3$. The peak marked * (2040 cm^{-1}, vw) is unassigned.

Protonation of Ia,b. Protonation of the alkoxyacetylide $[Fe_3(CO)_9CCOEt]^-$ produces the alkyne cluster compound $Fe_3(CO)_9HCCOEt$, which rapidly cleaves, even at low temperature, eq 1.[10] Protonation of Ia,b with triflic acid in CH_2Cl_2 also produces green-brown solutions of the alkyne clusters $Fe_3(CO)_9HCCSR$ (IIIa,b) (R = Me, IIIa; Et, IIIb). These 46-electron clusters are formally deficient by 2 electrons, and in contrast to the 48-electron phosphonium alkyne complexes, the alkyne coordinates in a perpendicular mode over one Fe–Fe bond; the correlation between electron count and alkyne bonding modes is understood.[9]

The thiolate alkynes are sufficiently stable to permit in situ spectroscopic characterization at room temperature. The IR spectra of IIIa,b are very similar in CH_2Cl_2 solutions (IIIa 2086 (vw), 2079 (w), 2033 (vs), 2021 (vs), 2013 (m) cm^{-1}; IIIb 2089 (vw), 2077 (w), 2033 (vs), 2020 (vs), 2005 (m) cm^{-1}). These spectra bear a strong resemblance to those of other $Fe_3(CO)_9RCCR'$ alkyne compounds.[9b] The ^{13}C NMR spectrum of IIIb, enriched with 30% ^{13}C on the acetylide and carbonyl carbons, was recorded at room temperature. This revealed characteristic[1,9,10] $\mu_3\text{-}\eta^2$ ($\perp$) alkyne ligand resonances at 271.4 and 75.5 ppm. The signals were spin–spin coupled, $^1J_{C-C} = 35$ Hz, and the upfield resonance was split into a doublet by the added proton, $^1J_{C-H} = 197$ Hz. These data indicate that formation of a H—C≡C—SEt moiety has occurred, and the thiolate is attached to the carbon directly over the metal triangle. The structural isomer with the alkyne reversed was not observed for IIIb or for $Fe_3(CO)_9HCCOEt$.[10] Other NMR data conform with the alkyne formulation. The ligand resonances for $Fe_3(CO)_9HCCSMe$ (IIIa) occur at 271.1 and 77.9 ppm, with $^1J_{C-H} = 198$ Hz.

The thiolate alkynes are unstable however, and within a few hours the green-brown alkyne solutions turned red and new $\nu(C{\equiv}O)$ IR bands appeared; those of IIIb are replaced with 2084 (vw), 2052 (vs), 2028 (vs), and 2010 (m) cm^{-1}. A new set of resonances also appeared in the ^{13}C NMR spectra. For IIIb, new ligand signals appeared at 274.4 and 101.4 ppm at the expense of the alkyne resonances (Figure 3). The new peaks were still coupled however, $^1J_{C-C} = 43$ Hz, clearly demonstrating that C≡C cleavage had not occurred. No alkylidyne carbon resonances were observed downfield beyond 400 ppm. The upfield resonance appeared as a widely separated doublet

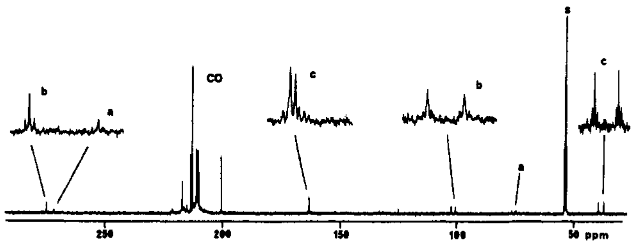


Figure 3. Proton-coupled ^{13}C NMR spectrum of protonated Ib, which contains ligand signals of (a) alkyne, (b) vinylidene, and (c) acetylide decomposition products. The peak marked s is the CD_2Cl_2 solvent resonance.

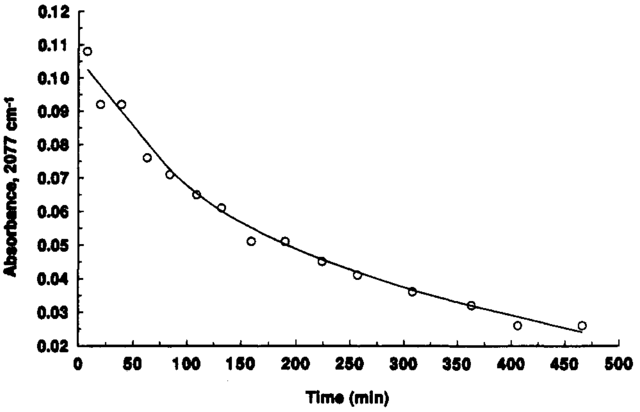
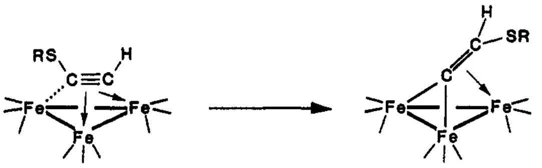


Figure 4. Plot of the IR absorption at 2077 cm^{-1} [$Fe_3(CO)_9HCCSEt$ concentration] versus time for a 7 mM CH_2Cl_2 cluster solution at room temperature.

($^1J_{C-M}$ = 175 Hz) of triplets. Apparently, hydrogen atom migration has occurred to produce a vinylidene ligand C=C(H)SEt, eq 4. Rearrangement of a coordinated terminal alkyne to a vinylidene is known to occur,[14,15] both on mononuclear complexes[16] and on a $Co_2Ru(CO)_9$ cluster.[17] The diminished $^1J_{C-H}$ and increased $^1J_{C-C}$ values are both consistent with rehybridization of the ligand from an sp–sp alkyne to an sp^2–sp^2 vinylidene.[18] The ligand carbons for the methane thiolate vinylidene resonate at 273.5 and 103.3 ppm, with $^1J_{C-H}$ = 179 Hz. The appearance of a single set of resonances in both cases indicates the ligands are highly fluxional, as observed for other trinuclear vinylidene cluster compounds.[15]



(4)

The conversion of IIIb to $Fe_3(CO)_9CC(H)SEt$ at room temperature in 7 mM CH_2Cl_2 solution was monitored as a function of time by IR spectroscopy (Figure 4). The amplitude of the relatively isolated 2077-cm^{-1} $\nu(C\equiv O)$ absorption was used to determine the concentration of the alkyne complex; however, growth of the very weak 2084 cm^{-1} vinylidene cluster $\nu(C\equiv O)$ band prevented absorbance at 2077 cm^{-1} from diminishing completely to the baseline. The data are not sufficiently precise to permit detailed kinetic analysis of the ligand conversion. Nonetheless, the observed half-life was roughly 85 min; we estimate this reaction would be a minimum of 100 times slower than cleavage of $Fe_3(CO)_9HCCOEt$ under comparable conditions, yet competitive formation of $Fe_3(CO)_9(\mu_3\text{-}CH)(\mu_3\text{-}CSR)$ products did not occur. This is attributed to relative destabilization of the cleavage transition state (Figure 1) due largely to decreased π donation from the thiolate compared to ethoxide.

Alkynes and vinylidenes are both 4-electron donors when ligated to $Fe_3(CO)_9$ frameworks. Therefore the vinylidene clusters remain electronically unsaturated with 46 valence electrons. A recent review catalogs known triiron carbonyl vinylidene compounds;[15] all have a full 48-electron count. By contrast, the 46-electron compound, $Fe_3(CO)_9CC(H)SEt$, was observed nevertheless by IR spectroscopy to be stable for days in the absence of excess acid.

A third species slowly appeared on some occasions, as judged by IR and NMR spectra. The ^{13}C NMR ligand resonances for this third product were observed at 163.1 ppm ($^2J_{C-H}$ = 16 Hz) and 38.5 ppm ($^1J_{C-H}$ = 231 Hz), with $^1J_{C-C}$ = 49 Hz. Peaks for the methane thiolate derivative lie at 163.4 and 39.3 ppm. The rather large J_{C-C} and J_{C-H} values and the chemical shifts suggest the formation of a C≡C—H acetylide ligand and a possible change in coordination from μ_3-η^2 ($\perp$). Therefore, these products are possibly the 50-electron species $(RS)Fe_3(CO)_9CCH$, which would result from an acid-catalyzed thiolate migration to the metal framework via free thiol. Such compounds are known to undergo substituent-dependent structural rearrangements,[19] so no geometry can be assigned from spectroscopic data alone. The C≡C—H acetylide species were the only cluster decomposition products to be repeatedly identified. However, deliberate addition of several equivalents of triflic acid to Ia,b and their derivatives prompts complete decomposition, which may result from loss of similarly protonated thiolate substituents.

Conclusions

The comparative ligand transformation chemistry of the acetylides $[Fe_3(CO)_9CCER]^-$ (E = O, S; R = Me, Et) is determined largely by the identity of the heteroatom, especially when π donation may affect ligand reactivity. Such π donation on an edge-bridging alkyne is proposed to account for the facile cleavage of $Fe_3(CO)_9HCCOEt$ and the lack of such reactivity in $Fe_3(CO)_9HCCSR$.

Another example of alkyne-to-vinylidene rearrangement was observed; like most alkynes, the vinylidene ligand is stable on electronically unsaturated $Fe_3(CO)_9$ clusters. However, loss of the thiolate substituent from Ia,b and their derivatives is readily induced by nucleophiles such as PMe_3, which cause thiolate displacement, and acid, which promotes loss of thiol.

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