

Photochemical C–C coupling reaction of an iron acetylide complex $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}\equiv\text{CPh})]$ with alk-1-ynes ($\text{RC}\equiv\text{CH}$) leading to cyclic compounds including paramagnetic iron(II) cyclopentadienone complexes $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-2-Ph-5-R-C}_5\text{H}_2\text{O})]$

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Photolysis of $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}\equiv\text{CPh})]$ with methyl propynoate which bears a coordinating substituent (CO_2Me) affords a metallabicyclic compound incorporating two molecules of the alkyne, whereas the reaction with alk-1-ynes ($\text{RC}\equiv\text{CH}$) bearing a non-coordinating substituent ($\text{R} = \text{alkyl, Ph, SiMe}_3$) produces paramagnetic 17e iron(II)-cyclopentadienone complexes $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-2-Ph-5-R-C}_5\text{H}_2\text{O})]$.

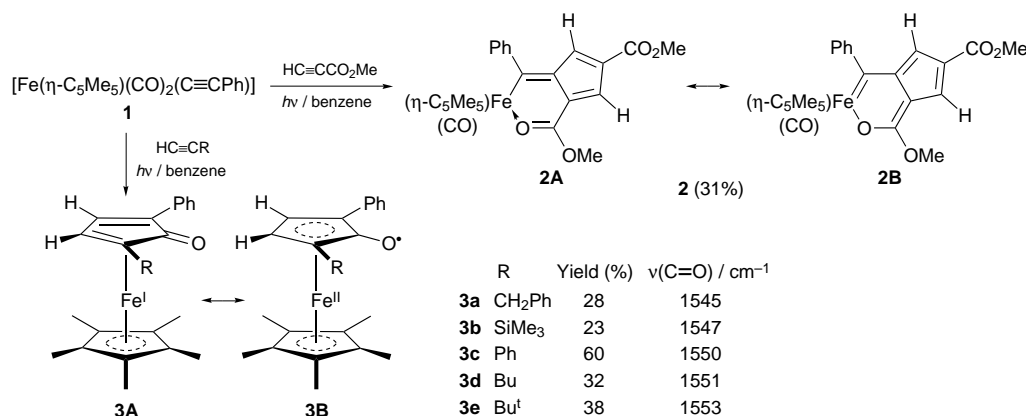
C–C coupling reactions of alkynes have been realized by the action of a transition-metal species.¹ One versatile transformation is insertion into an M–C bond leading to oligomeric or polymeric conjugated systems.² In a previous paper, we reported the photochemical dimerization of iron acetylides $[\text{Fe}(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}\equiv\text{CR})]$ ($\text{R} = \text{H, Ph}$), giving dinuclear complexes with an enyne ligand.³ The study reveals that, when a $\text{C}\equiv\text{C}$ group is introduced into the coordination sphere of the acetylide complex, insertion takes place quite readily. Herein we disclose photochemical reactions of the phenylacetylide complex with alk-1-ynes leading to cyclic products including iron(II) cyclopentadienone complexes.⁴

Irradiation of a benzene solution of $[\text{Fe}(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}\equiv\text{CPh})]$ **1** with a high-pressure mercury lamp in the presence of methyl propynoate (5 equiv.) afforded a red-brown complex **2** in 31% yield (Scheme 1). The NMR spectrum of the mononuclear complex **2**† showed two MeO signals [$\delta_{\text{H}}(\text{CDCl}_3)$ 3.74, 3.80] and revealed the incorporation of two molecules of the alkyne. The bicyclic structure of **2** has been determined by X-ray crystallography (Fig. 1)‡ and the contribution of a carbene structure **2B** in addition to the dominant resonance structure **2A** is evident as indicated by the structural parameters as well as the spectroscopic data [$\delta_{\text{C}}(\text{C}2)$ 280.7 (s), $\nu[\text{C}(23)=\text{O}(3)]$ 1600 cm^{-1}].

In contrast to the reaction with alk-1-yne bearing a coordinating substituent (CO_2R) mentioned above, the photochemical reaction with alk-1-ynes ($\text{RC}\equiv\text{CH}$) bearing a non-coordinating

substituent (R) afforded air-stable orange products **3** ($\text{R} = \text{CH}_2\text{Ph}$ **a**, SiMe_3 **b**, Ph **c**, Bu **d**, Bu^t **e**) after separation by alumina column chromatography. The striking features of **3** are (i) paramagnetism, (ii) loss of the $\nu(\text{C}\equiv\text{O})$ absorption, and (iii) the appearance of an IR absorption around 1550 cm^{-1} (KBr) which is assignable to a $\nu(\text{C}=\text{O})$ vibration. Complex **3** has been characterized as a 17e iron(II) cyclopentadienone complex, $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-2-Ph-5-R-C}_5\text{H}_2\text{O})]$, on the basis of the results of X-ray crystallography of the SiMe_3 and Ph derivatives **3b,c**.§ A view of **3c** is shown in Fig. 2. The Fe–C(1) distance [2.22(1) Å] is substantially longer than the Fe–C(2)–(5) distances [2.090(9), 2.029(9), 2.028(9), 2.075(9) Å; suggesting that the cyclopentadienone ring C(1)–(5) is coordinated to the Fe centre essentially in an η^4 -mode (**3A**) [C(1)–C(2) 1.43(1), C(1)–C(5) 1.48(1), C(2)–C(3) 1.42(1), C(3)–C(4) 1.50(1), C(4)–C(5) 1.42(1) Å], like an η^4 -diene ligand. However, the considerably elongated C(1)–O bond [1.26(1) Å] and the lowered wave-number of the $\nu(\text{C}=\text{O})$ vibration (Scheme 1) are indicative of a minor contribution of the iron(II) η^5 -cyclopentadienoxyl structure (**3B**), where the unpaired electron is localized on the oxygen atom and the Fe centre attains an 18e configuration. The cyclopentadienone ring is located virtually parallel to the C_5Me_5 ring [Fe–C(C_5Me_5) 2.06–2.10(1) Å], and the two Ph groups at the 2 and 5 positions are arranged almost coplanar with the central five-membered ring to extend the conjugated π system.

A possible formation mechanism of **2** and **3** is summarized in Scheme 2. Initial photodecarbonylation followed by coordination of the alk-1-yne gives an η^2 -alkyne intermediate **4**. Subsequent insertion of the $\text{C}\equiv\text{C}$ moiety into the Fe–C \equiv bond with the orientation of the substituent directing toward the metal centre gives an ynenyl species **5**. In the case of the reaction with methyl propynoate, a sequence of (i) further insertion of the acetylene substrate **6**, (ii) insertion of the terminal $\text{PhC}\equiv\text{C}$ part into the Fe–C(sp^2) bond, and (iii) coordination of the ester $\text{C}=\text{O}$ moiety would give **2**. On the other hand, the reaction of



Scheme 1

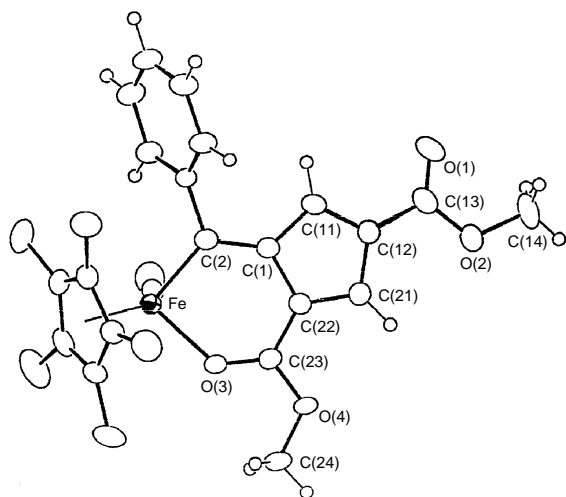


Fig. 1 Molecular structure of **2** with thermal ellipsoids drawn at the 30% probability level. Selected bond distances (Å): Fe–C(2) 1.922(4), Fe–O(3) 1.995(3), C(2)–C(1) 1.406(6), C(1)–C(11) 1.435(6), C(1)–C(22) 1.451(6), C(11)–C(12) 1.379(6), C(12)–C(21) 1.428(6), C(21)–C(22) 1.365(6), C(22)–C(23) 1.427(6), C(23)–O(3) 1.234(5), C(13)–O(1) 1.197(6).

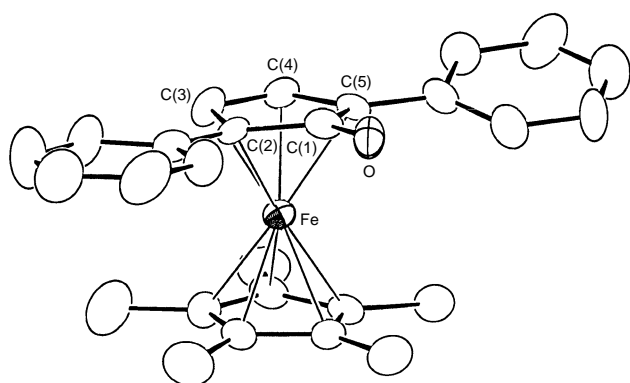
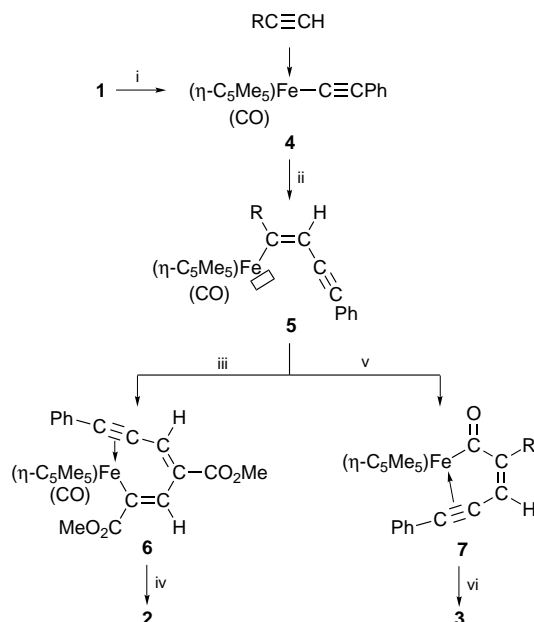


Fig. 2 An overview of **3c** with thermal ellipsoids drawn at the 30% probability level



Scheme 2 i, Photodecarbonylation and coordination of $\text{RC}\equiv\text{CH}$; ii, insertion of alk-1-yne; iii, insertion of a second molecule of alk-1-yne; iv, insertion of the $\text{PhC}\equiv\text{C}$ part and coordination of the ester $\text{C}=\text{O}$ group; v, CO insertion; vi, $\text{PhC}\equiv\text{C}$ insertion and H abstraction

alk-1-yne with a non-coordinating substituent follows CO insertion of the ynenyl moiety to form the acyl intermediate **7**. Successive ring closure *via* $\text{C}\equiv\text{C}$ insertion and H abstraction from the reaction medium gives the cyclopentadienone complex **3**. The reaction pathways may depend on the nucleophilicity of the α -carbon atom of the ynenyl group in **5** as well as the coordinating ability of the alk-1-yne substituent (R).

In summary, a $\text{C}\equiv\text{C}$ functional group incorporated in a metal coordination sphere readily inserts into the $\text{M}-\text{C}\equiv$ bond to form a conjugated system *via* $\text{C}-\text{C}$ coupling. The obtained 17e species **3**, which can be viewed as a dehydrogenated form of the classical hydroxyferrocene or a paramagnetic counterpart of well known cyclopentadienone complexes,⁴ belongs to a rare class of iron(i) compounds.⁶ Despite the paramagnetic character, **3** is air stable and passes through an alumina column. A study on the physical properties and reactivity of **3** is now under way.

Footnotes

† *Selected spectroscopic data for 2*: NMR data for the ring: $\delta_{\text{H}}(\text{CDCl}_3)$ 6.62, 7.64 [d \times 2, J 2 Hz, C(11 H) and C(21 H)], $\delta_{\text{C}}(\text{CDCl}_3)$ 280.7 [s, C(2)], 174.1 [s, C(23)], 166.6 [s, C(13)], 155.7 [t, J 7 Hz, C(12)], 148.9 [q, J 4 Hz, C(1)], 131.4, 118.3 [d \times 2, J 164 Hz, C(11) and C(21)], 116.4 [d, J 9 Hz, C(22)]. IR (KBr) $\nu(\text{C}=\text{O})$ 1927, $\nu(\text{C}=\text{O})$ 1703, 1600 cm^{-1} .

‡ *Crystallographic data: 2*: $\text{C}_{27}\text{H}_{28}\text{FeO}_5$, $M = 488.4$, triclinic, space group $P\bar{1}$, $a = 11.190(2)$, $b = 12.181(3)$, $c = 8.812(2)$ Å, $\alpha = 97.60(2)^\circ$, $\beta = 96.42(2)^\circ$, $\gamma = 90.21(2)^\circ$, $U = 1182.9(5)$ Å³, $Z = 2$, $D_{\text{c}} = 1.37$ g cm^{-3} , $R(R_{\text{w}}) = 0.046$ (0.049) for 2474 unique data with $I > 3\sigma(I)$ and 298 variables.

3c: $\text{C}_{26}\text{H}_{27}\text{FeO}$, $M = 423.4$, monoclinic, space group $P2_1/n$, $a = 11.901(5)$, $b = 9.235(6)$, $c = 19.77(1)$ Å, $\beta = 94.94(4)^\circ$, $U = 2165(2)$ Å³, $Z = 4$, $D_{\text{c}} = 1.30$ g cm^{-3} , $R(R_{\text{w}}) = 0.064$ (0.065) for 1711 unique data with $I > 3\sigma(I)$ and 262 variables.

3b: $\text{C}_{24}\text{H}_{31}\text{OSiFe}$, $M = 419.4$, monoclinic, space group $P2_1/n$, $a = 12.003(3)$, $b = 12.186(3)$, $c = 16.258(3)$ Å, $\beta = 104.90(3)^\circ$, $U = 2298(2)$ Å³, $Z = 4$, $D_{\text{c}} = 1.21$ g cm^{-3} , $R(R_{\text{w}}) = 0.078$ (0.081) for 1994 unique data with $I > 3\sigma(I)$ and 186 variables. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/320.

§ Slippage of the cyclopentadienone ring is more evident for the SiMe_3 derivative **3b** [Fe–C(1) 2.29(1), Fe–C(2) 2.09(1), Fe–C(3) 2.014(9), Fe–C(4) 1.996(9), Fe–C(5) 2.10(1) Å]; however, the relative arrangement of the ring with respect to the C_5Me_5 ligand can not be determined satisfactorily because of the severe disorder of the C_5Me_5 ligand, which was refined by using rigid models.

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