# A Versatile Synthetic Method for Diiron Bridging Allenylidene Complexes $(\eta^5\text{-}C_5Me_5)_2Fe_2(\mu\text{-}CO)(CO)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C{=}C{=}CR^1R^2)$ *via* Nucleophilic Addition to the Ethynediyldiiron Complex $(\mu\text{-}C{\equiv}C)[Fe(\eta^5\text{-}C_5Me_5)(CO)_2]_2$

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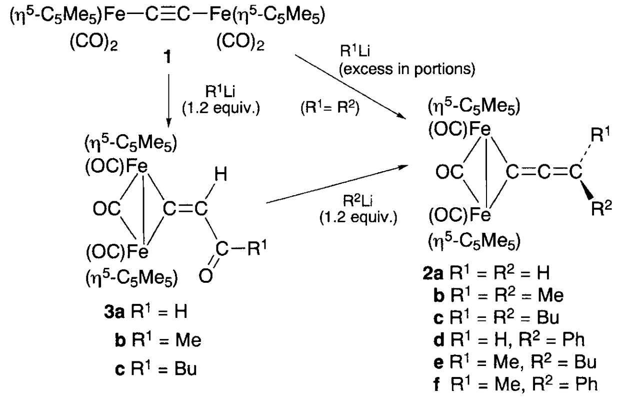
Addition of an excess amount of nucleophile (alkyllithium or $LiHBEt_3$) to the ethynediyldiiron complex $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{-}C{\equiv}C\text{-}Fe(\eta^5\text{-}C_5Me_5)(CO)_2$ **1** in portions, affords a variety of diiron bridging allenylidene complexes $(\eta^5\text{-}C_5Me_5)_2Fe_2(\mu\text{-}CO)(CO)_2(\mu\text{-}C{=}C{=}CR^1R^2)$ **2** ($R^1$, $R^2$ = H, Me, Bu, Ph) including the parent compound **2a** ($R^1$ = $R^2$ = 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 $[M_n(C{=}CR_2)]$,[2] the chemistry of their next higher homologues, *i.e.* allenylidene complexes $[M_n(C{=}C{=}CR_2)]$, 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.* $Pr^i$, $Bu^t$, 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 $(\eta^5\text{-}C_5Me_5)_2Fe_2(\mu\text{-}CO)(CO)_2(\mu\text{-}C{=}C{=}CR^1R^2)$ **2** *via* carbon chain elongation of the $C_2$ bridge in the ethynediyldiiron complex $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{-}C{\equiv}C\text{-}Fe(\eta^5\text{-}C_5Me_5)(CO)_2$ **1**,[3b] another carbon-rich metal complex (a carbon-metal rod).[1,3] The first example of the parent compound **2a** ($R^1$ = $R^2$ = 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 $(\eta^5\text{-}C_5Me_5)_2Fe_2(\mu\text{-}CO)(CO)_2[\mu\text{-}C{=}C(H)\text{-}C({=}O)\text{-}R]$ **3** (Scheme 1).[3c,d] However, when an excess amount of the nucleophile (RLi, $LiHBEt_3$) 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.* $(\eta^5\text{-}C_5Me_5)_2Fe_2(\mu\text{-}CO)(CO)_2(\mu\text{-}C{=}CH_2)$ $\nu(C{\equiv}O)$/IR(KBr) $cm^{-1}$ 1923 and 1772][3c] they are characterized as the diiron μ-allenylidene complexes $(\eta^5\text{-}C_5Me_5)_2Fe_2(\mu\text{-}CO)(CO)_2(\mu\text{-}C_\alpha{=}C_\beta{=}C_\gamma R_2)$ on the basis of (i) the spectroscopic data indicate a $C_2$ symmetrical structure and (ii) the three carbon signals appearing around $\delta_C$ 100 ($C_\gamma$), 200 ($C_\alpha$) and 210 ($C_\beta$). These signals are assigned unequivocally by the $J_{C\text{-}H}$ coupling of the parent allenylidene compound **2a** ($C_\gamma$ δ 77.6, t, ${}^1J$ 167 Hz) and the phenyl derivative **2d** ($C_\gamma$ δ 97.3, d, ${}^1J$ 161 Hz; $C_\alpha$ δ 193.8, s; $C_\beta$ 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 $\mu\text{-}\eta^1{:}\eta^1$-allenylidene complexes:[2] (i) linear C=C=C linkage: 179(1) **2a**, 176(1), 177.3(10)° (**2b** contains two independent molecules); (ii) $C_\beta\text{-}C_\gamma$ is slightly longer than $C_\alpha\text{-}C_\beta$: 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 $Fe_2C_\alpha$ plane lies almost perpendicular to the $C_\gamma R_2$ plane [Fig. 1(*b*)]. Although we anticipated that the allenylidene terminus might be sterically shielded by the $\eta^5$-



**3a** $R^1$ = H
**b** $R^1$ = Me
**c** $R^1$ = Bu

**2a** $R^1$ = $R^2$ = H
**b** $R^1$ = $R^2$ = Me
**c** $R^1$ = $R^2$ = Bu
**d** $R^1$ = H, $R^2$ = Ph
**e** $R^1$ = Me, $R^2$ = Bu
**f** $R^1$ = Me, $R^2$ = Ph

**Scheme 1**

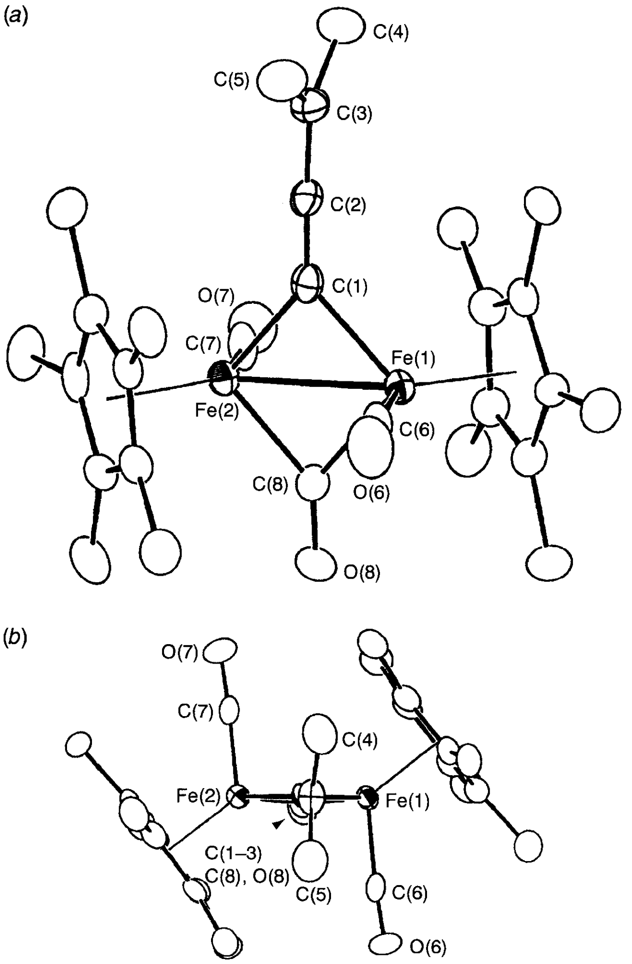


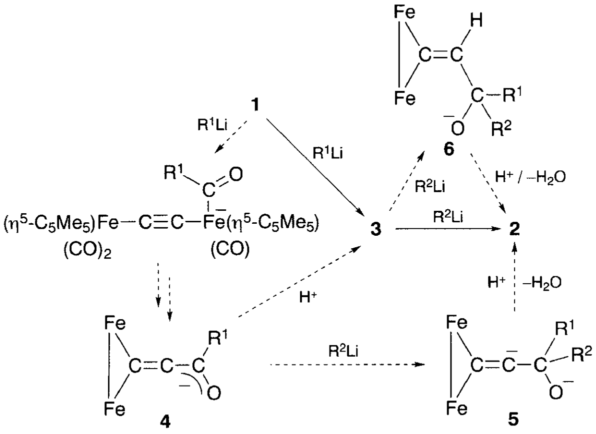
**Fig. 1** ORTEP views of **2b** drawn at the 30% probability level. (*a*) An overview. (*b*) A side view. Important bond lengths (Å) and angles (°): Fe(1)–Fe(2) 2.562(2), Fe(1)–C(1) 1.951(9), Fe(2)–C(1) 1.989(9), C(1)–C(2) 1.26(1), C(2)–C(3) 1.34(1), C(3)–C(4) 1.51(2), C(3)–C(5) 1.45(2); Fe(2)–Fe(1)–C(1) 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**

This work was supported financially by the Ministry of Education, Science and Culture of the Japanese Government (Grant-in-Aid for Scientific Research for Priority Area: No. 05236103).

*Received, 13th March 1995; Com. 5/01588J*

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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, $C_5$*Me*$_5$), 77.6 (t, *J* 167 Hz, =$CH_2$), 97.9 (s, $C_5Me_5$), 202.3 (s, $C_\alpha$), 206.5 (s, $C_\beta$), 214.7 (s, CO), 276.4 (s, μ-CO); IR (KBr) ν(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 °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, β = 99.16(2)°, $V$ = 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, β = 119.85(3)°, $V$ = 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. 3*c*.

¶ The reaction of **3a** with alkyllithiums such as MeLi and BuLi (R′$CH_2$Li) gave **2** in very low yields. Instead the alkenyl vinylidene complexes [($\eta^5$-$C_5Me_5)_2Fe_2(CO)_3${μ-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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