Journal of Organometallic Chemistry, 341 (1988) 421–437
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Synthesis and reactivity of (μ-σ,π-acetylide)(μ-alkane- and μ-arene-thiolate)bis(tricarbonyliron) complexes *

Dietmar Seyferth*, **Jeffrey B. Hoke and David R. Wheeler**

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received July 7th, 1987)

Abstract

The reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with bromoacetylenes, $R^1C{\equiv}CBr$, gives complexes of type $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR^1)(\mu\text{-}RS)Fe_2(CO)_6$ in good yield. Reactions of such complexes with Et_2NH, $PhNH_2$, t-$BuNH_2$ and Ph_3P involve attack of these nucleophiles at a carbon atom of the C≡C bond of the $R^1C{\equiv}C$ ligand.

Introduction

As reported in an earlier communication [1], the easily synthesized salts of the $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anion react with allylic and propargylic halides. The products obtained no longer contain the bridging CO ligand and have instead the new organic group as a σ,π-bridging ligand. Presumably, the first step involves S_N2' attack of the $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anion at the carbon–carbon multiple bond of the organic halide with displacement of halide ion, followed by displacement of CO by the unsaturated ligand now σ-bonded to iron.

We have extended these studies to include reactions of $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anions with bromoacetylenes. The expected products would be complexes with σ,π-bridging acetylide ligands and such complexes should show interesting reactivity.

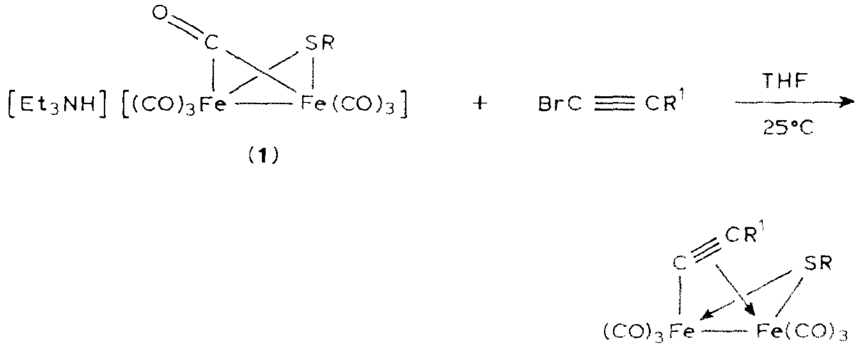
Results and discussion

Reaction of 1-bromoalkynes, $R^1C{\equiv}CBr$ (R^1 = Ph, ^tBu, $SiMe_3$), with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ (**1**) (R = ^tBu, Et, Ph), generated the expected acetylide-bridged

---

* Dedicated to Professor Colin Eaborn in recognition of his many contributions to Group IV organometallic chemistry on the occasion of his 65th birthday.

0022-328X/88/$03.50



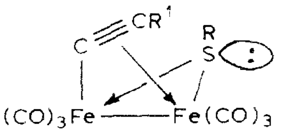
(1)

(1)

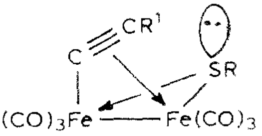
(2)

	R	R^1	Yield (%)
2a	^{t}Bu	Ph	88
2b	^{t}Bu	^{t}Bu	88
2c	^{t}Bu	SiMe	93
2d	Et	Ph	84
2e	Et	^{t}Bu	71
2f	Ph	^{t}Bu	66

diiron complexes, (μ-σ,π-C≡CR^1)(μ-RS)$Fe_2(CO)_6$ (**2**) in high yield (eq. 1). Addition of the acetylene to a brown-red THF solution of the thiolate anion typically resulted in rapid reaction with brisk gas evolution (CO), dramatic color change (cherry-red), and formation of a white precipitate ([Et_3NH][Br]). After chromatographic workup, the acetylide products were isolated as a mixture of two inseparable isomers (identified in the respective ^{1}H and ^{13}C NMR spectra). Presumably, these isomers

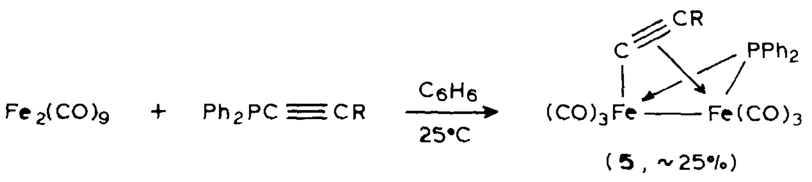


(**3** (*ax*))

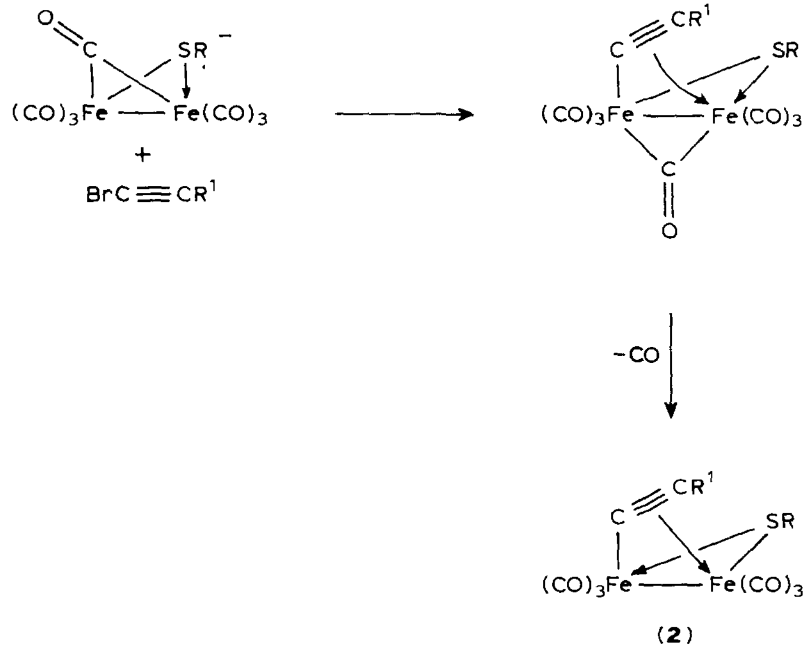


(**4** (*eq*))

arise from either an axial (*ax*) or equatorial (*eq*) orientation of the organic substituent and the lone electron pair on the bridging sulfur atom with respect to the Fe_2S plane (**3**,**4**). In general, the ^{1}H NMR spectra of these complexes show thiolate resonances of the major isomer shifted slightly downfield from those of the minor isomer. For instance, the major t-butyl resonance in complex **2a** appears at δ(H) 1.38 while the minor resonance appears at δ(H) 1.21. Prior correlations have shown that protons on axial thiolate ligands resonate at higher field than the corresponding equatorial protons [2]. Consequently, the high-field signals in our system can be attributed to the axial (minor) isomer and the low-field signals to the equatorial (major) isomer. The fact that the major isomer formed is that with the equatorial orientation seems reasonable based on steric arguments. In related work,


(2)

(R = Ph , ^tBu , ^iPr , c-C_6H_{11} , p-C_6H_4OMe , p-C_6H_4Br)


Scheme 1

Carty has reported the synthesis of analogous phosphido-bridged μ-σ,π-acetylide complexes by the reaction of diiron nonacarbonyl with phosphinoacetylenes (eq. 2) [3]. Other mono- and polynuclear acetylide species also are known [3d,e,4–11].

In line with proposed mechanisms for nucleophilic substitution of α-bromoacetylenes [12], the initial step in our system possibly results from attack of an iron-centered anion on the bromine atom of the acetylene (Scheme 1). Bridging of the terminal alkynyl moiety of the resulting heptacarbonyl intermediate with elimination of CO then produces **2**.

In the infrared spectra, only **2c** shows a band assignable to the carbon–carbon stretch of the triple bond (ν(C≡C) 1910 cm^{-1}). The appearance of this band is consistent with coordination of the alkynyl fragment resulting in a decrease of the stretching frequency from that of a free carbon–carbon triple bond (ca. 2100–2250 cm^{-1}) [13]. Similarly, Carty has observed this effect in the related phosphido-bridged complexes, (μ-σ,π-C≡CPh)(μ-Ph_2P)$Fe_2(CO)_6$ (**5a**) and (μ-σ,π-C≡CPh)(μ-

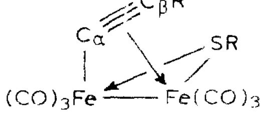
$Ph_2P)Fe_2(CO)_5PPh_3$ (**6**), where $\nu(C{\equiv}C)$ was observed at 1930 and 1900 cm^{-1}, respectively [3b]. The corresponding absorption in the other thiolate-bridged, μ-σ,π-acetylide complexes which we have prepared (**2a**,**b**,**d**–**f**) were not located due to overlap with the terminal carbonyl bands. Only the strongly electron-withdrawing trimethylsilyl group [14] in **2c** shifted $\nu(C{\equiv}C)$ far enough to lower frequency to be observed distinctly.

Although the alkynyl bond typically is not observable in **2** via IR spectroscopy, the acetylenic carbon atoms themselves are easily assigned in the corresponding ^{13}C NMR spectra (Table 1). In all cases except **2c** (where $R^1 = Me_3Si$), the acetylide carbon atoms (C_α and C_β) resonate in the range $\delta(C)$ 95–120. As expected, Carty has noted similar behavior in the series of related acetylides $(\mu$-σ,π-$C{\equiv}CR)(\mu$-$Ph_2P)Fe_2(CO)_6$ (**5**). However, whereas we cannot assign C_α and C_β unambiguously, Carty could differentiate between C_α and C_β based on differences in coupling constants to the bridged phosphorus atom. In addition, he noted that the relative position of C_α and C_β, and hence the charge distribution of the triple bond, depended on the group bonded to C_β. When R was t-butyl (charge donating), C_α was observed at higher field ($\delta(C)$ 98.4) than C_β ($\delta(C)$ 107.0). However, when R was phenyl (charge withdrawing), C_α was observed at lower field ($\delta(C)$ 110.4) than C_β ($\delta(C)$ 92.1). Whether this substituent derived reversal in polarization occurs in our acetylide system cannot be determined with certainty, although direct comparison to Carty's correlations seems reasonable. It is interesting to note that for **2c** ($R = Me_3Si$), C_α and C_β are separated by approximately 50 ppm, indicating a much larger degree of polarization than for the other acetylide complexes. This likely results from the strongly electron withdrawing nature of the trimethylsilyl group [14].

Structurally, complexes **2** are interesting in that the bridging acetylide ligand is fluxional. This is illustrated in the variable temperature ^{13}C NMR study $(\mu$-σ,π-$C{\equiv}CSiMe_3)(\mu$-$^tBuS)Fe_2(CO)_6$ (**2c**) (Fig. 1). At room temperature, the ^{13}C NMR spectrum shows two signals in the terminal carbonyl region ($\delta(C)$ 208.12, minor isomer; $\delta(C)$ 209.48, major isomer) each of which can be assigned to all the carbonyl ligands of each isomer. However, **2c** is a statically unsymmetrical molecule. The two tricarbonyliron fragments in each isomer are chemically inequivalent, and,

Table 1

^{13}C NMR data for **2**



Compound	R	R^1	$\delta(C_{\alpha/\beta})$
2a	^tBu	Ph	92.39, 95.43, 114.46, 114.95
2b	^tBu	^tBu	102.34, 109.60
2c	^tBu	$SiMe_3$	90.95, 95.27, 141.32, 143.24
2d	Et	Ph	93.09, 93.87, 113.21, 119.00
2e	Et	^tBu	101.50, 105.48, 107.72
2f	Ph	^tBu	100.85, 104.75, 108.26, 111.01

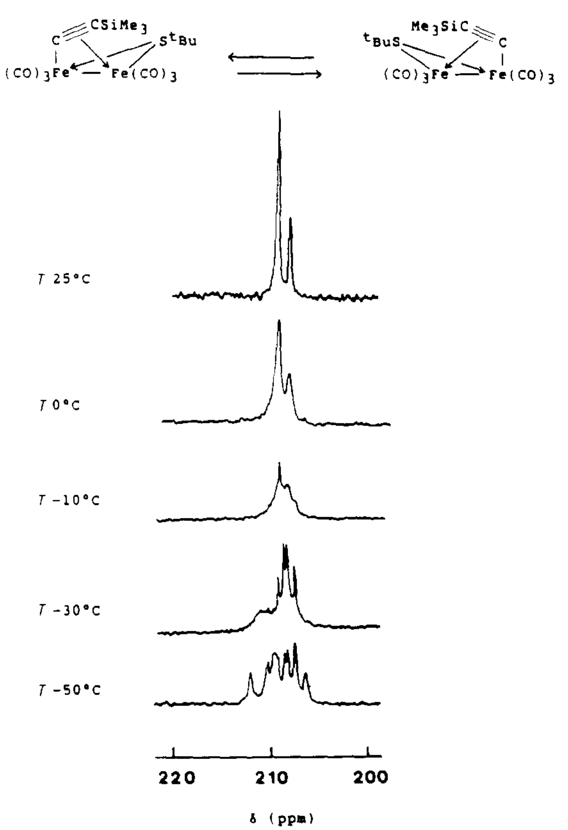
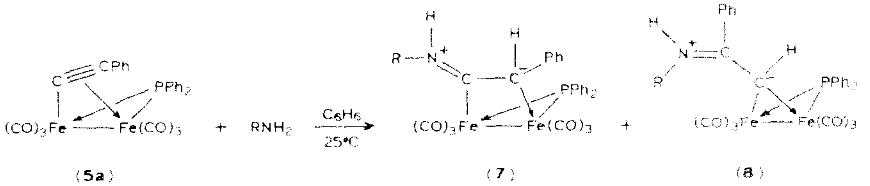


Fig. 1. Variable temperature ^{13}C NMR study for **2c**.

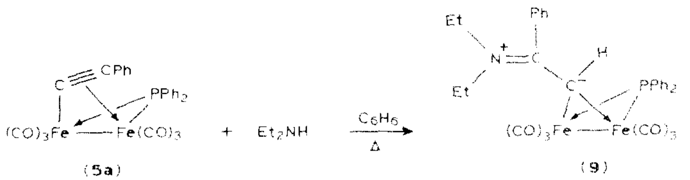
therefore, should give rise to *two* carbonyl resonances (a total of four including both isomers) assuming that the three carbonyl ligands on each metal center are locally equilibrated between themselves by rapid rotation. Consequently, some type of fluxional motion involving the bridging acetylide ligand must occur at room temperature which equilibrates the two tricarbonyliron fragments, and hence, all carbonyl ligands in each isomer on the NMR time scale. As illustrated in Fig. 1, the two inequivalent tricarbonyliron fragments of each isomer can be equilibrated by a flipping motion of the acetylide ligand over the face of the Fe_2S core. Not surprisingly, this motion can be frozen out at low temperature. As the temperature is lowered, the two singlets broaden, and then, at $-30\,^\circ C$, each is split into two distinct resonances ($\delta(C)$ 207.47 and 209.23, minor isomer; $\delta(C)$ 208.23 and 208.60, major isomer) corresponding to the now inequivalent $Fe(CO)_3$ fragments of each isomer. A broad hump has also begun to form to the left of these four peaks indicative of the slowing down of the localized carbonyl rotations on each iron center. Further cooling causes further slowing until at $-50\,^\circ C$, nine distinct CO peaks are visible in the range $\delta(C)$ 207.42–210.29. As expected, this fluxionality is reversible. Subsequent warming of the sample to room temperature results in the reappearance of the original two carbonyl signals. This type of fluxional process has been proposed for other bridged vinyl and acetylide complexes as well [15].

Because of the polarizable and relatively unhindered nature of their bridging acetylide ligands, complexes **2** appeared to be likely candicates for further reactivity studies. Carty has extensively explored the chemistry of the corresponding phosphido-bridged acetylide derivatives (μ-σ,π-C≡CR)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**5**). Included in these studies were the reactions of **5** with amines, phosphines, and phosphites. Depending on the particular amine or phosphine/phosphite utilized, new phosphido-bridged iron complexes were isolated resulting from nucleophilic attack on the triple bond with subsequent incorporation of the base into a new bridging ligand (eqs. 3–7) [3b,16]. Based on this precedent, it was of interest to see if (μ-σ,π-C≡CR^1)(μ-RS)Fe$_2$(CO)$_6$ (**2**) would react similarly.

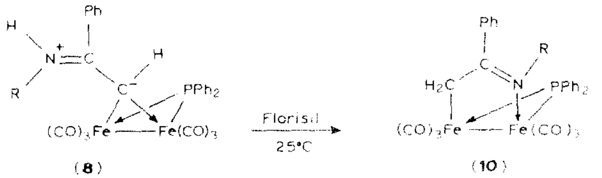


(3)

(R = Me, Et)

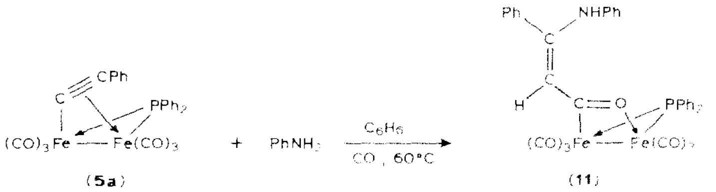


(4)

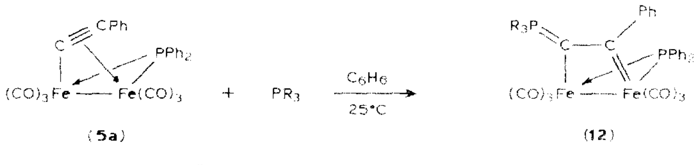


(5)

(R = Me, Et)



(6)



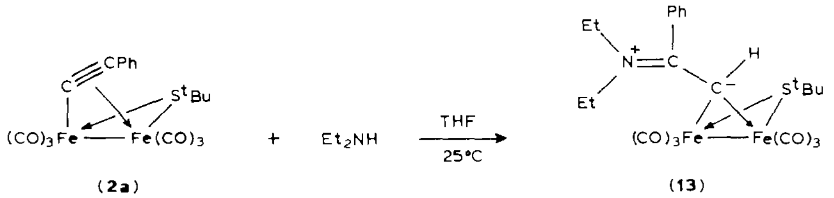
(7)

(R = OMe, OEt, O^{n}Bu, Ph)

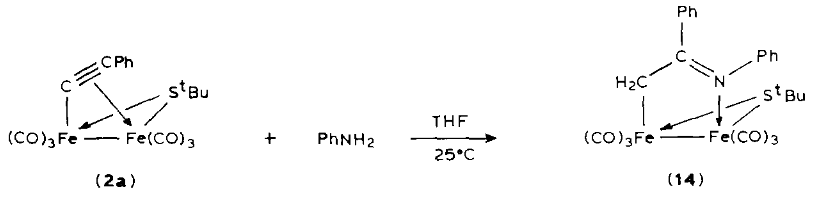
In general, reaction of $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ (**2a**) with amines was not as successful when compared to Carty's results. For many amines (e.g., bis(trimethylsilyl)amine, diphenylamine, methylamine, n-propylamine, dimethylamine, and diisopropylamine), reaction led to decomposition. However, diethylamine, aniline, and t-butylamine did react to yield isolable products analogous to those of type **9**, **10** and **11**, respectively. In the case of diethylamine, the one-carbon bridged, zwitterionic, imminium complex $(\mu\text{-}HCC(Ph){=}NEt_2)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ (**13**) was isolated in 71% yield (eq. 8). In the reaction of aniline, the iminoethyl bridged complex, $(\mu\text{-}CH_2C(Ph){=}NPh)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ (**14**) was isolated in 80% yield (eq. 9). Finally, in the case of t-butylamine, the α,β-unsaturated acyl complex, $(\mu\text{-}{}^tBuNH(Ph)C{=}CHC{=}O)(\mu\text{-}SBu^t)Fe_2(CO)_6$ (**15**) was isolated in 37% yield (eq. 10).

Surprisingly, however, the corresponding reactions of diethylamine with $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}C^tBu)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ (**2b**) or $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ (**2c**) only led to decomposition. Similarly, Carty has noted that nucleophilic addition of amines to $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}C^tBu)(\mu\text{-}Ph_2P)Fe_2(CO)_6$ (**5b**) did not occur [3e].

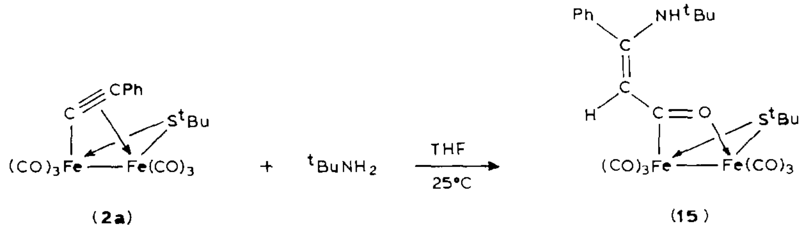
Products **13**, **14** and **15** all gave elemental carbon/hydrogen combustion analyses, infrared, mass, and ^1H and ^{13}C NMR spectra consistent with the structures given. Furthermore, these data were consistent with the limited spectroscopic evidence presented by Carty for the related phosphido-bridged complexes, **9**, **10**, and **11** (eqs. 4–6), whose structures were determined primarily by X-ray crystallography [16]. Furthermore, the spectroscopic data for the vinylacyl derivative, **15**, were in agreement with known α,β-unsaturated diiron acyl species [17]. Finally, as illustrated in



(8)



(9)

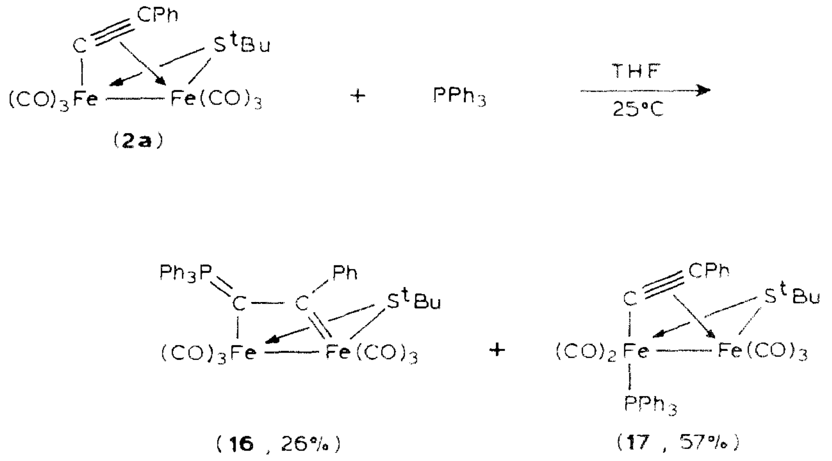


(10)

their ^1H and ^{13}C NMR spectra, **13** and **15** both were isolated as a mixture of two inseparable isomers presumably resulting from either an axial (*ax*) or equatorial (*eq*) orientation of the organic thiolate group.

Mechanistically, formation of **13**, **14** and **15** results from initial nucleophilic attack of the amine on the β-carbon atom of the acetylide ligand of **2a**. Surprisingly, this is not consistent with the assumed polarization of the triple bond. Based on the ^{13}C NMR correlations drawn by Carty and presented earlier in this discussion, the α-carbon atom of $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)(\mu\text{-}Ph_2P)Fe_2(CO)_6$ (**5a**) was found to be more "electrophilic" than the β-carbon atom [3e]. Thus, nucleophilic attack should be directed at the α-carbon atom of the acetylide ligand. In fact, Carty typically did not observe this tendency (eqs. 3–6), and we did not observe this orientation in the reactions of $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)(\mu\text{-}^tBuS)Fe_2(CO)_6$ as well. Nevertheless, β-addition of the amine to the acetylide ligand of **2a** followed by 1,3-hydrogen migration generated **13** in the case of diethylamine. In the case of t-butylamine, migration plus insertion of carbon monoxide gave **15**. Finally, in the case of aniline, 1,3-hydrogen migration of both amine protons produced the iminoethyl complex **14**.

In contrast to these findings, reaction of triphenylphosphine with $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)(\mu\text{-}^tBuS)Fe_2(CO)_6$ (**2a**) generated the phosphonium, ylide-carbene complex, $(\mu\text{-}Ph_3PC{=}CPh)(\mu\text{-}^tBuS)Fe_2(CO)_6$ (**16**) resulting from α-attack of the nucleophile (eq. 11). Based on the precedent established by Carty (eq. 7) [36,16e], characterization of **16** by the standard analytical and spectroscopic techniques was straightfor-

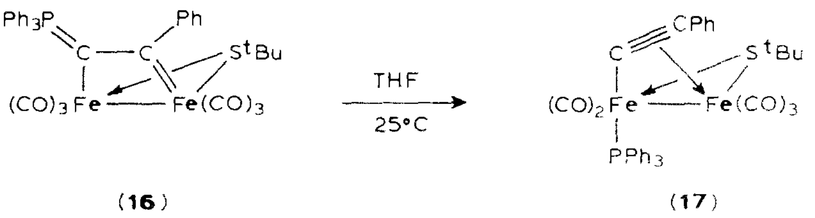


(**2a**)

(**16**, 26%)

(**17**, 57%)

(11)



(**16**)

(**17**)

(12)

ward. However, the isolation of **16** was complicated by its facile conversion to the substituted triphenylphosphine complex (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_5(PPh_3)$ (**17**). In fact, **16** decarbonylates to **17** in 88% yield at room temperature after stirring for 60 h in THF (eq. 12). Based on the crystal structure of (μ-σ,π-C≡CPh)(μ-Ph_2P)$Fe_2(CO)_5(PPh_3)$ reported by Carty and coworkers [3b], we suggest that phosphine substitution occurs at the iron atom bound to the α-carbon atom of the acetylide ligand.

Experimental

General comments

All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl and purged with nitrogen prior to use. Triethylamine, diethylamine, aniline, and t-butylamine were distilled under nitrogen from calcium hydride and purged with nitrogen prior to use. Triphenylphosphine was purchased from Aldrich and used as received. Ethyl, t-butyl, and phenyl mercaptans were purged with nitrogen and used without further purification. Phenylbromoacetylene (PhC≡CBr), trimethylsilylbromoacetylene (Me_3SiC≡CBr), and t-butylbromoacetylene (^{t}BuC≡CBr) all were prepared by a literature procedure [18] and purged with nitrogen prior to use. Triiron dodecacarbonyl ($Fe_3(CO)_{12}$) [19] was also prepared by a literature method.

The progress of all reactions was monitored by thin layer chromatography (Baker Flex – Silica Gel 1B-F). Purification by filtration chromatography in which the reaction products were dissolved in a suitable solvent and chromatographed on a bed of EM Science or Sigma 100–300 mesh silicic acid (ca. 200 ml) in a 350 ml glass fritted filter funnel was used in most cases. Further purification by medium pressure column chromatography was accomplished with a 300 × 25 mm column using Sigma 230–400 mesh silica gel. All chromatography was completed without exclusion of atmospheric moisture or oxygen. Solid products were recrystallized from deoxygenated solvents at $-20\,^\circ$C.

Solution infrared spectra (NaCl windows) were obtained using a Perkin–Elmer Model 1430 double beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a JEOL FX-90Q, a Bruker WM-250, or a Varian XL-300 NMR spectrometer operating at 90, 250, or 300 MHz respectively. Carbon-13 NMR spectra were obtained using a Bruker WH-270 NMR spectrometer operating at 67.9 MHz, phosphorus-31 NMR spectra using a JEOL FX-90Q spectrometer operating at 36.2 MHz. Electron impact mass spectra were obtained using a Finnigan-3200 mass spectrometer operating at 70 eV. Field desorption mass spectra were obtained using a Finnigan MAT-731 mass spectrometer operating in the positive ion mode. Masses were correlated using the following isotopes: ^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{28}Si, ^{31}P, ^{32}S, ^{56}Fe. Melting points were determined in air on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were perfomed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Standard in-situ preparation of [Et_3NH][(μ-CO)(μ-RS)$Fe_2(CO)_6$]

A 250 ml Schlenk flask equipped with a stir-bar and a rubber septum was charged with 1.52 g (3.02 mmol) of triiron dodecacarbonyl and degassed by three evacuation/nitrogen-backfill cycles. The flask was then charged sequentially with 30 ml of THF, 0.42 ml (3.00 mmol) of triethylamine, and 3.00 mmol of the appropriate thiol. The resulting mixture then was stirred for 20 min at room temperature during which time slow gas evolution and a gradual color change to brown-red were observed. The $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ reagent solution subsequently was used in-situ without further purification.

Synthesis of $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)(\mu\text{-}^tBuS)Fe_2(CO)_6$

To the standard $[Et_3NH][(\mu\text{-CO})(\mu\text{-}^tBuS)Fe_2(CO)_6]$ reagent solution (3.00 mmol) was added 0.37 ml (3.00 mmol) of phenylbromoacetylene by syringe at room temperature. An immediate reaction ensued with brisk gas evolution (CO), a gradual color change to cherry red, and formation of a white precipitate ($[Et_3NH][Br]$). After the reaction mixture had been stirred for 2 h at room temperature, the solvent was removed in vacuo, and the resulting cherry red tar was purified by filtration chromatography. Pentane eluted a minor pale orange band which was not collected. Further elution with pentane yielded a dark red band which gave 1.25 g (2.65 mmol, 88%) of $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)(\mu\text{-}^tBuS)Fe_2(CO)_6$ (**2a**) (a mixture of two inseparable isomers), as a slightly air-sensitive red oil.

Anal. Found: C, 46.15; H, 3.14. $C_{18}H_{14}Fe_2O_6S$ calc: C, 45.99; H, 3.00%. *IR*: Terminal carbonyl region (pentane): 2080s, 2042vs, 2018sh, 2009sh, 2002vs, 1980vw cm^{-1}. *^1H NMR* (acetone-d_6; 90 MHz): δ 1.21 (s, 9H, $SC(CH_3)_3$ minor isomer), 1.38 (s, 9H, $SC(CH_3)_3$ major isomer), 7.17–7.80 (br m, 10H, C_6H_5 both isomers). Ratio major/minor = 1.3/1.0. *^{13}C NMR* ($CDCl_3$; 67.9 MHz): δ 33.33 (q, J 127.8 Hz, $SC(CH_3)_3$ major isomer), 34.55 (q, J 128.1 Hz, $SC(CH_3)_3$ minor isomer), 47.94 (s, $SC(CH_3)_3$ minor isomer), 48.59 (s, $SC(CH_3)_3$ major isomer), 92.39 (s, acetylide C, minor isomer), 95.43 (s, acetylide C, major isomer), 114.46 (s, acetylide C, major isomer), 114.95 (s, acetylide C, minor isomer), 125.24 (s, *ipso*-C_6H_5), 127.93 (d, J 157.0 Hz, C_6H_5), 128.55 (d, J 160.6 Hz, C_6H_5), 131.80 (d, J 156.9 Hz, C_6H_5), 132.00 (d, J 160.5 Hz, C_6H_5), 207.90 (s, Fe-CO minor isomer), 209.24 (s, Fe-CO major isomer). *Mass spectrum (EI); m/z* (relative intensity): 470 (M^+, 15), 442 (M^+ − CO, 12), 414 (M^+ − 2CO, 38), 386 (M^+ − 3CO, 14), 358 (M^+ − 4CO, 41), 330 (M^+ − 5CO, 40), 302 (M^+ − 6CO, 84), 246 ($HSFe_2C{\equiv}CPh$, 100), 202 ($HCSFeC{\equiv}CPh$, 10), 190 ($HSFeC{\equiv}CPh$, 7), 189 ($SFeC{\equiv}CPh$, 16), 178 (HSFeCPh, 57), 169 ($HSFeC{\equiv}C$, 12), 157 ($FeC{\equiv}CPh$, 3), 145 ($HSFe_2$, 6), 144 (SFe_2, 50), 134 ($HSC{\equiv}CPh$, 24), 102 ($HC{\equiv}CPh$, 14), 89 (FeSH, 11), 57 (^{t}Bu, 29), 56 (Fe, 18).

Synthesis of other $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR^1)(\mu\text{-}RS)Fe_2(CO)_6$ *complexes*

The same procedure as that described above was used in the synthesis of the following complexes:

$(\mu\text{-}\sigma,\pi\text{-}C{\equiv}C^tBu)(\mu\text{-}^tBuS)Fe_2(CO)_6$ (**2b**) (a mixture of two inseparable isomers), as a dark red, air-stable solid, m.p. 56.0–60.0 °C after recrystallization from pentane.

Anal. Found: C, 42.52; H, 4.13. $C_{16}H_{18}Fe_2O_6S$ calc: C, 42.70; H, 4.03%. *IR*: Terminal carbonyl region (pentane): 2075s, 2038vs, 2000vs, 1980s, 1945w (C≡C?) cm^{-1}. *^1H NMR* ($CDCl_3$; 250MHz): δ 1.17 (s, 9H, $C(CH_3)_3$ minor isomer), 1.27 (s, 9H, $C(CH_3)_3$ major isomer), 1.28 (s, 9H, $C(CH_3)_3$ major isomer), 1.34 (s, 9H, $C(CH_3)_3$ minor isomer). Ratio major/minor = 7.9/1.0. *^{13}C NMR* ($CDCl_3$; 67.9 MHz): δ 31.60 (q, J 126.4 Hz, $C{\equiv}CC(CH_3)_3$ major isomer), 31.92 (q, J 127.0 Hz, $C{\equiv}CC(CH_3)_3$ minor isomer), 33.30 (q, J 127.2 Hz, $SC(CH_3)_3$ major isomer), 34.59

(q, *J* 127.0 Hz, $SC(CH_3)_3$ minor isomer), 36.70 (s, $C{\equiv}CC(CH_3)_3$), 48.16 s, $SC(CH_3)_3$), 102.34 (s, acetylide C), 109.60 (s, acetylide C), 208.48 (s, Fe-CO major isomer), 209.35 (s, Fe-CO minor isomer), 209.94 (s, Fe-CO minor isomer). *Mass spectrum (EI); m/z* (relative intensity): 450 (M^+, 13), 422 ($M^+ - CO$, 9), 394 ($M^+ - 2CO$, 25), 366 ($M^+ - 3CO$, 16), 338 ($M^+ - 4CO$, 42), 310 ($M^+ - 5CO$, 41), 282 ($M^+ - 6CO$, 100), 226 $HSFe_2C{\equiv}C^tBu$, 95), 184 ($HSFe_2C{\equiv}CMe$, 10), 170 ($HSFe_2C{\equiv}CH$, 69), 169 ($HSFe_2C{\equiv}C$, 12), 168 ($SFe_2C{\equiv}C$, 9), 145 ($HSFe_2$, 10), 144 (SFe_2, 34), 57(^tBu, 30), 56 (Fe, 10).

(μ-σ,π-$C{\equiv}CSiMe_3$)(μ-^tBuS)$Fe_2(CO)_6$ (2c) (a mixture of two inseparable isomers), as an air-stable, red solid, m.p. 58.0–59.0 °C after recrystallization from pentane.

Anal. Found: C, 38.73; H, 3.96. $C_{15}H_{18}Fe_2O_6SSi$ calc: C, 38.65; H, 3.89%. *IR* ($CHCl_3$): 1910vs ($C{\equiv}C$). Terminal carbonyl region (pentane): 2080m, 2040s, 2017sh, 2010sh, 2002s, 1995sh, 1978vw cm^{-1}. *^1H NMR* ($CDCl_3$; 90 MHz): δ 0.24 (s, 9H, $Si(CH_3)_3$ minor isomer), 0.28 (s, 9H, $Si(CH_3)_3$ major isomer), 1.17 (s, 9H, $SC(CH_3)_3$ minor isomer), 1.30 (s, 9H, $SC(CH_3)_3$ major isomer). Ratio major/minor = 2.3/1.0. *^{13}C NMR* ($CDCl_3$; 67.9 MHz): δ 0.11 (q, *J* 120.1 Hz, $Si(CH_3)_3$ major isomer), 0.40 (q, *J* 120.0 Hz, $Si(CH_3)_3$ minor isomer), 33.32 (q, *J* 128.1 Hz, $SC(CH_3)_3$ major isomer), 34.81 (q, *J* 122.5 Hz, $SC(CH_3)_3$ minor isomer), 48.55 (s, $SC(CH_3)_3$), 90.95 (s, acetylide C minor isomer), 95.27 (s, acetylide C major isomer), 141.32 (s, acetylide C minor isomer), 143.24 (s, acetylide C major isomer), 208.16 (s, Fe-CO minor isomer), 209.48 (s, Fe-CO major isomer). *Mass spectrum (EI); m/z* (relatively intensity): 466 (M^+, 7), 438 ($M^+ - CO$, 8), 410 ($M^+ - 2CO$, 18), 382 ($M^+ - 3CO$, 23), 354 ($M^+ - 4CO$, 24), 326 ($M^+ - 5CO$, 30), 298 ($M^+ - 6CO$, 85), 242 ($HSFe_2C{\equiv}CSiMe_3$, 100), 226 ($^tBuSFe_2C{\equiv}CH$, 20), 145 ($HSFe_2$, 3), 144 (SFe_2, 7), 112 (Fe_2, 4), 97 ($C{\equiv}CSiMe_3$, 6), 73 ($SiMe_3$, 41), 57 (^tBu, 49), 56 (Fe, 15).

(μ-σ,π-$C{\equiv}CPh$)(μ-EtS)$Fe_2(CO)_6$ (2d) (a mixture of two inseparable isomers), as a slightly air-sensitive red oil.

Anal. Found: C, 43.55; H, 2.45. $C_{16}H_{10}Fe_2O_6S$ calc: C, 43.48; H, 2.28%. *IR*: Terminal carbonyl region (pentane): 2080m, 2043vs, 2005s, 2002sh cm^{-1}. *^1H NMR* (CD_2Cl_2; 250 MHz): δ 1.11 (t, *J* 7.55 Hz, 3H, SCH_2CH_3 minor isomer), 1.29 (t, *J* 7.55 Hz, 3H, SCH_2CH_3 major isomer), 2.16 (q, *J* 7.37 Hz, 2H, SCH_2CH_3 minor isomer), 2.39 (q, *J* 7.37 Hz, 2H, SCH_2CH_3 major isomer), 7.28–7.58 (m, 10H, C_6H_5 both isomers). Ratio major/minor = 2.6/1.0. *^{13}C NMR* ($CDCl_3$; 67.9 MHz): δ 16.46 (q, *J* 127.6 Hz, SCH_2CH_3 minor isomer), 17.42 (q, *J* 128.6 Hz, SCH_2CH_3 major isomer), 23.46 (t, *J* 140.4 Hz, SCH_2CH_3 minor isomer), 34.18 (t, *J* 140.9 Hz, SCH_2CH_3 major isomer), 93.09 (s, acetylide C major isomer), 93.87 (s, acetylide C minor isomer), 113.21 (s, acetylide C major isomer), 119.00 (s, acetylide C minor isomer), 125.25 (s, *ipso*-C_6H_5), 128.57 (d, *J* 161.4 Hz, C_6H_5), 131.89 (d, *J* 161.6 Hz, C_6H_5), 132.24 (d, *J* 162.5 Hz, C_6H_5), 208.10 (s, Fe-CO minor isomer), 208.88 (s, Fe-CO major isomer). *Mass spectrum (EI); m/z* (relative intensity): 442 (M^+, 13), 414 ($M^+ - CO$, 12), 386 ($M^+ - 2CO$, 33), 358 ($M^+ - 3CO$, 15), 330 ($M^+ - 4CO$, 32), 302 ($M^+ - 5CO$, 33), 274 ($M^+ - 6CO$, 63), 246 ($HSFe_2C{\equiv}CPh$, 100), 245 ($SFe_2C{\equiv}CPh$, 34), 189 ($SFeC{\equiv}CPh$, 25), 178 (HSFeCPh, 60), 169 ($HSFe_2C{\equiv}C$, 15), 162 ($EtSC{\equiv}CPh$, 18), 157 ($FeC{\equiv}CPh$, 6), 145 ($HSFe_2$, 8), 144 (SFe_2, 48), 134 ($HSC{\equiv}CPh$, 27), 102 ($HC{\equiv}CPh$, 13), 89 (HSFe, 17), 56 (Fe, 7).

(μ-σ,π-$C{\equiv}C^tBu$)(μ-EtS)$Fe_2(CO)_6$ (2e) (a mixture of two inseparable isomers), as a slightly air-sensitive red oil.

Anal. Found: C, 39.64; H, 3.43. $C_{14}H_{14}Fe_2O_6S$ calc: C, 39.84; H, 3.34%. *IR*: Terminal carbonyl region (pentane): 2077vs, 2044vs, 2004vs, 1994vs, 1958sh, 1932sh(C≡C?) cm^{-1}. *^1H NMR* ($CDCl_3$; 250 MHz): δ 1.05 (t, *J* 7.53 Hz, 3H, $SCH_2C\mathit{H}_3$ minor isomer), 1.22 (t, *J* 7.40 Hz, 3H, $SCH_2C\mathit{H}_3$ major isomer), 1.28 (s, 9H, $C{\equiv}CC(CH_3)_3$ major isomer), 1.33 (s, 9H, $C{\equiv}CC(CH_3)_3$ minor isomer), 1.96 (q, *J* 7.42 Hz, 2H, $SC\mathit{H}_2CH_3$ minor isomer), 2.24 (q, *J* 7.36 Hz, $SC\mathit{H}_2CH_3$ major isomer). Ratio major/minor = 2.8/1.0. *^{13}C NMR* ($CDCl_3$; 67.9 MHz): δ 16.39 (q, *J* 127.0 Hz, $SCH_2\mathit{C}H_3$ major isomer), 17.36 (q, *J* 128.2 Hz, $SCH_2\mathit{C}H_3$ minor isomer), 22.64 (t, *J* 142.8 Hz, $S\mathit{C}H_2CH_3$ minor isomer), 31.70 (q, *J* 126.4 Hz, $C{\equiv}CC(\mathit{C}H_3)_3$), 33.40 (s, $C{\equiv}C\mathit{C}(CH_3)_3$), 34.30 (t, *J* 139.6 Hz, $S\mathit{C}H_2CH_3$ major isomer), 101.50 (s, acetylide C major isomer), 105.48 (s, acetylide C minor isomer), 107.72 (s, acetylide C major isomer), 208.53 (s, Fe-CO minor isomer), 209.37 (s, Fe-CO major isomer). *Mass spectrum (EI); m/z* (relative intensity): 422 (M^+, 3), 310 (M^+ − CO, 5), 366 (M^+ − 2CO, 12), 338 (M^+ − 3CO, 8), 394 (M^+ − 4CO, 15), 282 (M^+ − 5CO, 19), 254 (M^+ − 6CO, 36), 226 ($HSFe_2C{\equiv}C^tBu$, 41), 198 ($EtSFe_2C{\equiv}CH$, 5), 184 ($HSFe_2C{\equiv}CMe$, 5), 183 ($CH_2SFeC{\equiv}C^tBu$, 8), 170 ($HSFe_2C{\equiv}CH$, 38), 145 ($HSFe_2$, 12), 144 (SFe_2, 29), 57 (^tBu, 30).

(μ-σ,π-$C{\equiv}C^tBu$)(μ-PhS)$Fe_2(CO)_6$. After the reaction mixture had been stirred for 18 h at room temperature, the solvent was removed in vacuo, and the resulting red tar was dissolved in pentane and filtered through a thin pad of silicic acid. Removal of the solvent left a red oil which was purified by medium pressure chromatography. Pentane eluted three bands. The first brown-red band gave 0.14 g (0.29 mmol, 19%) of (μ-σ,π-$C{\equiv}C^tBu$)(μ-PhS)$Fe_2(CO)_6$ (**2f**) (*ax* isomer only), as an air-stable, red solid, m.p. 99.0–101.0 °C after recrystallization from pentane. The second cherry red band yielded 0.33 g (0.70 mmol, 47%) of (μ-σ,π-$C{\equiv}C^tBu$)(μ-PhS)$Fe_2(CO)_6$ (**2f**) (*eq* isomer only), as a slightly air-sensitive red oil. The third orange band gave 0.16 g (0.33 mmol, 22% based on S) of (μ-PhS)$_2Fe_2(CO)_6$ identified by its ^{1}H NMR and mass spectra [20]. Except where specified, all data are reported for the *eq/ax* isomer mixture.

Anal. Found (major isomer - *eq*): C, 46.22; H, 3.19. Found (minor isomer - *ax*): C, 45.96; H, 3.11. $C_{18}H_{14}Fe_2O_6S$ calc: C, 45.99; H, 3.00%. *IR*: Terminal carbonyl region (pentane): 2082s, 2042vs, 2003s, 1997sh, 1990sh cm^{-1}. *^1H NMR* (CD_2Cl_2; 250 MHz): δ 0.86 (s, 9H, $C(CH_3)_3$ minor isomer), 1.34 (s, 9H, $C(CH_3)_3$ major isomer), 7.20 (s, 10H, C_6H_5 both isomers). *^{13}C NMR* ($CDCl_3$; 67.9 MHz): δ 30.80 (q, *J* 128.0 Hz, $C(\mathit{C}H_3)_3$ minor isomer), 31.71 (q, *J* 127.8 Hz, $C(\mathit{C}H_3)_3$ major isomer), 100.85 (s, acetylide C major isomer), 104.75 (s, acetylide C minor isomer), 108.26 (s, acetylide C major isomer), 111.01 (s, acetylide C minor isomer), 127.57 (d, *J* 163.4 Hz, C_6H_5), 127.91 (d, *J* 160.8 Hz, C_6H_5), 128.48 (d, *J* 161.8 Hz, C_6H_5), 131.4 (d, *J* 161.9 Hz, C_6H_5), 133.87 (d, *J* 165.7 Hz, C_6H_5), 140.92 (s, *ipso*-C_6H_5), 208.37 (s, Fe-CO minor isomer), 209.06 (s, Fe-CO major isomer). *Mass spectrum (EI); m/z* (relative intensity): 470 (M^+, 5), 442 (M^+ − CO, 2), 414 (M^+ − 2CO, 23), 386 (M^+ − 3CO, 7), 358 (M^+ − 4CO, 4), 330 (M^+ − 5CO, 16), 302 (M^+ − 6CO, 100), 246 ($PhSFe_2C{\equiv}CH$, 23), 221 ($PhSFe_2$, 6), 190 ($PhSC{\equiv}C^tBu$, 5), 186 (PhSPh, 8), 169 ($SFe_2C{\equiv}CH$, 5), 158 ($PhC{\equiv}C^tBu$, 26), 144 (SFe_2, 10), 143 ($PhC{\equiv}CCMe_2$, 84), 128 ($PhC{\equiv}CCMe$, 39), 110 (PhSH, 10), 77 (Ph, 13), 57 (^tBu, 6).

Reaction of (μ-σ,π-$C{\equiv}CPh$)(μ-^tBuS)$Fe_2(CO)_6$ with Et_2NH

A 100 ml round-bottomed flask equipped with a stir-bar and a rubber septum was charged with 0.87 g (1.85 mmol) of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$ (**2a**) and degassed by three evacuation/nitrogen-backfill cycles. The flask was then charged with 30 ml of THF and 0.21 ml (2.00 mmol) of diethylamine by syringe at room temperature. After the reaction mixture had been stirred for 20 h at room temperature, the solvent was removed in vacuo and the resulting deep red oil was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Pentane/CH_2Cl_2 (3/1 v/v) eluted a pale yellow band which was not collected and purple band which gave 0.71 g (1.32 mmol, 71%) of (μ-HC-C(Ph)=NEt_2)(μ-^{t}BuS)$Fe_2(CO)_6$ (**13**) (a mixture of two inseparable isomers), as an air-stable, deep red solid, m.p. 117.0–119.0 °C after recrystallization from pentane/CH_2Cl_2.

Anal. Found: C, 48.79; H, 4.71. $C_{22}H_{25}Fe_2O_6NS$ calc: C, 48.64; H, 4.64%. *IR* ($CHCl_3$): 2980m, 2965m, 2940m, 2930m, 2900w, 2880w, 1505vs (C=N), 1495s (C=N), 1472s, 1468s, 1445s, 1388s, 1370s, 1355s, 1340s, 1325s, 1265s, 1165s, 1098w, 1075m, 1030vw, 995w, 980w, 865w, 620s, 600s cm^{-1}. Terminal carbonyl region (pentane): 2050s, 2010vs, 1970s, 1960s, 1950m cm^{-1}. *^1H NMR* (CD_2Cl_2; 250 MHz): δ 0.99 (s, 9H, $SC(CH_3)_3$ minor isomer), 1.05 (t, *J* 7.06 Hz, 6H, CH_2CH_3 both isomers), 1.30 (t, *J* 7.11 Hz, 6H, CH_2CH_3 both isomers), 1.39 (s, 9H, $SC(CH_3)_3$ major isomer), 1.42 (s, 1H, Fe_2CH - *endo* -major isomer), 3.01 (q, *J* 7.12 Hz, 4H, CH_2CH_3 both isomers), 3.54 (q, *J* 7.14 Hz, 4H, CH_2CH_3 both isomers), 3.92 (s, 1H, Fe_2CH - *endo* - minor isomer), 7.23–7.43 (m, 10H, C_6H_5 both isomers). Ratio major/minor = 1.4/1.0. *^{13}C NMR* ($CDCl_3$; 67.9 MHz): δ 11.71 (q, *J* 132.0 Hz, CH_2CH_3 both isomers), 13.66 (q, *J* 131.8 Hz, CH_2CH_3 both isomers), 32.57 (q, *J* 127.4 Hz, $SC(CH_3)_3$ minor isomer), 33.47 (q, *J* 126.8 Hz, $SC(CH_3)_3$ major isomer), 45.37 (t, *J* 138.4 Hz, CH_2CH_3 both isomers), 48.18 (t, *J* 134.7 Hz, CH_2CH_3 major isomer), 48.53 (t, *J* 140.0 Hz, CH_2CH_3 minor isomer), 63.78 (d, *J* 133.8 Hz, Fe_2CH minor isomer), 74.95 (d, *J* 134.4 Hz, Fe_2CH major isomer), 124.85–131.31 (m, C_6H_5), 136.31 (s, *ipso*-C_6H_5, minor isomer), 137.37 (s, *ipso*-C_6H_5, major isomer), 198.12 (s, Et_2N=CPh, major isomer), 200.96 (s, Et_2N=CPh, minor isomer), 214.28 and 214.71 (both s, Fe-CO). *Mass spectrum (EI); m/z* (relative intensity): 543 (M^+, 7), 487 ($M^+ - 2CO$, 7), 459 ($M^+ - 3CO$, 16), 431 ($M^+ - 4CO$, 9), 403 ($M^+ - 5CO$, 20), 375 ($M^+ - 6CO$, 100), 347 ($M^+ - 6CO - C_2H_4$, 6), 319 ($HSFe_2CHC(Ph)=NEt_2$, 63), 291 ($HSFe_2CHC(Ph)=NHEt$, 34), 263 ($HSFe_2CHC(Ph)=NH_2$, 7), 247 ($HSFe_2CHCPh$, 19), 221 (Fe_2SPh, 21), 185 ($SFe_2CHC=NH_2$, 20), 174 ($Et_2N=C(Ph)CH$, 27), 145 ($HSFe_2$, 16), 144 (SFe_2, 37), 105 ($PhC=NH_2$, 16), 104 (PhC=NH, 21), 103 (PhC=N, 19), 77 (Ph, 13), 57 (^{t}Bu, 37), 56 (Fe, 17).

Reaction of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$ with $PhNH_2$

In an experiment similar to the reaction of **2a** with diethylamine, a THF solution containing 0.94 g (2.00 mmol) of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$ (**2a**) and 0.18 ml (2.00 mmol) of aniline was stirred for 20 h at room temperature. Removal of the solvent in vacuo left a red oil which was purified by filtration chromatography. Pentane eluted a pale yellow band which was not collected. Pentane/CH_2Cl_2 (9/1 v/v) eluted a red band which gave 0.97 g (1.72 mmol, 86%) of (μ-$CH_2C(Ph)$=NPh)(μ-^{t}BuS)$Fe_2(CO)_6$ (**14**) as an air-stable, red solid, m.p. 118.0–121.0 °C (dec) after recrystallization from pentane/CH_2Cl_2.

Anal. Found: C, 51.22; H, 3.78. $C_{24}H_{21}Fe_2O_6NS$ calc: C, 51.18; H, 3.76%. *IR*

(CCl_4): 3090w, 3070w, 3035w, 3015w, 2970m, 2945m, 2930m, 2900m, 2870m, 1610m (Ph or C=N), 1490s, 1475m, 1460m, 1445m, 1390w, 1370m, 1330vw, 1265s, 1210vw, 1160s, 1077w, 1057w, 1030m, 1000vw, 910w, 885vw, 865vw, 760vs, 615vs, 605vs, 575vs cm^{-1}. Terminal carbonyl region (pentane): 2065s, 2025vs, 1988vs, 1967m cm^{-1}. *^1H NMR* (CD_2Cl_2; 300 MHz): δ 1.56 (s, 9H, $SC(CH_3)_3$), 1.89 and 2.02 (AB quartet, J 18.31 Hz, 2H, $FeCH_2$), 6.68–7.14 (m, 10H, C_6H_5). *^{13}C NMR* ($CDCl_3$; 67.9 MHz): δ 26.37 (t, J 131.5 Hz, $FeCH_2$), 34.39 (q, J 126.8 Hz, $SC(\mathit{C}H_3)_3$), 48.18 (s, $S\mathit{C}(CH_3)_3$), 121.09–129.77 (m, C_6H_5), 140.51 (s, *ipso* C_6H_5), 154.99 (s, *ipso* C_6H_5), 198.00 (s, C=N), 209.93, 210.99, 211.78, and 218.06 (all s, Fe-CO).

Mass spectrum (EI); m/z (relative intensity): 563 (M^+, 0.3), 535 ($M^+ - CO$, 0.1), 507 ($M^+ - 2CO$, 13), 479 ($M^+ - 3CO$, 5), 451 ($M^+ - 4CO$, 2), 423 ($M^+ - 5CO$, 17), 395 ($M^+ - 6CO$, 44), 339 ($HSFe_2CH_2C(Ph)$=NPh, 75), 235 (SFe_2NPh, 12), 221 ($PhSFe_2$, 14), 195 (MeC(Ph)=NPh, 53), 180 PhC=NPh, 100), 144 (Fe_2S, 26), 77 (Ph, 83), 57 (^tBu, 22), 56 (Fe, 14).

Reaction of (μ-σ,π-C≡CPh)(μ-^tBuS)$Fe_2(CO)_6$ with $^tBuNH_2$

In an experiment similar to the reaction of **2a** with diethylamine, a THF solution containing 0.97 g (2.07 mmol) of (μ-σ,π-C≡CPh)(μ-^tBuS)$Fe_2(CO)_6$ (**2a**) and 0.32 ml (3.00 mmol) of t-butylamine was stirred for 1 h at −78 °C and then 18 h at room temperature. Removal of the solvent in vacuo left a brown oil which was purified by filtration chromatography. Pentane/CH_2Cl_2 (9/1 v/v) eluted an orange band which gave 0.23 g (0.50 mmol, 48% based on S) of (μ-^tBuS)$_2Fe_2(CO)_6$ [21], identified by its ^1H NMR spectrum. Pentane/CH_2Cl_2 (9/1 v/v) then eluted a second orange band which gave 0.44 g (0.77 mmol, 37%) of (μ-HC(=C(Ph)NH^{t}Bu)C=O)(μ-^tBuS)$Fe_2(CO)_6$ (**15**) (a mixture of two inseparable isomers), as an air-stable, red solid mp 138 °C (dec.) after recrystallization from pentane/CH_2Cl_2.

Anal. Found: C, 48.03; H, 4.56. $C_{23}H_{25}Fe_2O_7NS$ calc: C, 48.36; H, 4.41%. *IR* (CCl_4): 3240vw-br (NH), 3065vw, 2975m, 2940m, 2925m, 2900w, 2870w, 1610m (C=C), 1585sh (acyl C=O), 1573 vs (acyl C=O), 1512m (Ph), 1475s, 1460s, 1445sh, 1400m, 1370s, 1308vs, 1265m, 1240m, 1200vs, 1160m, 1080s, 1037w, 1003w, 980w, 920w, 850m, 705m, 652m, 625sh, 595s, 565sh cm^{-1}. Terminal carbonyl region (pentane): 2070m, 2030vs, 2000s, 1987s, 1965m cm^{-1}. *^1H NMR* (acetone-d_6; 300 MHz): 1.037 (s, 9H, $NC(CH_3)_3$ minor isomer), 1.044 (s, 9H, $NC(CH_3)_3$ major isomer), 1.47 (s, 9H, $SC(CH_3)_3$ major isomer), 1.55 (s, 9H, $SC(CH_3)_3$ minor isomer), 4.93 (s, 1H, *H*C=CPh minor isomer), 5.14 (s, 1H, *H*C=CPh major isomer), 6.96–7.48 (m, 10H, C_6H_5 both isomers), 9.49 (broad s, 1H, NH minor isomer), 9.55 (s, 1H, NH major isomer). Ratio major/minor = 1.5/1.0. *^{13}C NMR* ($CDCl_3$; 67.9 MHz): δ 31.36 (q, J 126.8 Hz, $NC(\mathit{C}H_3)_3$ both isomers), 34.32 (q, J 127.8 Hz, $SC(\mathit{C}H_3)_3$ both isomers), 47.45 (s, $S\mathit{C}(CH_3)_3$ minor isomer), 48.67 (s, $S\mathit{C}(CH_3)_3$ major isomer), 54.41 (s, $N\mathit{C}(CH_3)_3$ both isomers), 113.94 (d, J 168.2 Hz, H*C*=CPh minor isomer), 114.55 (d, J 167.6 Hz, H*C*=CPh major isomer), 127.77 (d, J 162.8 Hz, C_6H_5), 128.19 (d, J 164.4 Hz, C_6H_5), 129.21 (d, J 158.9 Hz, C_6H_5), 135.69 (s, *ipso*-C_6H_5), 156.45 (s, HC=*C*Ph major isomer), 157.64 (s, HC=*C*Ph minor isomer), 207.32, 210.83, 211.68, 213.05, and 214.24 (all s, Fe-CO both isomers), 253.41 (s, acyl C=O minor isomer), 257.19 (s, acyl C=O major isomer).

Mass spectrum (EI); m/z (relative intensity): 571 (M^+, 4), 543 ($M^+ - CO$, 4), 515 ($M^+ - 2CO$, 7), 487 ($M^+ - 3CO$, 15), 459 ($M^+ - 4CO$, 8), 431 ($M^+ - 5CO$, 17), 403 ($M^+ - 6CO$, 47), 375 ($M^+ - 7CO$, 22), 347 ($HSFe_2HC(=C(Ph)NH^tBu)C{=}O$, 100), 319 ($HSFe_2HC{=}C(Ph)NH^tBu$, 28), 291 ($HSFe_2HC(=C(Ph)NH_2)C{=}O$, 23), 263 ($HSFe_2HC{=}C(Ph)NH_2$, 55), 221 ($PhSFe_2$, 27), 202 ($HC(=C(Ph)NH^tBu)C{=}O$, 33), 185 ($HSFe_2C{=}CNH_2$, 19), 145 ($HSFe_2$, 13), 144 ($SFe_2$, 41), 104 (PhCNH, 44), 57 (^{t}Bu, 65), 56 (Fe, 16).

Reaction of (μ-σ,μ-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$ with PPh_3

In an experiment similar to the reaction of **2a** with diethylamine, a THF solution containing 4.42 g (9.41 mmol) of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$ (**2a**) and 2.53 g (9.64 mmol) of triphenylphosphine was stirred for 1 h at room temperature. Removal of the solvent in vacuo left a purple, foamy solid which was purified by filtration chromatography. Pentane eluted a pale, brownish-yellow band which was not collected. Pentane/CH_2Cl_2 (4/1 v/v) eluted dark purple and purple-red bands which were collected together. Repeated filtration chromatography achieved a satisfactory separation between the two. However, the second product converted readily to the first during chromatographic workup. Subsequently, the residue from the second band was extracted with pentane to yield a purplish solution (first product) and an insoluble orange solid (second product). Ultimately, the first band yielded 3.90 g (5.54 mmol, 57%) of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_5(PPh_3)$ (**17**) (a mixture of two inseparable isomers), as an air-stable, purple solid, m.p. 145.0 °C (dec) after recrystallization from pentane/CH_2Cl_2.

Anal. Found: C, 59.32; H, 4.21. $C_{35}H_{29}Fe_2O_5PS$ calc: C, 59.68; H, 4.15%.

IR ($CHCl_3$): 3070m, 2977w, 2955w, 2938w, 2908w, 2878vw, 1599m (Ph), 1576w (Ph), 1485vs, 1461m, 1435vs, 1395vw, 1368s, 1311vw, 1185vw, 1160s, 1092vs, 1072vw, 1028vw, 1001w, 630s, 619vs, 608vs, 580vs, 515vs cm^{-1}. Terminal carbonyl region (pentane): 2050vs, 2001vs, 1992s, 1972m, 1952w cm^{-1}.

^1H NMR (CD_2Cl_2; 250 MHz): δ 1.04 (s, 9H, $SC(CH_3)_3$ minor isomer), 1.08 (s, 9H, $SC(CH_3)_3$ major isomer), 7.11–7.78 (m, 40H, C_6H_5 both isomers). Ratio major/minor = 8.5/1.0. *^{13}C NMR* (CD_2Cl_2; 67.9 MHz): δ 33.43 (q, J 128.0 Hz, $SC(\mathit{C}H_3)_3$ major isomer), 34.14 (q, J 125.2 Hz, $SC(\mathit{C}H_3)_3$ minor isomer), 47.87 (s, $S\mathit{C}(CH_3)_3$), 97.13 (s, acetylide C), 125.68–136.80 (m, C_6H_5), 212.52, 215.59, 215.76, 216.40, and 216.57 (all s, Fe-CO). *^{31}P NMR* (CD_2Cl_2; 36.2 MHz): δ 62.72 (s, PPh_3 major isomer), 65.41 (s, PPh_3 minor isomer). *Mass spectrum (FD); m/z* (relative intensity): 704 (M^+).

Ultimately, the second band yielded 1.86 g (2.54 mmol, 26%) of (μ-$Ph_3P{=}CCPh$)(μ-^{t}BuS)$Fe_2(CO)_6$ (**16**) as an air-stable, orange solid, m.p. 108.0–115.0 °C (dec) after recrystallization from pentane/CH_2Cl_2.

IR ($CHCl_3$): 3070w, 2973w, 2957w, 2937w, 2910w, 2867vw, 1599w (Ph), 1580vw (Ph), 1500vs, 1473vs, 1440vs, 1392vw, 1367w, 1320vw, 1267vw, 1185vw, 1160s, 1104s, 1073vw, 1030vw, 1002w, 895w, 640vs, 631vs, 611vs, 599vs, 510vs cm^{-1}. Terminal carbonyl region (pentane): 2085vw, 2050m, 2009vs, 1975m, 1962m, 1945w cm^{-1}. *^1H NMR* (CD_2Cl_2; 90 MHz): δ 1.37 (s, 9H, $SC(CH_3)_3$), 6.72–7.80 (m, 20H, C_6H_5). *^{13}C NMR* (CD_2Cl_2; 67.9 MHz): δ 33.89 (q, J 126.7 Hz, $SC(\mathit{C}H_3)_3$), 45.80 (s, $S\mathit{C}(CH_3)_3$), 118.72–136.10 (m, C_6H_5), 145.31 (d, J(PC) 20.4 Hz, $Ph_3P\mathit{C}{=}CPh$), 214.30 and 214.71 (both s, Fe-CO), 292.41 (s, $Ph_3PC{=}\mathit{C}Ph$). ^{31}P NMR (CD_2Cl_2; 36.2 MHz): δ 0.54 (s, PPh_3). *Mass spectrum (FD); m/z*: 732 (M^+).

Decarbonylation of $(\mu\text{-}Ph_3P{=}CCPh)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$

A 100 ml round-bottomed flask equipped with a stir-bar and rubber septum was charged with 0.17 g (0.24 mmol) of $(\mu\text{-Ph}_3\text{PC{=}CPh})(\mu\text{-}{}^t\text{BuS})\text{Fe}_2(\text{CO})_6$ (**16**) and degassed by three evacuation/nitrogen-backfill cycles. Subsequently, 30 ml of THF was added by syringe. After the reaction mixture had been stirred for 90 h at room temperature, the solvent was removed in vacuo, and the resulting purple tar was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Pentane/CH_2Cl_2 (5/1 v/v) eluted a dark purple band which gave 0.15 g (0.21 mmol, 88%) of $(\mu\text{-}\sigma,\pi\text{-C}{\equiv}\text{CPh})(\mu\text{-}{}^t\text{BuS})\text{Fe}_2(\text{CO})_5\text{PPh}_3$ (**17**) identified by its ^{1}H and ^{31}P NMR spectra.

Acknowledgements

The authors are grateful to the National Science Foundation for generous support of this work and to the M.I.T. Mass Spectrometry Facility (supported by N.I.H. Division of Research Resources, Grant No. RR 00317; K. Biemann, principal investigator) for mass spectra.

References

1 D. Seyferth, G.B. Womack and J.C. Dewan, Organometallics, 4 (1985) 398.

2 (a) R.B. King, J. Am. Chem. Soc., 84 (1962) 2460; (b) G.B. Womack, Ph. D. Dissertation The Massachusetts Institute of Technology: Cambridge, MA, 1984, pp. 25, 26, 225.

3 (a) H.A. Patel, R.G. Fischer, A.J. Carty, D.V. Naik and G.J. Palenik, J. Organomet. Chem., 60 (1973) C49; (b) W.F. Smith, J. Yule, N.J. Taylor, N.H. Paik and A.J. Carty, Inorg. Chem., 16 (1977) 1593; (c) A.J. Carty, H.N. Paik and G.J. Palenik, Inorg. Chem., 16 (1977) 300; (d) A.J. Carty, ACS Adv. Chem. Ser., 196 (1981) 163; (e) A.J. Carty, Pure and Appl. Chem., 54 (1982) 113.

4 (a) P.W. Jolly and R. Pettit, J. Organomet. Chem., 12 (1968) 491; (b) M.L.H. Green and T. Mole, J. Organomet. Chem., 12 (1968) 404; (c) A. Davison and J.P. Selegue, J. Am. Chem. Soc., 100 (1978) 7763; (d) R.A. Bell, M.H. Chisholm, D.A. Couch, and L.A. Rankel, Inorg. Chem., 16 (1977) 677.

5 P.O. Nubel and T.L. Brown, Organometallics, 3 (1984) 29.

6 (a) D. De Montauzon and R. Mathieu, J. Organomet. Chem., 252 (1983) C83; (b) M.K. Alami, F. Dahan and R. Mathieu, Organometallics, 4 (1985) 2122.

7 (a) K. Yasufuku and H. Yamazaki, Bull. Chem. Soc. Jpn., 45 (1972) 2664; (b) K. Yasufuku and H. Yamazaki, Bull. Chem. Soc. Jpn., 48 (1975) 1616.

8 (a) M. Catti, G. Gervasio and S.A. Mason, J. Chem. Soc., Dalton Trans., (1977) 2260; (b) E. Sappa, O. Gambino, L. Milone and G. Cetini, J. Organomet. Chem., 39 (1972) 169; (c) A.J. Deeming, S. Hasso and M. Underhill, J. Chem. Soc., Dalton Trans., (1975) 1614; (d) S. Ermer, R. Karpelus, S. Miura, E. Rosenberg, A. Tiripicchio and A.M.M. Lanfredi, J. Organomet. Chem., 187 (1980) 81.

9 (a) A.J. Carty, S.A. MacLauglin and N.J. Taylor, J. Organomet. Chem., 204 (1981) C27; (b) A.J. Carty, N.J. Taylor and W.F. Smith, J. Chem. Soc., Chem. Commun., (1979) 750.

10 (a) R.W.M. ten Hoedt, J.G. Noltes, G. van Koten and A.L. Spek, J. Chem. Soc., Dalton Trans., (1978) 1800; (b) O.M. Abu Salah, M.I. Bruce, M.R. Churchill and S.A. Bezman, J. Chem. Soc., Chem. Commun., (1972) 858; (c) O.M. Abu Salah, M.I. Bruce, M.R. Churchill and B.G. De Boer, J. Chem. Soc., Chem. Commun., (1974) 688.

11 J. Hriljac and D.F. Shriver, Organometallics, 4 (1985) 2225.

12 S.Y. Delavarenne and H.G. Viehe, in H.G. Viehe (Ed.), Chemistry of Acetylenes, Marcel Dekker, New York, 1969, pp. 691–693.

13 R.M. Silverstein, G.C. Bassler, T.C. Morrill, (Eds.), Spectrometric Identification of Organic Compounds, John Wiley and Sons, Inc., New York, 1981, p. 10.

14 P.D. Magnus, T. Sarkar and S. Djuric, in G. Wilkinson, F.G.A. Stone, E.W. Abel, (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, New York, 1982, 7, pp. 517–519.

15 (a) S. Aime, L. Milone, E. Sappa, A. Tiripicchio and M.T. Camellini, J. Chem. Soc., Dalton Trans., (1979) 1155; (b) J.P. Hickey, J.C. Huffman and L.J. Todd, Inorg. Chim. Acta, 28 (1978) 77; (c) P.O. Nubel and T.L. Brown, J. Am. Chem. Soc., 106 (1984) 3474; (d) P.O. Nubel and T.L. Brown, Organometallics, 3 (1984) 29; (e) M.D. Fryzuk, T. Jones and F.W.B. Einstein, Organometallics, 3 (1984) 185; (f) J.R. Shapley, S.I. Richter, M. Tachikawa and J.B. Keister, J. Organomet. Chem., 94 (1975) C43; (g) A.D. Clauss, M. Tachikawa, J.R. Shapley and C.G. Pierpoint, Inorg. Chem., 20 (1981) 1528; (h) Reference 2b, p. 288; (i) A.F. Dyke, S.A.R. Knox, P.J. Naish and G.E. Taylor, J. Chem. Soc., Chem. Commun., (1980) 409.

16 (a) A.J. Carty, G.N. Mott, N.J. Taylor and J.E. Yule, J. Am. Chem. Soc., 100 (1978) 3051. (b) A.J. Carty, N.J. Taylor, H.N. Paik, W. Smith and J.G. Yule, J. Chem. Soc., Chem. Commun., (1976) 41; (c) A.J. Carty, G.N. Mott and N.J. Taylor, J. Organomet. Chem., 182 (1979) C69; (d) G.N. Mott, R. Granby, S.A. MacLaughlin, N.J. Taylor and A.J. Carty, Organometallics, 2 (1983) 289; (e) Y.S. Wong, H.N. Paik, P.C. Chieh and A.J. Carty, J. Chem. Soc., Chem. Commun., (1975) 309.

17 (a) J.B. Hoke, Chapters 3 and 4 of Ph.D. Dissertation, M.I.T., 1987; (b) C.M. Archer, Ph. D. Dissertation. The Massachusetts Institute of Technology, Cambridge, MA, 1986, p. 218.

18 L. Brandsma, H.D. Verkruijsse, (Eds.), Synthesis of Acetylenes, Allenes, and Cumulenes, Elsevier Pub. Co., New York, 1981, p. 98.

19 W. McFarlane and G. Wilkinson, Inorg. Synth., 8 (1966) 181.

20 S.F.A. Kettle and L.E. Orgel, J. Chem. Soc., (1960) 3890.

21 J.A. deBeer and R.J. Haines, J. Organomet. Chem., 24 (1970) 757.