Acetylene–Acetylide Coupling *via* Reactions of Phosphido-bridged σ–π-Acetylides with Alkynes. *X*-Ray Crystal Structures of $[Fe_2(CO)_5\{PPh_2C(O)C(Bu^t)CC(CO_2Et)C(CO_2Et)\}]$ and $[Fe_2(CO)_5\{PPh_2C(Ph)C(CO_2Et)CC(Bu^t)CO\}]$

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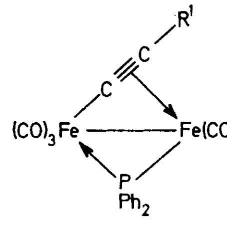
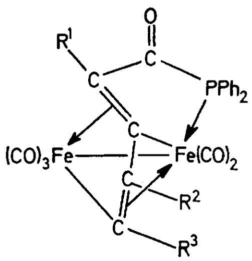
Summary Reactions of σ–π-acetylides $[Fe_2(CO)_6(C_2R^1)(PPh_2)]$ with acetylenes $R^2C{\equiv}CR^3$ leads to acetylide–acetylene coupling and insertion into iron–phosphorus bonds generating novel organometallic derivatives $[Fe_2(CO)_5\{PPh_2C(O)C(R^1)CC(R^2)C(R^3)\}]$ ($R^1 = Bu^t$; $R = R^3 = CO_2Et$) and $[Fe_2(CO)_5\{PPh_2C(R^2)C(R^3)CC(R^1)C(O)\}]$ ($R^1 = Bu^t$; $R^2 = Ph$; $R^3 = CO_2Et$) characterised by *X*-ray diffraction.

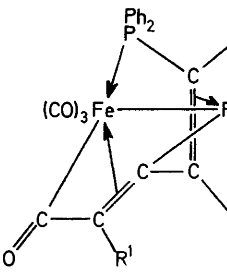
ALTHOUGH insertion of an acetylene into the metal–carbon (*sp*) bond of a σ-acetylide is a key step in the proposed mechanisms of acetylene oligomerisation by transition metal catalysts,[1] few attempts have been made to isolate σ-acetylide intermediates and study their reactivity.[2] We have synthesised a range of activated acetylides of type (I) and investigated coupling reactions with disubstituted acetylenes. Carbon–carbon bond formation at the α-carbon atom of the acetylide and insertion of unsaturated species into metal–phosphorus bonds are features of these reactions.



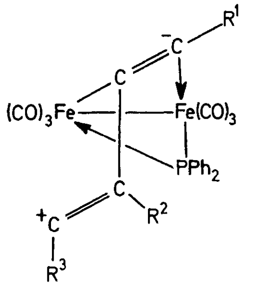
(I)



(II)



(III)

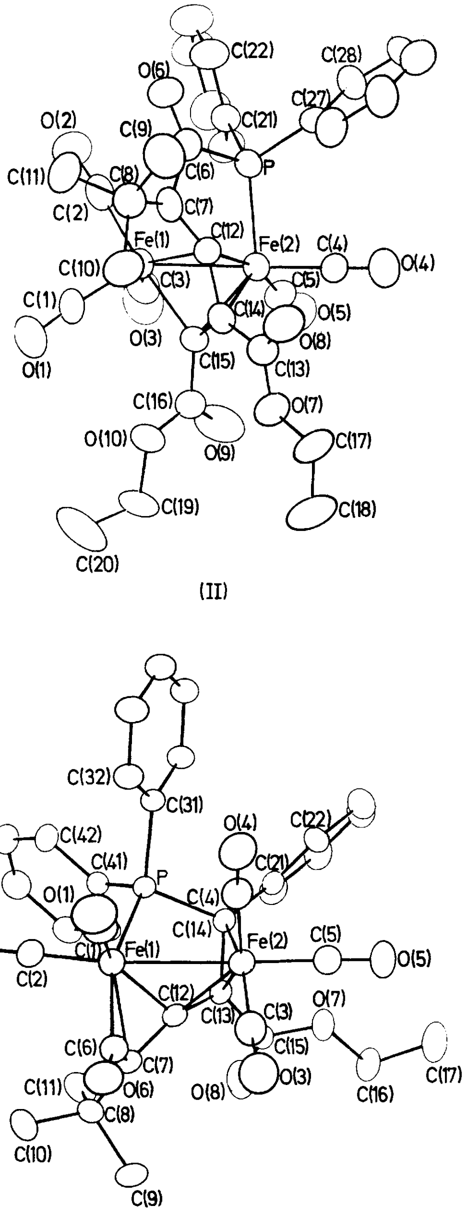


(IV)

Reaction of (I; R^1 = Bu^t) with R^{2}C$\equiv$CR^3 (R^2 = R^3 = CO$_2$Et; R^2 = R^3 = CF$_3$; R^2 = R^3 = Et; R^2 = R^3 = Ph; R^2 = CO$_2$Et, R^3 = Ph) at or slightly above 25 °C led to high yields (90% for R^1 = R^2 = CO$_2$Et) of air-stable purple crystalline complexes (II). Mass spectral analysis established the retention of 6 CO groups, one of which was ketonic [i.r. (C$_6$H$_{12}$) (II; R^2 = R^3 = CF$_3$) ν(CO) 1699w cm^{-1}]. Mössbauer spectra show 4 lines indicative of non-equivalent iron sites. The structure of (II; R^2 = R^3 = CO$_2$Et) was elucidated by *X*-ray crystallography. *Crystal data*: monoclinic, space group $P2_1$, $Z = 2$, $a = 11{\cdot}474(4)$, $b = 16{\cdot}779(5)$, $c = 9{\cdot}926(3)$ Å; $\beta = 97{\cdot}35(4)^\circ$, $R = 0{\cdot}044$ for 3314 observed diffractometer reflections. A short Fe–Fe bond [2·524(1) Å] (Figure) is bridged by a new ligand built up from the original acetylido and phosphido groups, the incoming acetylene, and a molecule of CO. The α-ketophosphine group is attached to the β-carbon atom of the original acetylide, with the alkyne linked to the α-carbon atom. Although the synthesis of phosphorus heterocycles from PF$_3$ complexes has been reported,[3] to our knowledge insertion into the metal–phosphorus bond of a phosphido bridge is unprecedented.

Compounds (II) can be converted into new derivatives (III) on refluxing in benzene. These reactions are clean and there is no loss of CO. The presence of a different type of ketonic CO group is indicated by a new ν(CO) absorption between 1775 and 1805 cm^{-1} for all complexes of type (III).

In contrast to those for (II), Mössbauer spectra for (III) are deceptively simple with only two slightly broadened



(II)

(III)

FIGURE

The molecular structure of [Fe$_2$(CO)$_5${PPh$_2$C(O)C(Bu^t)CC(CO$_2$Et)C(CO$_2$Et)}] (II) and [Fe$_2$(CO)$_5${PPh$_2$C(Ph)C(CO$_2$Et)CC(Bu^t)CO}] (III) as determined by *X*-ray diffraction. Important bond lengths are: (II); Fe(2)–P 2·193(2), P–C(6) 1·918(6), C(6)–C(7) 1·530(8), C(7)–C(12) 1·341(8), C(12)–C(14) 1·455(8), C(14)–C(15) 1·400(9), Fe(1)–C(7) 2·405(6), Fe(1)–C(12) 2·159(5), Fe(1)–C(15) 2·022(6), Fe(2)–C(12) 1·931(6), Fe(2)–C(14) 2·090(6), Fe(2)–C(15) 2·089(6) Å. (III); Fe(1)–P 2·2537(7), Fe(1)–C(6) 1·946(3), Fe(1)–C(7) 2·131(2), Fe(1)–C(12) 1·955(2), P–C(14) 1·830(3), C(14)–C(13) 1·456(3), C(13)–C(12) 1·405(4), C(12)–C(7) 1·396(4), C(6)–C(7) 1·450(4), Fe(2)–C(13) 2·042(2), Fe(2)–C(14) 2·123(2), Fe(2)–C(12) 2·016 Å.

lines apparent. Compound (III; $R^2 = CO_2Et$, $R^3 = Ph$) has been characterised by *X*-ray diffraction. *Crystal data*: triclinic, space group $P\bar{1}$, $a = 11{\cdot}308(6)$, $b = 14{\cdot}343(12)$, $c = 11{\cdot}424(14)$ Å, $\alpha = 86{\cdot}68(16)$, $\beta = 69{\cdot}93(6)$, $\gamma = 104{\cdot}87(11)°$; $Z = 2$; $R = 0{\cdot}029$ on 4408 observed diffractometer data. All hydrogen atoms were refined. The structure (Figure) shows that the carbon atom of the incoming alkyne with the most electron-withdrawing substituent is linked to the α-carbon atom of the acetylide with the other alkyne terminus bonded to the phosphido group. A carbonyl group has inserted between the β-carbon of the acetylide and Fe(1). Conversion of (II) into (III) thus involves cleavage of the P–C(6) and Fe(1)–C(15) bonds, formation of a new P–C(acetylene) link, and a rearrangement.

Several aspects of these reactions deserve comment: (a) The original α-carbon atom of the acetylide in (I) [C(12) in (II) and (III); Figure] remains bonded to both iron atoms in the coupled products, contrary to the usual mechanisms for acetylene–acetylide coupling.[1] (b) The ready, high-yield coupling of two bridging ligands, one of which (PPh_2) is generally considered to be inert, with an unsaturated substrate $R^2C{\equiv}CR^3$ suggests a potential for organic synthesis. (c) Substituent orientation in (II) and (III) ($R^2 = CO_2Et$, $R^3 = Ph$; $R^2 = COMe$, $R^3 = Ph$), the lack of isomers in these cases, and the propensity of (I) for nucleophilic attack by weak nucleophiles at the α-carbon atom of the acetylide rather than the iron atoms,[4] favours an ionic coupling mechanism involving a 1,4-dipolar species (IV). (d) The σ–π-co-ordination of an acetylide unit as in (I) confers an unusual pattern of reactivity[4] which appears to have a direct analogy in the recently explored chemistry of structurally related cluster compounds.[5]

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