Binuclear Iron Carbonyl Complexes with 1,3-Dipoles as Bridging One-carbon, Three-electron Ligands; *X*-Ray Structure of $[Fe_2(CO)_6\{CH{\cdot}C(Ph){:}NEt_2\}(PPh_2)]{\cdot}C_6H_6$

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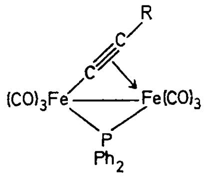
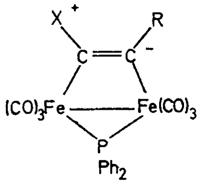
Summary Binuclear iron carbonyl complexes containing ammonium 1,3-dipoles as bridging one-carbon, three electron ligands have been synthesised; the complex $[Fe_2(CO)_6\{CH{\cdot}C(Ph){:}NEt_2\}(PPh_2)]{\cdot}C_6H_6$ (III) has been characterised by single crystal *X*-ray diffraction.

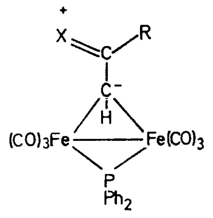
THE σ–π-acetylide $[Fe_2(CO)_6(C{\equiv}CPh)PPh_2]$ (I; R = Ph)[1] reacts with trialkyl phosphites at room temperature or below *via* attack on the α-carbon of the alkyne to yield the phosphonium–betaine (ylide–carbene) complexes [II; X = $(RO)_3P$] in which a two-carbon bridge behaves as a three-electron (σ-vinyl + σ-carbanion or σ-vinyl + σ-carbene) donor.[2] We now report a new class of organometallic compounds (III) and (IV), containing one-carbon, three-electron ligands. The single bridging carbon atom in these new compounds is part of an ammonium 1,3-dipole stabilised by co-ordination and formally derived from (I) by nucleophilic attack at the β-carbon atom of the acetylide. Unstable ammonium 1,3-dipoles related to the trapped ligands in (III) and (IV) are postulated intermediates in the reactions of secondary amines with activated acetylenes.[3] Moreover, to our knowledge, metal carbyne complexes[4] are the only examples where a single carbon atom behaves as a 3-electron donor.



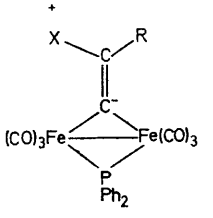
(I)



(II)



(III)



(IV)

The complexes (III; X = NEt_2; R = Ph, Bu^t, or C_6H_{11}) and (IV; X = Et_3N, R = Ph or C_6H_{11}) can be obtained as red, air-stable crystals *via* the direct reaction of (I) with amines in hot benzene (0·5 h) followed by chromatography, or by first synthesising the yellow compounds of the type (II; X = Et_2NH) followed by thermal isomerisation in warm benzene. In the latter case CO is not evolved and the conversion can be monitored by solution i.r. spectroscopy. Formulation of the compounds as 1 : 1 adducts was established by microanalytical and mass spectroscopic data. I.r. spectra [*e.g.*, $\nu_{C=O}$ (C_6H_{12}): (III; X = Et_2N), 2035s, 1997vs, 1966s, 1943s and 1934m] have a characteristic intensity pattern. Mössbauer spectra consist of doublets (III; X = Et_2N) indicative of two iron sites with distorted octahedral stereochemistry.

The molecular structure of (III; X = Et_2N) was established by single crystal *X*-ray diffraction. *Crystal Data:* $C_{36}H_{32}Fe_2NO_6$, monoclinic, space group $P2_1/n$, a = 14·694(7), b = 13·653(7), c = 17·787(7) Å, β = 99·03(7)°; D_m = 1·36, D_c = 1·352 g cm^{-3}; Z = 4. The structure was solved by conventional heavy atom methods using 3760 observed [$I > 3\sigma(I)$] diffractometer data measured to $2\theta = 50°$ (Mo-K_α radiation). Full-matrix least-squares refinement with anisotropic temperature coefficients for non-hydrogen atoms and isotropic factors for hydrogen atoms has reduced R to 0·035. In the binuclear molecule (Figure) a short Fe–Fe bond [2·548(1) Å] is bridged by a diphenylphosphido group and C(7) of the dipolar ligand.

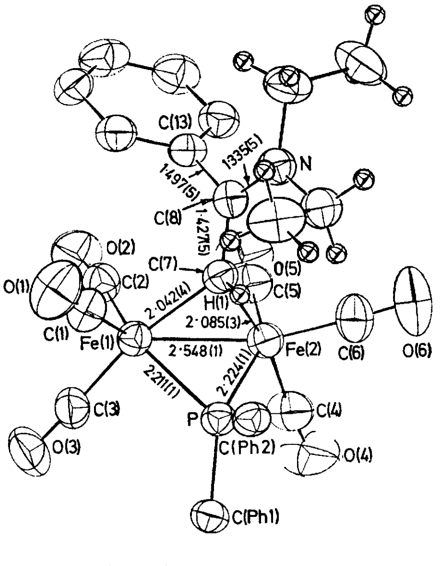


FIGURE. A perspective view of the molecular structure of $[Fe_2(CO)_6\{CH{\cdot}C(Ph){:}NEt_2\}(PPh_2)]$; only one carbon atom of each phenyl ring of the bridging phosphido group is shown.

The location of a hydrogen atom on C(7) and the tetrahedral stereochemistry at C(7), and the planar stereochemistry at (C(8) and N, show that the bridging ligand is a 1,3-dipole best represented by the canonical form (III). The formation of this ligand proceeds *via* attack by Et_2NH on the β-carbon of the alkyne in (I) followed by hydrogen transfer to C(7). The Fe(1)–C(7)–Fe(2) bridge is slightly asymmetric with an angle [76·2(0)°] which is the smallest yet reported for a bridging carbon atom, differing by 1·4° from the value in $[Fe_2(CO)_9]$[5]. The bridging carbanionic ligand in (III) can be considered formally analogous to the

$R\underset{\cdot}{\ddot{N}}H$ radical; for (IV) a similarity to alkylideneamido ($R_2C{=}\underset{\cdot}{\ddot{N}}$) and nitric oxide ligands, both of which exhibit terminal and bridging co-ordination modes, is apparent. Few examples of co-ordination stabilised 1,3-dipoles have been described, notable exceptions being complexes of thio- and seleno-ketocarbenes.[6]

The conversion of a compound of the type (II) into type (III) or (IV) represents a novel isomerisation of a two-carbon, 3-electron ligand to a one-carbon, 3-electron donor.† Finally, characterisation of the complexes of types (II), (III), and (IV) provides compelling structural evidence for the proposed mechanisms of reactions of activated acetylenes with Group V donors in which reactive 1,3-dipoles are initial intermediates.[3]

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† Yellow compounds [II; X = PR_3 or $P(OR)_3$] are converted into red complexes with i.r. spectra very similar to those of (III; X = NEt_2). However, an *X*-ray analysis of [$Fe_2(CO)_5(C_2Ph)PPh_3$] has shown that these derivatives are derived from (I) by substitution of CO by PR_3 or $P(OR)_3$.

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