

A Versatile Synthetic Method for Diiron Bridging Allenylidene Complexes ($\eta^5\text{-C}_5\text{Me}_5$)₂Fe₂($\mu\text{-CO}$)(CO)₂($\mu\text{-}\eta^1$: $\eta^1\text{-C=C=CR}^1\text{R}^2$) via Nucleophilic Addition to the Ethynediyliron Complex ($\mu\text{-C}\equiv\text{C}$)[Fe($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂]₂

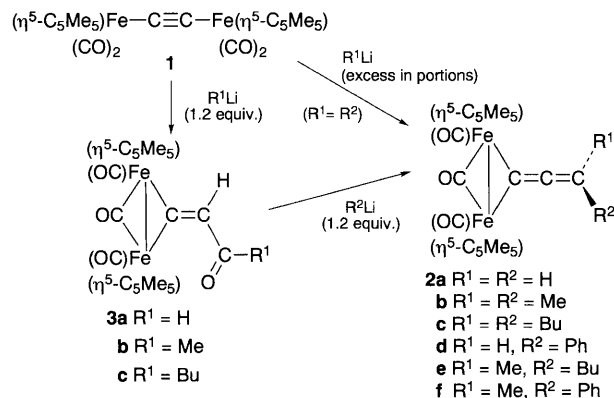
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Addition of an excess amount of nucleophile (alkyllithium or LiHBEt₃) to the ethynediyliron complex ($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂Fe-C≡C-Fe($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂ **1** in portions, affords a variety of diiron bridging allenylidene complexes ($\eta^5\text{-C}_5\text{Me}_5$)₂Fe₂($\mu\text{-CO}$)(CO)₂($\mu\text{-C=C=CR}^1\text{R}^2$) **2** (R¹, R² = H, Me, Bu, Ph) including the parent compound **2a** (R¹ = R² = H).

Unsaturated, carbon-rich hydrocarbyl species attached to a transition metal system have been recently attracting increasing attention because of their reactivity relevant to surface species as well as their unique physical properties.¹ In sharp contrast to the well-established vinylidene complexes [M_n(C=CR₂)],² the chemistry of their next higher homologues, *i.e.* allenylidene complexes [M_n(C=C=CR₂)], is not so extensively explored, mainly owing to their limited accessibility. In addition, most of the previous examples contain sterically demanding or unsaturated substituents (*e.g.* Pr^t, Bu^t, Ph, CN) that may hinder attack at the allenylidene terminus and, to our knowledge, even the mono-substituted derivative [M_n(C=C=CHR)] has not been reported so far.² Herein we report a novel synthetic method for diiron μ -allenylidene complexes ($\eta^5\text{-C}_5\text{Me}_5$)₂Fe₂($\mu\text{-CO}$)(CO)₂($\mu\text{-C=C=CR}^1\text{R}^2$) **2** via carbon chain elongation of the C₂ bridge in the ethynediyliron complex ($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂Fe-C≡C-Fe($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂ **1**,^{3b} another carbon-rich metal complex (a carbon-metal rod).^{1,3} The first example of the parent compound **2a** (R¹ = R² = H) has also been prepared and fully characterised.

Previously we disclosed the nucleophilic addition reaction of alkyllithiums (1 equiv.) to the ethynediyl complex **1** giving the acyl-substituted μ -vinylidene complexes ($\eta^5\text{-C}_5\text{Me}_5$)₂Fe₂($\mu\text{-CO}$)(CO)₂($\mu\text{-C=C(H)-C(O)-R}$) **3** (Scheme 1).^{3c,d} However, when an excess amount of the nucleophile (RLi, LiHBEt₃) was added to a THF solution of **1** in portions, sequential formation of **3** followed by deep red-purple complexes **2a-c**† were observed. The amount of the nucleophile was adjusted to maximize the yield of **2**, because addition of too much nucleophile would decompose the product. Compounds **2** were obtained in moderate yields [**2b** (29%), **2c** (35%)] after chromatographic separation. Although the IR spectra of **2** are very close to those of the vinylidene complexes [*cf.* ($\eta^5\text{-C}_5\text{Me}_5$)₂Fe₂($\mu\text{-CO}$)(CO)₂($\mu\text{-C=CH}_2$) $\nu(\text{C}\equiv\text{O})/\text{IR}(\text{KBr})$ cm⁻¹ 1923 and 1772]^{3c} they are characterized as the diiron μ -allenylidene complexes ($\eta^5\text{-C}_5\text{Me}_5$)₂Fe₂($\mu\text{-CO}$)(CO)₂($\mu\text{-C}_\alpha\text{=C}_\beta\text{=C}_\gamma\text{R}_2$) on the basis of (i) the spectroscopic data indicate a C₂ symmetrical structure and (ii) the three carbon signals appearing around δ_{C} 100 (C_γ), 200 (C_α) and 210 (C_β). These signals are assigned unequivocally by the J_{C-H} coupling of the



parent allenylidene compound **2a** (C_γ δ 77.6, t, ¹J 167 Hz) and the phenyl derivative **2d** (C_γ δ 97.3, d, ¹J 161 Hz; C_α δ 193.8, s; C_β δ 200.6, d, ²J 9.8 Hz). The molecular structures of **2a**, **b** determined by X-ray crystallography (Fig. 1; see also the structure of **2a** in the graphical abstract)[†] exhibits the features of the dinuclear $\mu\text{-}\eta^1$: η^1 -allenylidene complexes:² (i) linear C=C=C linkage: 179(1) **2a**, 176(1), 177.3(10)° (**2b** contains two independent molecules); (ii) C_β-C_γ is slightly longer than C_α-C_β: 1.32(2) > 1.29(1) Å **2a**, 1.34(1) > 1.26(1) Å, 1.38(1) > 1.26(1) Å **2b**; (iii) the Fe₂C_α plane lies almost perpendicular to the C₁R₂ plane [Fig. 1(b)]. Although we anticipated that the allenylidene terminus might be sterically shielded by the η^5 -

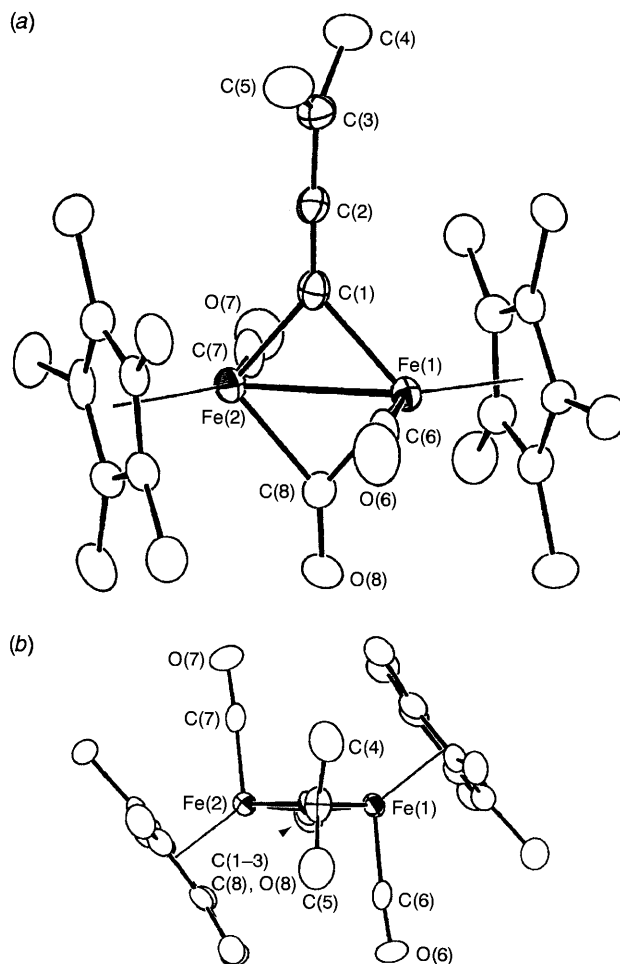


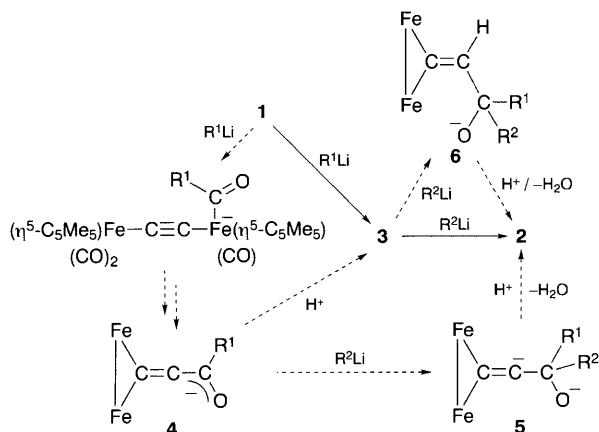
Fig. 1 ORTEP views of **2b** drawn at the 30% probability level. (a) An overview. (b) A side view. Important bond lengths (Å) and angles (°): Fe(1)-Fe(2) 2.562(2), Fe(1)-C(1) 1.951(9), Fe(2)-C(1) 1.989(9), C(1)-C(2) 1.26(1), C(2)-C(3) 1.34(1), C(3)-C(4) 1.51(2), C(3)-C(5) 1.45(2); Fe(2)-Fe(1)-C(1) 50.1(3), Fe(1)-Fe(2)-C(1) 48.8(3), Fe(1)-C(1)-Fe(2) 81.1(4), Fe(1)-C(1)-C(2) 139.1(7), Fe(2)-C(1)-C(2) 139.8(7), C(1)-C(2)-C(3) 176(1), C(2)-C(3)-C(4) 123(1), C(2)-C(3)-C(5) 126(1), C(4)-C(3)-C(5) 111(1).

C_5Me_5 rings, no apparent interaction was detected as can be seen from the side view. Similar structural features were observed for **2a**.

These aspects of the reaction suggested that the acylated vinylidene complex **3** might be an intermediate in the formation of **2**. Therefore, a sample of **3**§ was subjected to the nucleophilic reaction. As a result, the allenylidene complexes **2** were obtained [**2a** (53% based on **3a**), **2d** (39% based on **3a**), **2e** (52% based on **3b**), **2f** (80% based on **3b**)] after simple extraction followed by recrystallisation. A pure sample of **2a** was obtained by this method, because, in the one-pot synthesis, **2a** decomposed to a considerable extent during chromatographic separation. In addition, the monosubstituted ($R^1 = H$) and unsymmetrically substituted complexes ($R^1 \neq R^2$) **2d-f** have been prepared successfully through this two-step procedure.

A plausible mechanism for the formation of the allenylidene complexes **2** is summarized in Scheme 2. Treatment with the first equivalent of nucleophile results in the formation of the anionic intermediate **4** by nucleophilic addition to CO followed by coupling of the resultant acyl functional group and the $(\eta^5-C_5Me_5)-C=C$ moiety|| as discussed previously.^{3c} Protonation of **4** leads to the formation of **3**, whereas subsequent addition of the second equivalent of nucleophile to the acyl part in **4** may form the dianionic alkoxide intermediate **5**, which is transformed to **2** by sequential protonation and dehydration. In the conversion of **3** into **2**, the similar monoanionic species **6** may be an intermediate. The most popular synthetic method of allenylidene complexes is formal dehydration of prop-2-ynyl alcohol derivative within a metal coordination sphere.² The present method is also recognised as a variation of this process, *i.e.* dehydration of the prop-2-ynyl alcohol-type skeleton resulting from the intramolecular coupling of the acetylide and the acyl functional group.||

Thus the reaction of **1** with RLi affords different types of products depending on the addition procedure.^{3c,d†} It has proved that the present method serves as a versatile synthetic method for a variety of μ -allenylidene complexes **2**.



Scheme 2

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Footnotes

† Selected spectral data for **2a**: 1H NMR (C_6D_6) δ 1.59 [30 H, s, $(\eta^5-C_5Me_5)_2$], 5.47 (2 H, s, CH_2); ^{13}C NMR (C_6D_6) δ 9.1 (q, J 127 Hz, C_5Me_5), 77.6 (t, J 167 Hz, $=CH_2$), 97.9 (s, C_5Me_5), 202.3 (s, C_α), 206.5 (s, C_β), 214.7 (s, CO), 276.4 (s, $\mu-CO$); IR (KBr) $\nu(C=O)/cm^{-1}$ 1928 and 1767. Typical experimental procedure—the one-pot synthesis of **2c**: To a stirred THF solution (16 cm^3) of **1** (253 mg, 0.49 mmol) cooled at $-78^\circ C$ was added BuLi (1.6 mol dm^{-3} hexane solution, 0.40 cm^3 , 0.64 mmol). After 10 min the mixture was stirred for 1 h at ambient temperature and then recooled. The addition was then repeated with the same amounts of BuLi until the amount of **2c** became maximum (TLC). MeOH-treatment (2 cm^3) and diethyl ether extraction followed by alumina column chromatography (hexane elution) afforded the deep-purple complex **2c** (106 mg, 0.17 mmol, 35%). Addition of excess RLi in one portion produced another product.

‡ Crystal data for **2a**: $C_{26}H_{32}O_3Fe_2$, $M = 504.2$, space group $P2_1/n$, $a = 10.212(2)$, $b = 13.787(2)$, $c = 17.235(4)$ Å, $\beta = 99.16(2)^\circ$, $V = 2395.7(9)$ cm^3 , $Z = 4$, $D_c = 1.40$, $R(R_w) = 0.047$ (0.041) for 1507 unique reflections with $I > 3\sigma(I)$ and 288 variables. For **2b**: $C_{28}H_{36}O_3Fe_2$, $M = 532.3$, space group Cc , $a = 9.592(4)$, $b = 64.74(2)$, $c = 9.626(4)$ Å, $\beta = 119.85(3)^\circ$, $V = 5185(3)$ cm^3 , $Z = 8$, $D_c = 1.36$, $R(R_w) = 0.044$ (0.046) for 3847 unique reflections with $I > 3\sigma(I)$ and 593 variables (the unit cell contains two independent molecules). The data were collected on a Rigaku AFC5R diffractometer, and the structure was solved by a combination of the direct methods (SAPI91) and Fourier syntheses. All the non-hydrogen atoms were refined anisotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The new compounds **3a,b** were prepared by the reaction of **1** with $LiHBEt_3$ and MeLi, respectively, following the procedure described in ref. 3c.

¶ The reaction of **3a** with alkylolithiums such as MeLi and BuLi ($R'CH_2Li$) gave **2** in very low yields. Instead the alkenyl vinylidene complexes [$(\eta^5-C_5Me_5)_2Fe_2(CO)_3\{\mu-C=C(H)-C(H)=C(H)R'\}$] were obtained as predominant products.

|| Mononuclear acetylide complexes also reacted with RLi to give alkenyl complexes *via* a similar C-C coupling reaction. See ref. 4.

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