A Novel C=C Bond Cleavage in Hexacarbonyl(hexapentaene)diiron: X-Ray Crystal Structure of a Bis(μ_3,η^2-allenylidene)–Iron Complex

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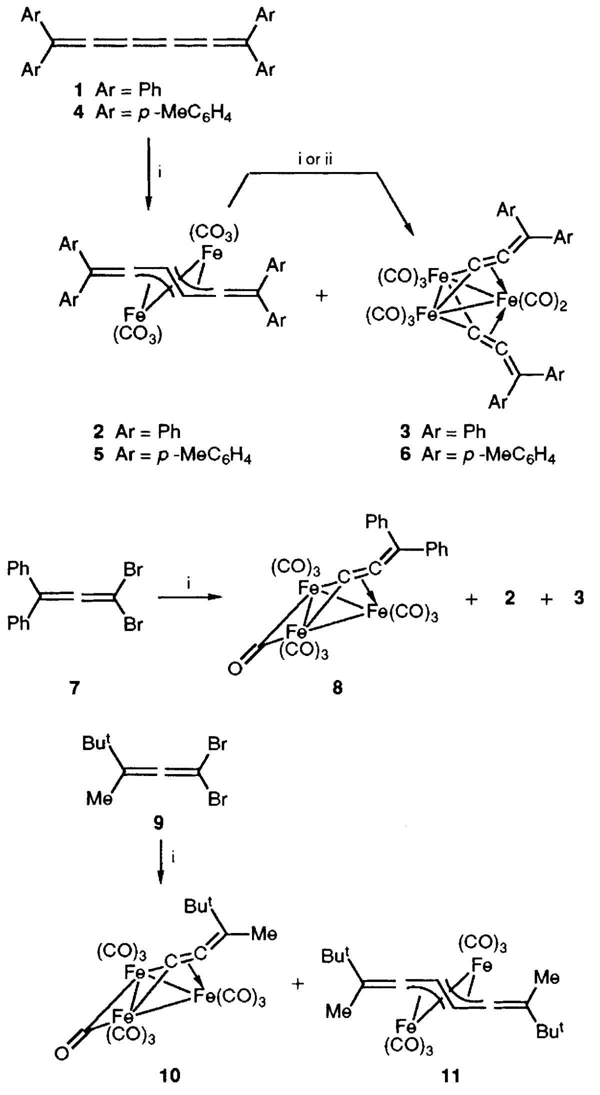
Aryl-substituted hexacarbonyl(hexapentaene)diiron complexes undergo facile intramolecular C=C bond cleavage on treatment with $[Fe_3(CO)_{12}]$ to yield the corresponding bis(μ_3,η^2-allenylidene)–iron complexes; the X-ray crystal structures of phenyl-substituted bis(μ_3,η^2-allenylidene)–iron and related allenylidene complexes are determined.

Although [5]cumulenes (hexapentaenes) have a wide variety of potential coordination sites, the structures and properties of transition metal complexes of [5]cumulenes have been little explored to date.[1] Recently, we have reported the synthesis and structures of two isomers of dodecacarbonyl(hexapentaene)tetrairon.[2] We now report a novel cleavage of the central cumulenic double bond in hexacarbonyl(tetraphenylhexapentaene)diiron.

C–C bond cleavage has been reported to occur for several transition metal complexes of electron-rich alkenes,[3] alkynes[4] and butadiynes[5] to form carbene complexes and mixed-metal clusters. In connection with our interest in the chemistry of transition metal–cumulene complexes, we have examined the reaction of tetraarylhexapentaenes with $[Fe_3(CO)_{12}]$.



Scheme 1 *Reagents and conditions*: i, $[Fe_3(CO)_{12}]$, benzene, reflux; ii, $[Fe_3(CO)_{12}]$, isooctane, reflux

Treatment of tetraphenylhexapentaene **1** with 1 equiv. of $[Fe_3(CO)_{12}]$ in refluxing benzene for 2 h produces hexacarbonyl(tetraphenylhexapentaene)diiron **2** (red prisms, m.p. 79.5–81.0 °C) in 55% yield, together with a small amount of the trinuclear complex **3** as a by-product [dark red prisms, m.p. 175–178 °C (decomp.), 4%]. The trinuclear complex **3** can be prepared in 27–44% yields by the reaction of **2** with 1 equiv. of $[Fe_3(CO)_{12}]$ in refluxing benzene or isooctane. Similar treatment of tetrakis(*p*-tolyl)hexapentaene **4** with 1 equiv. of $[Fe_3(CO)_{12}]$ in refluxing benzene for 2 h also produces the dinuclear complex **5** in 61% yield (red needles, m.p. 128–129.5 °C) and the trinuclear complex **6** in 7% yield (dark red prisms, decomp. above 185 °C). The dinuclear complex **4** can be converted into the trinuclear complex **5** in 34% yield by treatment with $[Fe_3(CO)_{12}]$ (1 equiv.) in refluxing isooctane.

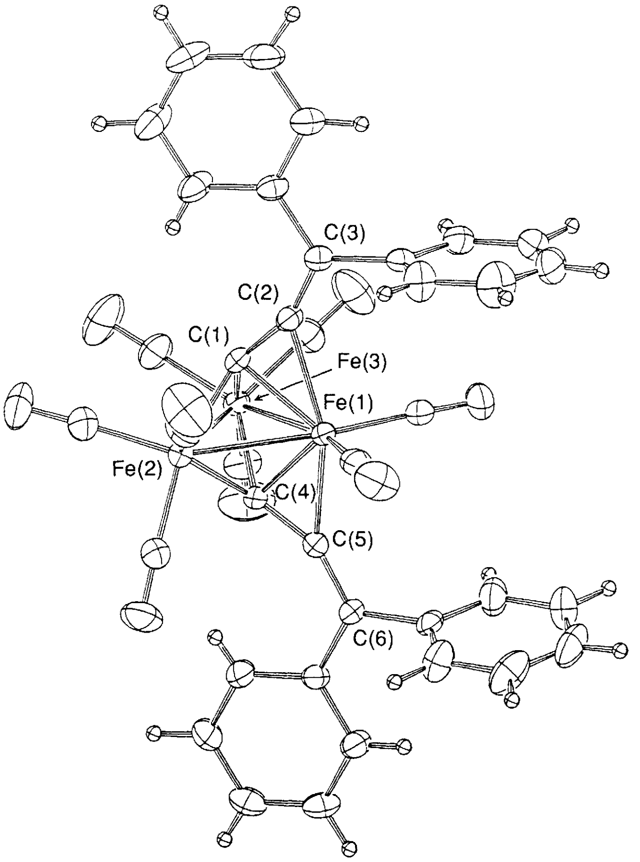


Fig. 1 ORTEP drawing of **3**. Selected bond distances (Å) and angles (°) are as follows: Fe(1)–Fe(2) 2.534(1), Fe(1)–Fe(3) 2.537(1), Fe(2)–Fe(3) 2.537(1), Fe(1)–C(1) 1.989(3), Fe(1)–C(2) 2.157(4), Fe(1)–C(4) 1.900(3), Fe(1)–C(5) 2.098(4), Fe(2)–C(1) 1.948(4), Fe(2)–C(4) 1.941(4), Fe(3)–C(1) 1.955(4), Fe(3)–C(4) 1.935(4), C(1)–C(2) 1.334(5), C(2)–C(3) 1.325(5), C(4)–C(5) 1.337(5), C(5)–C(6) 1.333(5), Fe(1)–Fe(2)–Fe(3) 60.04(2), Fe(2)–Fe(1)–Fe(3) 60.05(2), Fe(1)–Fe(3)–Fe(2) 59.91(2), Fe(2)–C(1)–Fe(3) 81.1(1), Fe(2)–C(4)–Fe(3) 81.8(1), C(1)–C(2)–C(3) 157.7(4), C(4)–C(5)–C(6) 152.8(4).

Interestingly, the reaction of 1,1-dibromo-3,3-diphenylallene **7** with 1 equiv. of $[Fe_3(CO)_{12}]$ in refluxing benzene for 3 h yields the allenylidene complex **8** [dark green prisms, m.p. 131–133 °C (decomp.), 1.5%], **2** (4%) and **3** (1%). Similarly, the reaction of 1,1-dibromo-3,4,4-trimethylpenta-1,2-diene **9** with 1 equiv. of $[Fe_3(CO)_{12}]$ in refluxing benzene produces the allenylidene complex **10** (black crystals, m.p. 88–89 °C) in 17% yield with the corresponding hexapentaene complex **11** (dark red crystals, m.p. 146.5–148 °C, 1.5%). The formation of **2** and **11** can be explained by dimerization of **8** and **10**, respectively, and further reaction of **2** with $[Fe_3(CO)_{12}]$ results in the formation of **3**.

The NMR spectra of **3** and **6** reflect their symmetrical structures. Thus, the ^1H and ^{13}C NMR spectra of **3** and **6** show the presence of two different aromatic rings and only three signals of the allenylidene carbon skeleton (**3**, δ 293.2, 160.0 and 124.3; **6**, 292.5, 158.7 and 124.3). In addition, only two carbonyl carbon ^{13}C NMR signals are observed. The ^{13}C NMR spectrum of **8** reveals three allenylidene carbons (δ 233.4, 169.1 and 122.9), as for **3**. The IR spectrum of **8** shows an absorption at 1870 cm^{-1} which indicates the existence of a carbonyl bridge.

The molecular structure of **3** was confirmed by X-ray diffraction.† As shown in Fig. 1, **3** has approximate C_{2v} symmetry. The three iron atoms are arranged at the vertices of an equilateral triangle and the two carbonyl groups attached to Fe(1) are located in the plane defined by the three iron atoms. Two phenyl groups located above and below Fe(1) are parallel to this plane at a distance of about 3.3 Å from each other. The α-carbon atoms C(1) and C(4) are attached to Fe(2) and Fe(3) with a 'carbene-like' bond, and both C(1)–C(2) and C(4)–C(5) bonds are η^2-coordinated to Fe(1). The distance between C(1) and C(4) is 2.56 Å, indicating definitely that C=C bond cleavage has occurred. The two η^2-ligands are coordinated to Fe(1) on each side of the iron triangle, and the six carbon atoms of the two allenylidene moieties and Fe(1) are coplanar. The maximum deviation from the least-squares plane of the seven atoms is 0.02 Å and this plane is perpendicular (89.6 °) to the iron triangle.

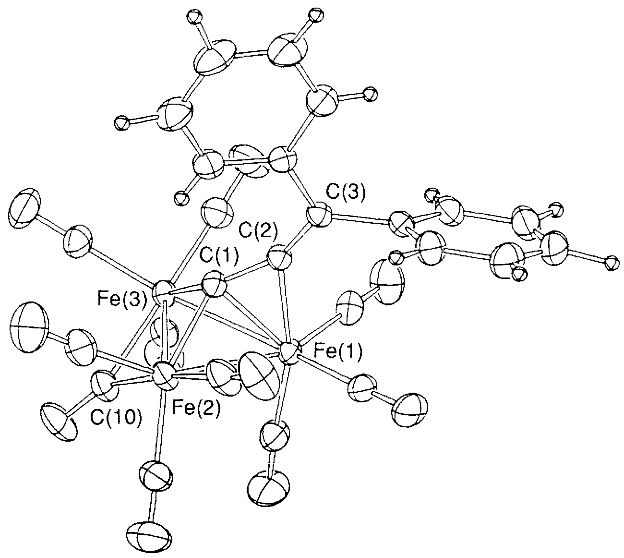


Fig. 2 ORTEP drawing of **8**. Selected bond distances (Å) and angles (°) are as follows: C(1)–C(2) 1.338(4), C(2)–C(3) 1.331(3), Fe(1)–Fe(2) 2.603(1), Fe(1)–Fe(3) 2.613(1), Fe(2)–Fe(3) 2.559(1), Fe(1)–C(1) 2.004(3), Fe(1)–C(2) 2.119(3), Fe(2)–C(1) 1.917(3), Fe(2)–C(10) 1.983(3), Fe(3)–C(1) 1.899(3), Fe(3)–C(10) 2.015(3), Fe(2)–Fe(1)–Fe(3) 58.77(2), Fe(1)–Fe(2)–Fe(3) 60.82, Fe(1)–Fe(3)–Fe(2) 60.41(2), Fe(2)–Fe(1)–C(1) 46.98(8), Fe(2)–Fe(1)–C(2) 77.09(7), Fe(3)–Fe(1)–C(1) 46.28(7), Fe(3)–Fe(2)–C(2) 78.09(7), C(1)–Fe(1)–C(2)—37.8(1), Fe(2)–C(1)–Fe(3) 84.2(1).

The X-ray structure of **8** has also been determined (Fig. 2).† The three iron atoms form a triangle, in which two are chemically equivalent, and Fe(2) and Fe(3) are linked by a symmetrical carbonyl bridge with Fe(2)–C(10) and Fe(3)–C(10) bonds. The triangle is capped by an allenylidene moiety, and the α-carbon atom C(1) is bound to Fe(2) and Fe(3) symmetrically with very short 'carbene-like' distances. The C(1)–C(2) bond is η^2-coordinated to Fe(1), and the C(2)–Fe(1) distance is longer than that of the other carbon–iron bonds. However, this distance is nearly 0.1 Å shorter than that in vinylidene complexes,[6] owing to the sp character of C(2). Although the synthesis of an allenylidene–triiron derivative has already been reported,[7] our results disclose a novel structural feature of (μ_3,η^2-allenylidene)–iron complexes.

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† *Crystal data* for **3**: $C_{38}H_{20}O_8Fe_3$, M = 772.1, triclinic, space group $P\bar{1}$, a = 12.436(2), b = 14.988(2), c = 10.105(1) Å, α = 108.14(1), β = 106.66(1), γ = 97.26(1)°, U = 1665.9(4) Å^3. Z = 2, D_c = 1.539 g cm^{-3}, F(000) = 780, λ = 0.71069 Å, μ(Mo-Kα) = 13.40 cm^{-1}, crystal dimensions 0.20 × 0.25 × 0.35 mm. The structure was solved by direct methods (MITHRIL based TEXRAY system) and refined by full-matrix least-squares analysis. Measurements were made on a Rigaku AFC-5R diffractometer using Mo-Kα radiation (graphite monochromator) in the range $3 < 2\theta < 60°$. From 9790 measured reflections, 4917 with $|F_o| > 3\sigma(F_o)$ were used in the refinement. All atoms including hydrogens were found; all non-hydrogen atoms were refined anisotropically and all hydrogen atoms isotropically; 522 parameters were refined. The final residuals R and R_w were 0.041 and 0.042, respectively.

Crystal data for **8**: $C_{25}H_{10}O_{10}Fe_3$, M = 637.9, triclinic, space group $P\bar{1}$, a = 11.091(2), b = 12.294(2), c = 10.219(1) Å, α = 94.52(1), β = 107.58(1), γ = 74.02(1)°, U = 1277.0(4) Å^3, Z = 2, D_c = 1.659 g cm^{-3}, F(000) = 636, λ = 0.71069 Å, μ(Mo-Kα) = 17.35 cm^{-1}, crystal dimensions 0.20 × 0.25 × 0.35 mm. The structure was solved by analysing the Patterson function and refined by full-matrix least-squares analysis using absorption-corrected data. Measurements were made on a Rigaku AFC-5R diffractometer using Mo-Kα radiation (graphite monochromator) in the range $3 < 2\theta < 60°$. From 7520 measured reflections, 5501 with $|F_o| > 3\sigma(F_o)$ were used in the refinement. All atoms including hydrogens were found; all non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically; 383 parameters were refined. The final residuals R and R_w were 0.039 and 0.050, respectively.

Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, Issue No. 1.