

C-C Bond-making by Trapping of a Nucleophilic Carbene (from an Electron-rich Olefin) by a σ - π -Acetylide(hexacarbonyl)di-iron Complex; X-Ray Crystal and Molecular Structure of
 $[(OC)_3FeC(\overset{+}{\text{C}}NMeCH_2CH_2NMe)\overset{-}{\text{C}}(Ph)Fe(CO)_3PPh_2]^\dagger$

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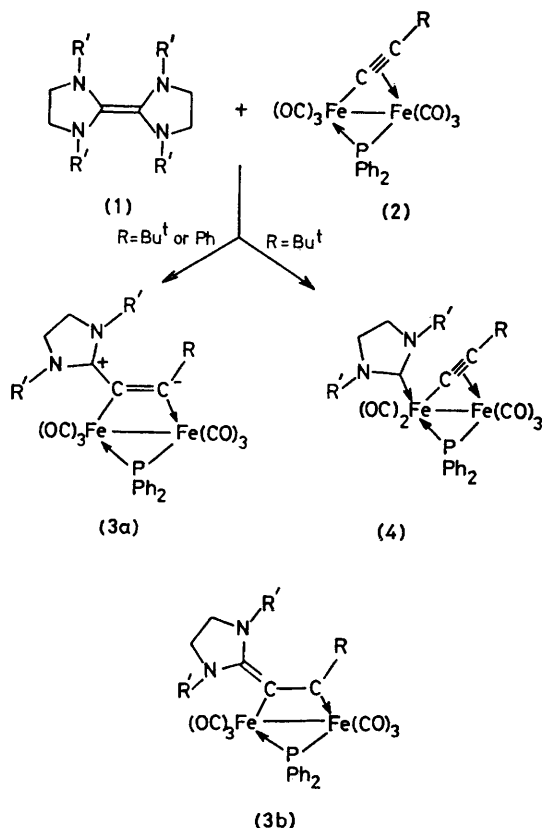
Summary Reaction of an electron-rich olefin $[\text{CNR}'(\text{CH}_2)_2\text{NR}']_2$ ($R' = \text{Me, Et, or CH}_2\text{Ph}$) with the σ - π -acetylide $[\text{Fe}_2(\text{CO})_6(\text{C}\equiv\text{CR})(\text{PPh}_2)]$ ($R = \text{Ph or Bu}^\dagger$) yields the novel mesoionic complex $[\text{Fe}_2(\text{CO})_6(\text{C}_2\text{R})(\text{PPh}_2)(\text{CNR}'(\text{CH}_2)_2\text{NR}')] \text{ via carbene-acetylide coupling; X-ray analysis reveals that the carbene species is attached$

$[\text{C}-\text{C}, 1.56(1) \text{ \AA}]$ to the α -carbon atom [attached to $\text{Fe}(1)$] of the acetylide with the β -carbon atom bonded to $\text{Fe}(2)$.

We describe reactions between an electron-rich olefin (**1**) and a binuclear σ - π -acetylide (**2**)¹ which lead *inter alia* to a novel mesoionic complex (**3**) containing a newly-made

† No reprints available.

three-carbon fragment derived from a nucleophilic carbene and the acetylide (Scheme), and the X-ray structural analysis of one such compound ($R = \text{Ph}$, $R' = \text{Me}$).



SCHEME

Although carbenes have been widely used in organic synthesis, particularly for the generation of cyclopropanes from acetylenes or cyclopropanes from olefins,² there are to our knowledge no examples of simple carbon-carbon bond formation *via* attack of a carbene on an olefin or acetylene (whether free or co-ordinated to a metal). The reverse addition, *i.e.*, the [2+2]-cycloaddition of a carbene-metal complex with an olefinic or acetylenic substrate has, however, been proposed to constitute an integral part of olefin or acetylene metathesis.³ The formation of complexes of type (3) provides (i) additional evidence for the unusual reactivity associated with σ - π -bound acetylide or alkenyl groups,⁴ and (ii) an example of a new class of transition metal reaction of an electron-rich olefin.⁵

Treatment of the acetylide (2; $R = \text{Ph}$) (toluene solvent, 50–60 °C, 5 h) with 0.5 equiv. of the olefin (1) affords in high yield (*ca.* 80%) the yellow crystalline adduct $[\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Ph})(\text{PPh}_2)\{\text{CNR}'(\text{CH}_2)_2\text{NR}'\}]$ (3; $R' = \text{Me}$, Et, or

CH_2Ph) which from spectroscopic data [*e.g.*, for (3; $R' = \text{Et}$), $\nu(\text{CO})$ (C_6H_{12}): 2040m, 1994s, 1969m, 1950w, 1946m, and 1921w cm^{-1} ; M^+ , 692; Mössbauer, 2 lines, $\delta = 0.19$, $\Delta = 0.21$ mm s^{-1} (w.r.t. sodium nitroprusside)] has structural similarity to $[\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Ph})(\text{PPh}_2)\text{P}(\text{OEt})_3]$.^{4a}

For the reaction between the acetylide (2; $R = \text{Bu}^t$) and the olefin (1) ($R' = \text{Me}$, Et, or CH_2Ph) (80 °C, 8 h), i.r. monitoring suggested the presence of two products, (3) and (4). Pure complexes (3) and (4) were separated by dry column chromatography (Florisil). Microanalysis, i.r. [$\nu(\text{CO})$, 2025s, 1979vs, 1958s, 1945s, and 1923m cm^{-1}] and Mössbauer spectra [4 lines, $\delta = 0.20$, $\Delta = 1.03$ mm s^{-1} , Fe(1); $\delta = 0.20$, $\Delta = 0.64$ mm s^{-1} , Fe(2)] suggest that complex (4) is a carbene-substitution product of complex (2) in which the carbene ligand is *trans* to the phosphido bridge, *cf.*, $[\text{Fe}_2(\text{CO})_5(\text{C}_2\text{Ph})(\text{PPh}_2)\text{PPh}_3]$.¹

The structure of complex (3; $R = \text{Ph}$, $R' = \text{Me}$) was finally determined by single crystal X-ray diffraction. Crystals[‡] are monoclinic, space group $P2_1/c$ with $a = 9.992(9)$, $b = 16.292(12)$, $c = 23.129(18)$ Å; $\beta = 99.64(8)^\circ$, $Z = 4$, $D_m = 1.37$, $D_c = 1.353$ g cm^{-3} . The structure was solved by Patterson and Fourier methods using 1436 observed data [$I > 2.5\sigma(I)$] measured on a GE-XRD-6 diffractometer (Mo- K_α radiation). Refinement has proceeded to $R = 0.071$.[¶] An ORTEP II plot of the structure is illustrated in the Figure.[§] The carbene fragment is attached to the α -acetylenic carbon atom by a long C(8)–C(9) bond [1.58(3) Å]; in contrast, the C(9)–N(1) and C(9)–N(2) bonds [av.

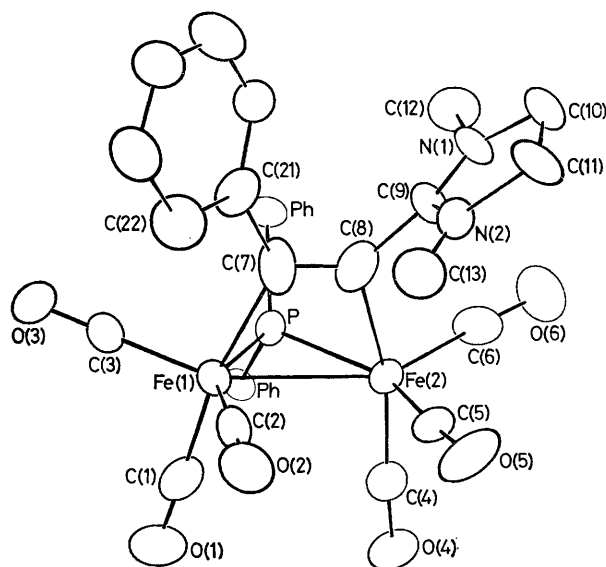


FIGURE. A perspective view of the molecular structure of $[\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Ph})(\text{PPh}_2)\{\text{CNMe}(\text{CH}_2)_2\text{NMe}\}.\text{PhMe}]$. For the sake of clarity, only one carbon atom of each phenyl ring of the phosphido bridge is shown. The half molecules of toluene of solvation are not included.

[‡] The asymmetric unit contains two half molecules of toluene located about centres of symmetry.

[§] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[¶] An improved refinement based on 3377 observed reflections from a new data set, has yielded $R = 0.056$; C(8)–C(9), 1.56(1) and C(7)–C(8), 1.24(1) Å (footnote added in proof).

1.32(3) Å] have considerable multiple bond character as in related carbene complexes.⁵ The stereochemistry at the original acetylide carbon atoms C(7) and C(8) in complex (2) is dramatically modified in complex (3), with C(8) bonded only to Fe(2) and C(7) to Fe(1), and internal angles Fe(1)–C(7)–C(8) and Fe(2)–C(8)–C(7) of 110.3(8) and 110.3(9)°, respectively. Nevertheless the C(7)–C(8) bond retains acetylenic character [C(7)–C(8), 1.21(3) Å]. These results point to a major contribution from the dipolar canonical form (3a) to the ground state of complex (3) with little evidence for the alternative form (3b), *cf.*, [Fe₂(CO)₈{CP(OEt)₃CPh}(PPh₂)].^{4a} Another difference between complex (3) and the structurally related [Fe₂(CO)₈{CP(OEt)₃CPh}(PPh₂)] is that whereas the latter can be converted into the red CO substitution product [Fe₂(CO)₈(C≡CPh)(PPh₂){P(OEt)₃] by warming in benzene, complex (3) shows no evidence of conversion into other products even in refluxing toluene.

It is apparent that the σ - π -acetylide in complex (2; R = Ph) exhibits remarkable reactivity towards neutral phosphorus,^{4a,c,d} nitrogen,^{4b,e} and now carbon nucleophiles. A few addition reactions of neutral metal π -complexes with neutral group 5 nucleophiles are known [*e.g.*,⁶ C₅H₅N with a Pt^{II}(η -C₂H₄) complex], but for carbonyl derivatives such reactivity is usually restricted to cations.⁷ The easy coupling of carbenes and acetylides observed here may, by analogy, be capable of extension to carbon-carbon bond-making *via* reaction of an electron-rich olefin with a cationic complex such as [Mo(η ²-C₇H₇)(CO)₃][BF₄] or [Fe(η ⁵-C₆H₇)(CO)₃][BF₄].

This work was supported by grants from N.A.T.O. (to A.J.C. and M.F.L.) and the National Research Council of Canada (A.J.C.). We thank Dr. J. Jeffery for technical assistance (to W.F.S.) in the initial stages of the project.

(Received, 9th August 1978; Com. 875.)

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