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Carbon–carbon bond formation at diiron centres

VII *. New routes to anionic alkenyl-bridged diiron complexes, and reactions of the latter with propargyl chloride

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Abstract

New routes to $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CR'H)]^-$ anions have been devised, and compared with those previously described. Reaction of $[HFe_2(CO)_8]^-$ with the alkynes RC≡CR′ (R = R′ = H (**1**), Ph (**2**) and Me_3Si (**3**)) gives the dinuclear alkenyl-bridged complexes in 80% yield, but with PhC≡CH a mixture of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CPh{=}CH_2)]^-$ (**4a**) and $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CH{=}CPhH)]^-$ (**4b**) is formed. Reaction of $Na[BH_4]$ with PhC≡CPh and $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ gives **2** in 40–45% yield. Treatment of PhC≡CPh with a $[Fe(CHO)(CO)_4]^-/Fe_2(CO)_9$ mixture in THF gives an 80% yield of **2**. Cinnamoyl chloride and $[Fe_2(CO)_8]^{2-}$ react to give **2** in 50% yield. Reaction of propargyl chloride with the $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CRH)]^-$ (R = H and Ph) complexes in CH_2Cl_2 yields the complexes $Fe_2(CO)_6(\mu\text{-}CR{=}CRH)(\mu\text{-}CHCCH_2)$ (R = H (**5**) and Ph (**6**)), the structures of which are suggested on the basis of IR and NMR data.

Introduction

The reaction of metal hydrides with alkynes provides a general route to alkenyl ligands [1]. Usually, the insertion of alkynes into mononuclear hydride complexes gives η^1-alkenyl ligands [2], whereas with hydride clusters μ,η^2-alkenyl ligands are formed [3].

We previously described the synthesis of the anionic alkenyl-bridged diiron complexes $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CR'H)]^-$ by two routes involving the reaction of the anionic cluster $[HFe_3(CO)_{11}]^-$ with alkynes in acetone [4] and the other

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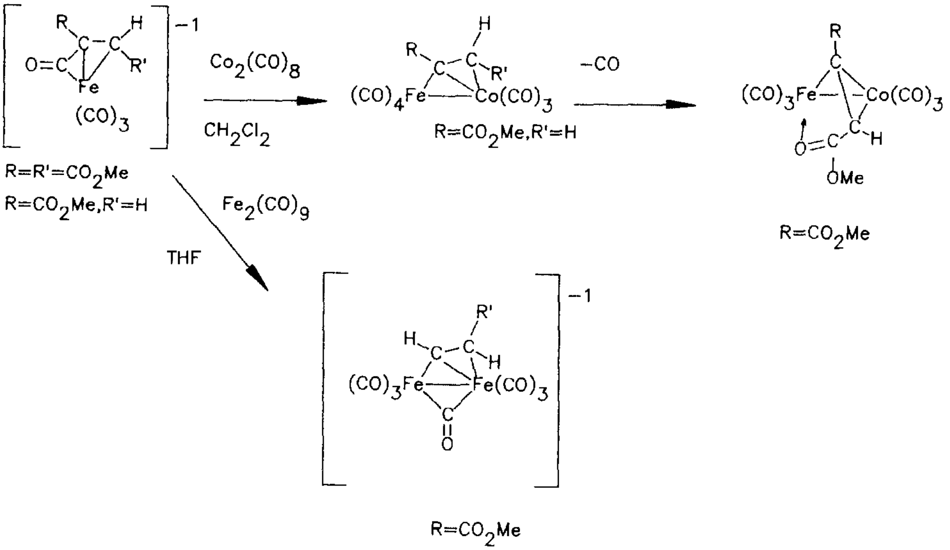
* For Part VI see ref. 9.

involving equimolar mixtures of $Fe_2(CO)_9$, RC≡CR; and $[HFe(CO)_4]^-$ in THF [5]. The second route gives the dinuclear anionic complexes as the only products. By contrast, the reaction of $[HFe_3(CO)_{11}]^-$ with alkynes provides anionic alkenyl-bridged trinuclear complexes at room temperature, but in refluxing acetone a mixture of dinuclear alkenyl-bridged and trinuclear compounds is formed. The method was extended to the synthesis of mixed dinuclear alkenyl-bridged complexes of the type $FeM(\eta\text{-}C_5H_5)(CO)_4(\mu\text{-}CO)(\mu\text{-}CR{=}CR'H)]$ (M = Fe or Ru) but yields were low [6]. The formation of complexes seems to involve an activation of the alkyne by $Fe_2(CO)_9$ and a subsequent reaction with the metal hydride. In order to throw light on the mechanism of formation of alkenyl-bridged compounds, we have carried out a study of the synthesis of these complexes based on the reaction of iron carbonyls with alkynes and hydrides.

We showed recently that reactions of the $[Fe_2(CO)_6(\mu\text{-}CO)(CR{=}CR'H)]^-$ complexes with alkynes and electrophiles give C–C bond formation [7–9]; in extension of that study we have now examined the reaction of complexes of this type with propargyl chloride.

Results and discussion

The reactions of $[HFe(CO)_4]^-$ with activated alkynes was described by Mitsudo [10], who showed that acryloyl complexes of the type $[Fe(\eta^3\text{-}R'HC{=}CRC{=}O)(CO)_3]^-$ are formed. Terminal alkynes RC≡CH (R = CO_2Me or CHO) give rise to acryloyl groups with geminal hydrogens and when R = R' = CO_2Me the methoxycarbonyl groups are in a *trans* disposition. The acryloyl ligands in these compounds are readily decarbonylated, allowing their use as a source of alkenyl-bridged diiron [5] and iron-cobalt [11] complexes by treatment with $Fe_2(CO)_9$ and $Co_2(CO)_8$, respectively (see Scheme 1).



Scheme 1.

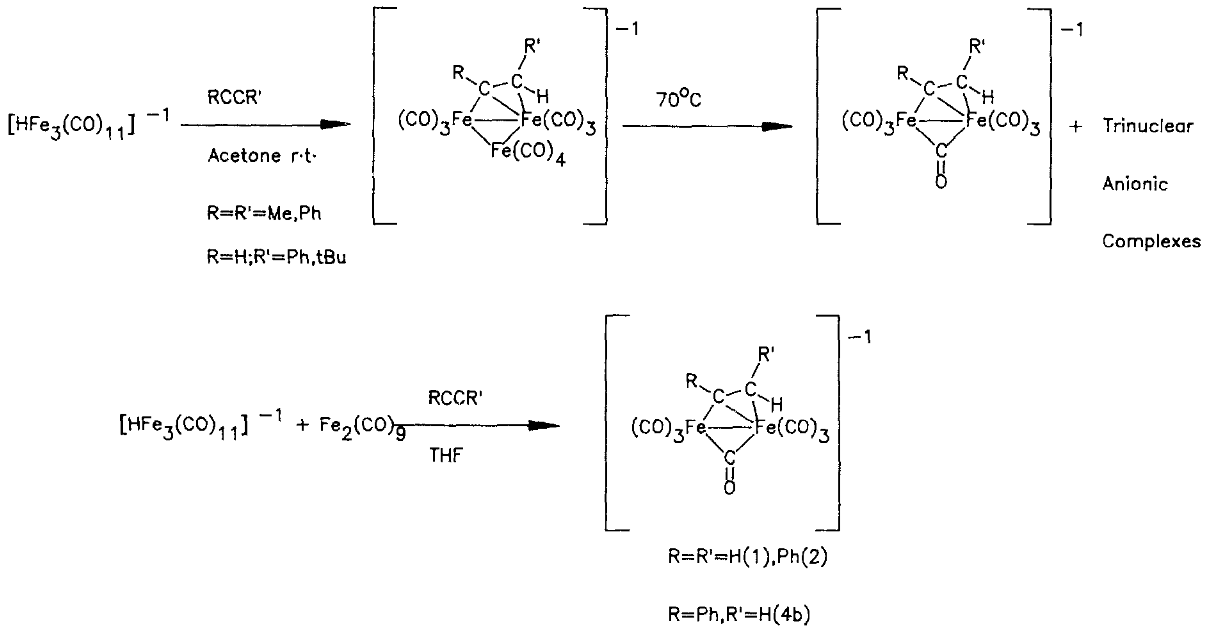
The related recently-described reaction of $Fe_2(CO)_9$/RC≡CR′/$[HFe(CO)_4]^-$ mixtures in THF [5] (Method A) gives the $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CR'H)]^-$ complexes, whose stereochemistry is different from that of compounds obtained from $[HFe_3(CO)_{11}]^-$ and alkynes when R′ = H (Method B) [4]. Thus, in reactions with terminal alkynes, Method A gives $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CH_2)]^-$ complexes but Method B gives $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CH{=}CR'H)]^-$ compounds. In two cases the insertion into the Fe–H bond seems to be *cis*, as can be deduced from the structure of products resulting from the reactions with electrophiles (see Scheme 2) [8]. In continuation of our studies on the preparation of anionic alkenyl-bridged diiron complexes and with the aim of explaining the mechanisms of formation of these complexes, we examined the following reactions: (a) $[HFe_2(CO)_8]^-$ with alkynes (Method C); (b) $Fe_2(CO)_9$ with PhC≡CPh and $Na[BH_4]$ (Method D); (c) $Fe_3(CO)_{12}$ with PhC≡CPh and $Na[BH_4]$ (Method E); (d) $[Fe(CO)_4CHO]^-$ with PhC≡CPh and $Fe_2(CO)_9$ (Method F); (e) $[Fe_2(CO)_8]^{2-}$ with cinnamoyl chloride (Method G).

Reaction of $[HFe_2(CO)_8]^-$ with alkynes (Method C)

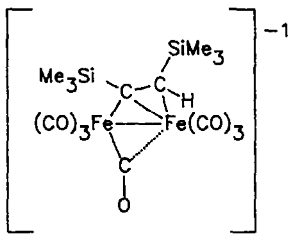
We examined the reaction of $[HFe_2(CO)_8]^-$ with alkynes. The reaction was performed by keeping a mixture of equimolar quantities of $[Fe_2(CO)_8]^{2-}$, trifluoroacetic acid, and alkynes RC≡CR′ (R = R′ = H, Ph or $SiMe_3$; R = H and R′ = Ph or ^tBu) in THF at room temperature for 15 min. After this time the reaction was complete and the IR spectrum of the mixture showed that the anionic alkenyl-bridged diiron complexes $[Fe_2(CO)(\mu\text{-}CO)(\mu\text{-}CR{=}CR'H)]^-$ were the only products. The yields are high, and comparable with those obtained by Method A (ca 80%). The IR and ^1H NMR data for the products obtained when R = R′ = H (**1**) or Ph (**2**) are identical to those of samples previously obtained [5]. The complex with R = R′ = $SiMe_3$ (**3**), which was not previously reported, is rather unstable, and decomposes slowly in THF solution at room temperature. Its IR spectrum in dichloromethane displays $\nu(C{\equiv}O)$ bands at 2013w, 1974vs, 1919vs and 1877s cm^{-1} positions different from those for the other $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CR'H)]^-$ complexes. In particular, the frequency of 1877 cm^{-1} is high enough to be assigned to a symmetric bridging carbonyl in an anionic complex [12]. The steric requirements of the $SiMe_3$ groups presumably lead to formation of a semi-bridging carbonyl ligand which may display a higher frequency $\nu(C{\equiv}O)$ band (Fig. 1). A related situation was found with phosphine disubstituted iron-cobalt complexes, where steric requirements probably promotes formation of a bridging CO [13]. The ^1H NMR spectrum of product **4** obtained from PhC≡CH exhibits signals corresponding to the formation of two isomers previously obtained by other methods, namely $[Fe_2(CO)_6(\mu\text{-}CO)(RC{=}CH_2)]^-$ (**4b**) and $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}HC{=}CRH)]^-$ (**4b**), with geminal and *trans* hydrogen atoms, respectively (Scheme 3).

Reaction of $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with PhC≡CPh and $Na[BH_4]$ (Methods D and E)

A more direct synthesis of the $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CR'H)]^-$ from iron carbonyls, alkynes and $Na[BH_4]$ as a source of hydride was devised. Reaction of PhC≡CPh with $Na[BH_4]$ and $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ gave similar yields of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CPh{=}CPhH)]^-$ (40 and 45%, respectively), isolated as $[PPh_4]^+$ salts. There are some earlier reports of the reactions of iron carbonyls with borohydrides to give of carbonyl iron hydrides ($[HFe(CO)_4]^-$ or $[HFe_3(CO)_{11}]^-$, depending on the reaction conditions) [14]. For example, a standard route to


[HFe3(CO)11] −1
RCCR'
Acetone r·t·
R=R'=Me,Ph
R=H;R'=Ph,tBu
R
R'
H
(CO)3Fe
Fe(CO)3
Fe(CO)4
−1
70°C
C
O
+ Trinuclear
Anionic
Complexes
[HFe3(CO)11] −1 + Fe2(CO)9
RCCR'
THF
R=R'=H(1),Ph(2)
R=Ph,R'=H(4b)

Scheme 2.

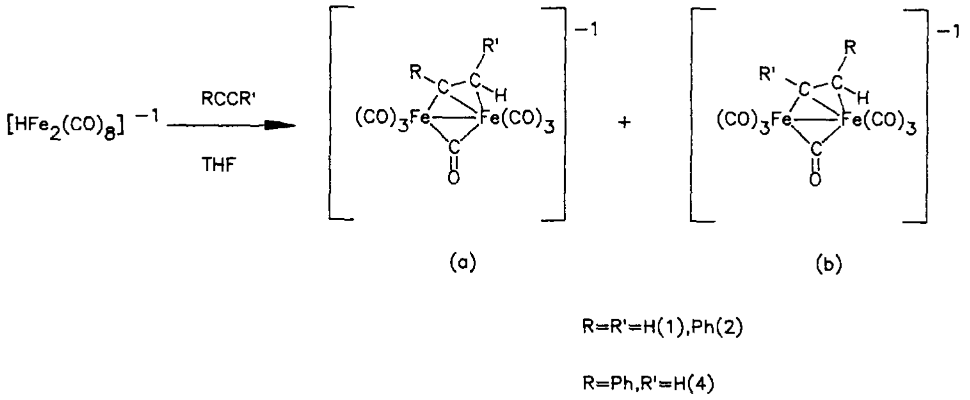


(3)

Fig. 1.

$[HFe_3(CO)_{11}]^-$ is based on the reaction of $Fe(CO)_5$ with $Na[BH_4]$ and subsequent addition of acetic acid [15]. On the other hand, it is known that the reaction of iron carbonyls ($Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$) with mild reducing agents such as $Na[BH_4]$ or Na/Hg in ethers gives a mixture of $[Fe(CO)_4]^{2-}$, hydrides and polynuclear species [16]. The reaction of $Fe(CO)_5$ with $Na[BH_4]$ in n-butyl alcohol gives the formyl complex $[Fe(CO)_4(CHO)]^-$, revealing that H^- attacks a bound CO ligand [17]. However, the conversion of the formyl anion $[Fe(CO)_4(CHO)]^-$ into the $[HFe(CO)_4]^-$ complex at room temperature was reported by other authors [18].

In these reactions, the alkenyl bridging ligand must be formed by insertion of PhC≡CPh into the Fe–H bond. As in method A for the synthesis of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}RC{=}CR'H)]^-$ [5], the PhC≡CPh is probably activated by coordination to the "$Fe(CO)_4$" fragment coming from the breakdown of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ upon treatment with $Na[BH_4]$. In order to throw light on possible mechanisms of formation of the alkenyl bridging ligands we treated $[HFe(CO)_4]$ with an equimolar amount of PhC≡CPh in the presence of $Fe(CO)_5$ in THF but observed no reaction at room temperature. However, when $Fe_2(CO)_9$ was added to the solution, formation of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PhC{=}CPhH)]^-$ (**2**) was complete in 2 h. This indicates that fragmentation of $Fe_2(CO)_9$ in THF is responsible for the activation of the alkyne, which subsequently reacts with $[HFe(CO)_4]^-$. The cluster anion $[HFe_3(CO)_{11}]^-$ was also treated with PhC≡CPh in the presence of $Fe_2(CO)_9$ in THF at room temperature, but the complex $[Fe_3(CO)_{10}(\mu\text{-}PhC{=}CPhH)]^-$, previ-



Scheme 3.

ously reported by Mathieu, was formed [4]. From these results it appears that the $Fe_2(CO)_9$/alkyne mixture in THF reacts only with mononuclear hydrides such as $[HFe(CO)_4]^-$ [5] or $MH(C_5H_5)(CO)_2$ (M = Fe or Ru) [6].

Reaction of $[Fe(CO)_4(CHO)]^-$ with $Fe_2(CO)_9$ and PhC≡CPh (Method F)

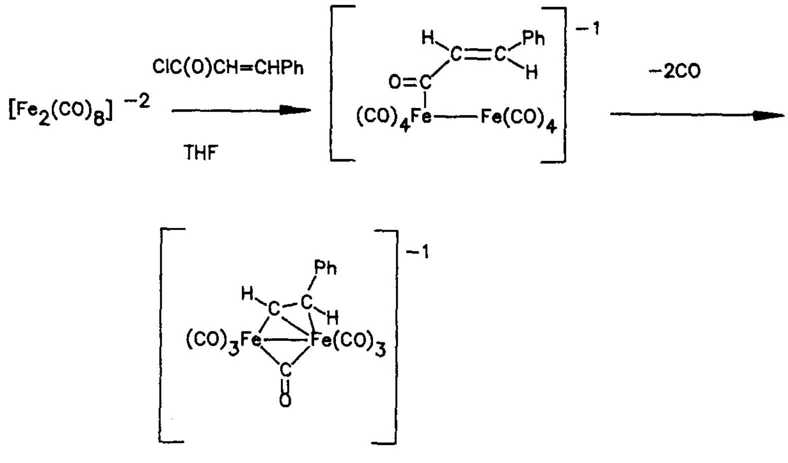
The formyl anion $[Fe(CO)_4(CHO)]^-$ is readily obtained by reduction of $Fe(CO)_5$ with $Na[BH_4]$ in n-butyl alcohol, but it decomposes to $[HFe(CO)_4]^-$ in ethers or in refluxing n-butyl alcohol. This instability allows the high yield synthesis of *trans*-$Fe(CO)_3(PR_3)_2$ compounds [17]. We recently showed that the treatment of $[Et_3O][BF_4]$ with a mixture resulting from the reaction of alkynes with $[HFe_3(CO)_{11}]^-$ gives the complexes $Fe_2(CO)_6(\mu\text{-}CRCR'C(OEt)H)$ (R = R′ = Ph and R = Ph, R′ = Me) [19]. During our investigations we tried unsuccessfully to isolate the assumed intermediate $[Fe_2(CO)_6(\mu\text{-}CRCR'C(H){=}O)]^-$, ethylation of which should lead to the formation of the complexes $Fe_2(CO)_6(\mu\text{-}CRCR'C(OEt)H)$. These neutral complexes seem to be formed by an alkyne insertion into Fe–C(formyl) bond with subsequent ethylation of the acyl carbon in the manner observed for the acryloyl complexes $[Fe(\eta^3\text{-}R'HC{=}CRC{=}O)(CO)_3]^-$ [10]. For this reason we treated the formyl complex $[Fe(CO)_4CHO]^-$ with PhC≡CPh and $Fe_2(CO)_9$ in THF, and this gave the alkenyl bridged compound $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CPh{=}CPhH)]^-$ (**2**) in 80% yield. There is no doubt that the formyl anion $[Fe(CO)_4(CHO)]^-$ decomposes at room temperature to give the $[HFe(CO)_4]^-$ complex, which reacts with the alkyne and $Fe_2(CO)_9$ as in Method A.

Reaction of $[Fe_2(CO)_8]^{2-}$ with cinnamoyl chloride (Method G)

Another possible route to the intermediate species $[Fe_2(CO)_6(\mu\text{-}CRCR'C(H){=}O)]^-$ is the reaction of $[Fe_2(CO)_8]^{2-}$ with an α,β-unsaturated acyl halide such as cinnamoyl chloride. Watanabe et al. recently reported the reaction of this type of acyl halide with the anion cluster $[Fe_3(CO)_{11}]^{2-}$, obtained the $[\mu_3\text{-}RCH{=}CHCOOCFe_3(CO)_{10}]^-$ complexes, which decompose slowly at room temperature by decarbonylation of the organic ligand and breakdown of the cluster to give the alkenyl bridged complexes $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CR'H)]^-$ [20]. When we treated $[Fe_2(CO)_8]^{2-}$ with cinnamoyl chloride in THF for 12 h we isolated the $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CH{=}CPhH)]^-$ anion complex (**4a**) in 50% yield. The IR and ^1H NMR data for the complex are identical with those for the complex obtained from $[HFe_3(CO)_{11}]^-$ and PhC≡CH by Mathieu [4]. The formation of the bridging alkenyl ligand suggests that the alkylation occurs at an iron center, forming an η^1-alkeneacyl ligand, decarbonylation of which gives the $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CH{=}CPhH)]^-$ complex (Scheme 4).

Reaction of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CRH)]^-$ with propargyl chloride

The anionic nature of complexes $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CRH)]^-$ leads to interesting reactions with electrophiles involving introduction or formation of three-electron bridges such as carbyne [8], phosphide [21] or chloride [22]. In the case of alkenyl-carbyne complexes the two groups are readily coupled to form a five-electron hydrocarbon bridge. In order to introduce other unsaturated moieties into the anionic diiron alkenyl complexes we studied the reactions of these complexes with propargyl chloride. When equimolar amounts of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CRH)]^-$ (R = H or Ph) and $ClCH_2C{\equiv}CH$ were mixed in dichloromethane at



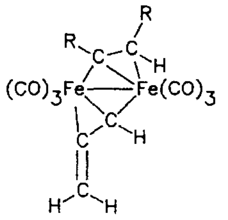
(4a)

Scheme 4.

room temperature in the presence of Tl[BF$_4$], red products of formula $Fe_2(CO)_6(\mu$-CR=CRH)(μ-CHCCH$_2$) (R = H (**5**) or Ph(**6**)) were obtained in moderate (ca 30%) yields. The elemental analyses of these new complexes are consistent with the presence of the $CH_2C{\equiv}CH$ fragment and the loss of one molecule of CO. The IR spectra of products in the ν(CO) region exhibit bands of terminal carbonyl ligands. The ^{1}H NMR spectra of $Fe_2(CO)_6(\mu$-CH=CH$_2$)(μ-CHCCH$_2$) (**5**) in CDCl$_3$ solution displays signals from the vinyl bridge at 8.15 (dd), 3.37 (d) and 2.38 (d) ppm with $J(H{-}H_{cis})$ of 8.8 Hz and $J(H{-}H_{trans})$ of 13.5 Hz. These values are similar to those for other neutral vinyl-bridged diiron complexes [21]. The signals of the propargyl ligands appear at 7.39 (t), 5.45 (t) and 4.81 (t) ppm, with a J(H–H) of 4.4 Hz. The ^{13}C NMR spectrum of the compound **5** contains signals from the coordinated ligands at 72.9 (t), 93.19 (t), 127.82 (d), 170.40 (d), 175.5 (s) and 209.59 (br, CO), with normal J(C–H) couplings for this type of ligand [23]. The ^{1}H NMR spectrum of $Fe_2(CO)_6(\mu$-CPh=CPh)(μ-CHCCH$_2$) (**6**) displays signals from the propargyl ligand at 7.46 (t), 5.71 (t) and 5.06 (t) ppm, whereas the alkenyl hydrogen signal is observed at 3.26 ppm. These spectroscopic data suggest that the two complexes (**5** and **6**) have the same structure, in which the two bridging alkenyl and propargyl ligands act as three-electron groups (Fig. 2). Very similar compounds $Fe_2(CO)_6(\mu$-SR)(μ-CHCCH$_2$) were previously prepared by Seyferth et al. [23], and gave comparable ^{13}C NMR data, but in the ^{1}H NMR spectrum the =CH$_2$ protons give rise to a triplet ($J = 4.9$ Hz). This equivalence of methylene hydrogens was attributed to the dynamic behaviour of the propargyl group [24].

Experimental

All manipulations were performed under nitrogen by conventional Schlenk techniques. IR spectra were recorded on a Perkin–Elmer 1710 FT spectrometer with THF (anionic compounds) or hexane (neutral compounds) solutions. ^{1}H NMR spectra were recorded on a Bruker WM 250 or Bruker AM 400 spectrometer with



R=H(5);R=Ph(6)

Fig. 2.

$CDCl_3$ solutions, and the ^{13}C spectra on the former instrument. Elemental analyses were performed with a Perkin–Elmer 240B analyzer.

The $Na_2[Fe_2(CO)_8]$ [25], $[PPh_4][HFe(CO)_4]$ [10], and $[PPh_4][Fe(CHO)(CO)_4]$ [17] were prepared by published procedures. Complexes **1**, **2**, **4a** and **4b** were also synthesized by other methods [4,5].

Synthesis of $[PPh_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)]$ (1)

A stoichiometric amount of trifluoroacetic acid was slowly added to a suspension of 0.32 g (0.83 mmol) of $Na_2[Fe_2(CO)_8]$ in 30 ml of THF. The solution was stirred and acetylene $HC{\equiv}CH$ was bubbled in for 5 min. Stirring was continued for 15 min and the solution was then filtered and evaporated to dryness. The residue was dissolved in a minimum of dichloromethane, and addition of PPh_4Br in methanol produced a precipitate of the crystalline complex **1**, which was filtered off and washed with methanol; yield, 90%.

Synthesis of $[PPh_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CRH)]$ ($R = Ph$ (2) and Me_3Si (3))

A mixture of 0.32 g (0.83 mmol) of $Na_2[Fe_2(CO)_8]$ and an equimolar quantity (0.83 mmol) of $RC{\equiv}CR$ ($R = Ph$ or Me_3Si) in 30 ml of THF was stirred and a stoichiometric amount of trifluoroacetic acid was slowly added. After 15 min the solution was filtered and evaporated to dryness, and the residue dissolved in a minimum of dichloromethane. Addition of PPh_4Br led to precipitation of the salt **2** or **3**, which was filtered off and washed with methanol. The yields were 85 ($R = Ph$ (**2**)) and 40% ($R = Me_3Si$ (**3**)).

3: IR: ν(CO) 2013w, 1974vs, 1919vs, 1877s cm^{-1}. ^1H NMR (ppm): 7.72 (m, 20H); 1.67 (s, 1H); 0.2 (s, 9H). Anal. Found: C, 58.1; H, 4.34. $C_{39}H_{39}O_7PSiFe_2$ calc. C, 57.1; H, 4.77%.

Synthesis of $[PPh_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CPh{=}CPhH)]$ (2) by Methods D and E

$Na[BH_4]$ (0.05 g) was added to a solution of 0.5 g (1.37 mmol) of $Fe_2(CO)_9$ (Method D) or 0.7 g (1.37 mmol) of $Fe_3(CO)_{12}$ (Method E) and 0.24 g (1.37 mmol) of $PhC{\equiv}CPh$ in 30 ml of THF. The mixture was stirred for 1 h, filtered through Celite, and the filtrate evaporated to dryness. The solid residue was dissolved in a minimum of methanol and a slight excess of PPh_4Br in methanol was added. A red crystalline solid **2** which separated was filtered off and washed with methanol. The yields were 40 (Method D) and 45% (Method E).

Synthesis of $[PPh_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CPh{=}CPhH)]$ *(2) by Method F*

To a THF solution (30 ml) containing 0.5 g (0.93 mmol) of $[PPh_4][Fe(CHO)(CO)_4]$ and 0.5 g (1.37 mmol) of $Fe_2(CO)_9$ was added 0.18 g (1 mmol) of $PhC{\equiv}CPh$. The mixture was stirred for 1 h, filtered through Celite, and the filtrate evaporated to dryness. The residue **2** was recrystallized from dichloromethane–methanol; yield, 80%.

Synthesis of $[PPh_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CH{=}CPhH)]$ *(4a) by Method G*

A mixture of 0.32 g (0.83 mmol) of $Na_2[Fe_2(CO)_8]$ and 0.14 g (0.83 mmol) of $ClC(O)CH{=}CPhH$ in 30 ml of THF was stirred for 12 h then filtered. The filtrate was evaporated to dryness and the residue dissolved in a minimum of dichloromethane. A slight excess of PPh_4Br in methanol was added, and the resulting precipitate was filtered off and dried *in vacuo*; yield, 50%.

Synthesis of $Fe_2(CO)_6(\mu\text{-}CR{=}CRH)(\mu\text{-}CHCCH_2)$ *(R = H (5) and Ph (6))*

To a solution of 2.4 mmol of $[PPh_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CRH)]$ (R = H and Ph) in 30 ml of CH_2Cl_2 were added 0.69 g (2.4 mmol) of $TlBF_4$ and 0.3 ml (4.2 mmol) of $ClCH_2C{\equiv}CH$. The mixture was stirred for 2 h and then evaporated to dryness. The residue was chromatographed on a silica column with hexane as eluent. The orange fractions were evaporated to dryness and the products recrystallized from dichloromethane–methanol. The yields were 35 (R = H (**5**)) and 26% (R = Ph (**6**)).

5: IR; ν(CO) 2078s, 2044vs, 2012vs, 2010vs, 2000sh cm^{-1}. ^1H NMR (ppm): 8.15 (dd, J_1 8.8, J_2 13.5 Hz, 1H); 7.39 (t, J 4.4 Hz, 1H); 5.45 (t, J 4.4 Hz, 1H); 4.81 (t, J 4.4 Hz, 1H); 3.37 (d, J 8.8 Hz, 1H); 2.38 (d, J 13.5 Hz, 1H). ^{13}C NMR (CD_2Cl_2) (ppm): 209.59 (br, CO); 175.5 (s, CH–*C*=); 170.40 (d, J 152.5 Hz, *C*H=CH_2); 127.82 (d, J 163.5 Hz, *C*H–C=); 93.19 (d, J 165.9 Hz, C=*C*H_2); 72.91 (t, J 160.9 Hz, CH=*C*H_2). Anal. Found: C, 37.9; H, 1.78. $C_{11}H_6O_6Fe_2$ calc.: C, 38.20; H, 1.74%.

6: IR: ν(CO) 2069s, 2044vs, 2008vs, 2003vs, 1990sh cm^{-1}. ^1H NMR (ppm): 7.46 (t, J 4.4 Hz, 1H); 6.5–7.1 (m, 10H); 5.71 (t, J 4.7 Hz, 1H); 5.06 (t, J 4.7 Hz, 1H); 3.26 (s, 1H). Anal. Found: C, 55.1; H, 2.8. $C_{23}H_{14}O_6Fe_2$ calc.: C, 55.48; H, 2.81%.

Acknowledgements

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