# Formation of Metal Acetylides *via* Complexes of Molecular Hydrogen

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Terminal acetylenes react with $[FeH_2(dmpe)_2]$ [dmpe = bis(dimethylphosphino)ethane] to form metal acetylides and diacetylides; the crystal structure of *trans*-$Fe(C{\equiv}CPh)_2(dmpe)_2$ shows that the seven atoms of the C–C≡C–Fe–C≡C–C grouping are colinear and the bond lengths indicate a strong Fe–C bond and an unusually short C–C triple bond.

It is now well established that a variety of metal hydrides can be protonated by strong acids to give molecular hydrogen complexes.[1] In previous work, we reported[2] that the dihydrides of bis(dialkylphosphino)ethaneiron complexes, *cis*-$[FeH_2(PP)_2]$, [(PP) = $R_2PCH_2CH_2PR_2$, where R = methyl (PP = dmpe), ethyl (PP = depe), and n-propyl (PP = dprpe)] are basic and are reversibly protonated by ethanol and other simple alcohols to yield the corresponding molecular hydrogen complexes *trans*-$[FeH(H_2)(PP)_2]^+$. At least in alcohol solution, these dihydrides exhibit a basicity comparable to that of alkoxides.

The complex *trans*-$[FeH(H_2)(dmpe)_2]^+$ (**2**) undergoes substitution by a variety of species including halides and tertiary phosphines with loss of $H_2$.[2,3] For inorganic and organometallic synthesis, $\eta^2$-co-ordinated $H_2$ is a ligand which can be introduced easily under very mild reaction conditions and affords a relatively inert leaving group. If the conjugate base ($B^-$) of the protonating acid (B–H) is itself a good ligand, protonation followed by $H_2$ displacement leads effectively to the substitution of a hydride ligand by $B^-$. Terminal acetylenes are sufficiently acidic to protonate $[FeH_2(dmpe)_2]$ to form the molecular hydrogen complex. In this communication we describe the reaction of $[FeH_2(dmpe)_2]$ (**1**) with terminal acetylenes to give initially the acetylide metal hydride and eventually metal diacetylide.

Phenyl[$^2H_1$]acetylene, deuteriated at the terminal acetylenic position, rapidly exchanges deuterium for the metal bound hydrides of $[FeH_2(dmpe)_2]$ at 0 °C in an aprotic solvent. This is consistent with the protonation/deprotonation of $[FeH_2(dmpe)_2]$ to exchange hydrogen for deuterium *via* the $\eta^2$-HD complex.

*trans*-$[FeH(H_2)(dmpe)_2]^+$
**(2)**

*trans*-$[FeH(PhC{\equiv}C)(dmpe)_2]$
**(3)**

In the presence of excess of phenylacetylene (10 equiv.) in aprotic solvents such as tetrahydrofuran (THF), benzene, or pentane, $[FeH_2(dmpe)_2]$ reacts to form the known iron acetylide hydride, *trans*-$[FeH(PhC{\equiv}C)(dmpe)_2]$ (**3**)[4] as the major product after 48 h. In neat phenylacetylene, *trans*-$[Fe(C{\equiv}CPh)_2(dmpe)_2]$, (**4**)†‡ is the major organometallic product and crystallises from the reaction mixture in about 40% isolated yield.

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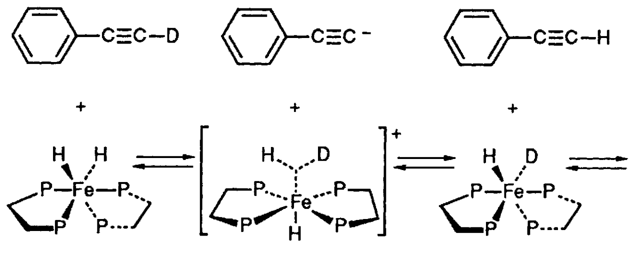
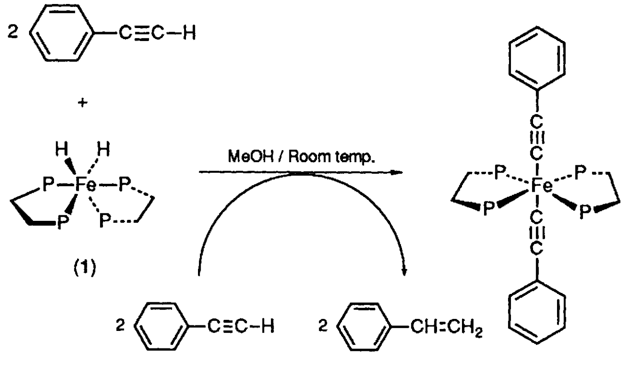
† $^{31}P$ NMR spectra (162.0 MHz) were referenced to external, neat, trimethyl phosphite, taken as 140.85 ppm. $^1H$ NMR (400.1 MHz) and $^{13}C$ NMR (100.6 MHz) spectra were referenced to solvent resonances.

‡ *Selected data* for *trans*-$[Fe(C{\equiv}CPh)_2(dmpe)_2]$ (**4**): $^{31}P\{^1H\}$ NMR ($C_6D_6$) δ 64.7; $^1H$ NMR ($C_6D_6$) δ 1.61 (br.s, 24H, $CH_3$), 1.72 (br.s, 8H, $CH_2$), 7.18 (m, 2H, CH), 7.38 (m, 4H, CH), and 7.54 (m, 4H, CH); $^{13}C\{^1H,^{31}P\}$ NMR ([$^2H_8$]tetrahydrofuran) δ 17.6 ($CH_3$), 32.7 ($CH_2$), 117.1 ($C{\equiv}\mathit{C}C$), 123.9 (CH), 129.4 (CH), 131.7 (CH), 133.1 ($C{\equiv}\mathit{C}Ph$), and 140.0 ($\mathit{C}{\equiv}CPh$); $\lambda_{max}$ (THF, log ε) 215 (3.63), 260 (4.05), and 365 (4.26) nm; $\nu_{C\equiv C}$ (Nujol) 2037 $cm^{-1}$; satisfactory elemental analyses were obtained.



(1)

P⌒P ≡ $Me_2PCH_2CH_2PMe_2$ (dmpe)



(4)

The reaction between excess of phenylacetylene and $[FeH_2(dmpe)_2]$ is much more rapid in alcohol solvents. In methanol, where $[FeH_2(dmpe)_2]$ is almost completely protonated,[2] the diacetylide (**4**) crystallises directly from the reaction mixture during a few minutes following the addition to phenylacetylene. In the reaction of phenylacetylene with (**1**) to form (**4**), two equivalents of styrene are formed as a byproduct. This would indicate that the terminal acetylene can function not only as a proton source but also serves to remove $H_2$. Hydrogenation of acetylenes has recently been observed in the presence of a ruthenium dihydride complex.[5]

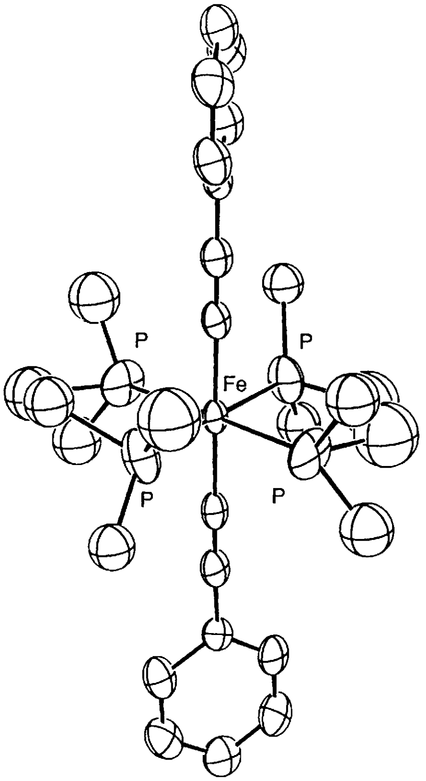


**Figure 1.** ORTEP plot of *trans*-$[Fe(C{\equiv}CPh)_2(dmpe)_2]$.

The crystal structure of (**4**) (Figure 1)§ shows that the seven atoms of the C–C≡C–Fe–C≡C–C grouping are colinear and the bond lengths indicate a strong Fe–C bond, an unusually short C–C triple bond (1.21 Å) and a significant amount of delocalization into the C–C(Ph) bond (1.438 Å). Each of the phenyl rings is planar to within 0.016 Å; the two rings are not coplanar, however, being twisted by 69.7°.

In an exactly analogous reaction sequence, $[FeH_2(dmpe)_2]$ reacts with the di- and tri-functional acetylenes, 1,4-diethynylbenzene[6] and 1,3,5-triethynylbenzene,[7] in methanol solution to give the corresponding metal diacetylides (**5**) and (**6**).¶ The functionalised metal diacetylides (**5**) and (**6**) provide the obvious possibility of forming oligomeric and polymeric organometallic species with metal centres separated by conjugated organic fragments.

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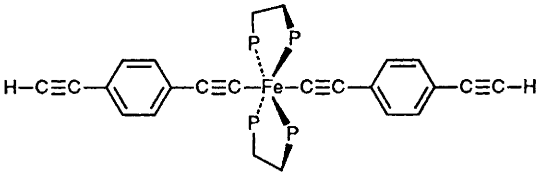
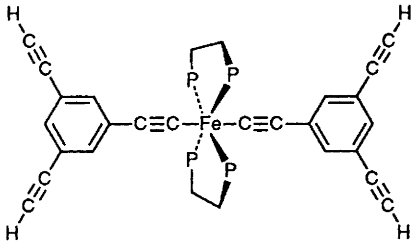
§ *Crystal data* for $Fe(C{\equiv}CPh)_2(dmpe)_2$ (**1**): $C_{28}H_{42}FeP_4$, $M = 558.39$, monoclinic, space group $C2/c$, $a = 23.239(4)$, $b = 10.429(2)$, $c = 18.660(3)$ Å, $\beta = 138.84(2)°$, $Z = 4$, $R = 0.069$ (1414 $F$). Cell constants were determined by a least-squares fit to the $\theta$ values of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer with a graphite monochromator. Data were reduced and Lorentz, polarization, and decomposition corrections were applied using the Enraf-Nonius Structure determination Package.[8] The structure was solved by Patterson methods and was refined by full-matrix least-squares analysis with SHELX-76.[9] The Fe atom was found to lie on a two-fold rotation axis. Two P atoms of different dmpe ligands also lie on this axis which can only be accommodated by statistical disorder of the ligand about the axis. Refinement of the structure was attempted in the lower symmetry space group $Cc$ but the disorder persisted. Also, analysis of the $E$ values suggested a centrosymmetric space group so refinement was continued in the original space group. In addition to this disorder of the dmpe ligands, minor sites for four P atoms (giving 8 sites after application of the symmetry operation) were observed. No disorder was observed in the phenylacetylide ligands. The Fe atom, the C atoms of the phenylacetylide ligand, and the major contributors to the P atoms were refined anisotropically; all other atoms were refined isotropically. Hydrogen atoms of the phenylacetylide ligand were included at calculated sites (C–H 0.97 Å) with individual isotropic thermal parameters. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (see Notice to Authors Issue No. 1).

¶ *Selected spectroscopic data* for *trans*-$[Fe(C{\equiv}CC_6H_4C{\equiv}CH)_2(dmpe)_2]$ (**5**): $^{31}P\{^1H\}$ NMR ($C_6D_6$) $\delta$ 67.9; $^1H$ NMR ($C_6D_6$) $\delta$ 1.54 (br.s, 24H, $CH_3$), 1.67 (br.s, 8H, $CH_2$), 3.38 (s, 2H, $C{\equiv}CH$), 7.25 (m, 4H, CH), and 7.57 (m, 4H, CH); $^{13}C\{^1H,^{31}P\}$ NMR ([$^2H_8$]tetrahydrofuran) $\delta$ 17.4 ($CH_3$), 32.5 ($CH_2$), 79.1 (ArC≡*C*H), 86.6 (Ar*C*≡CH), 117.7 (FeC≡C*C*), 117.9 (*C*C≡CH), 130.8 (CH), 133.3 (FeC≡*C*Ar), 134.2 (CH), and 147.2 (Fe*C*≡CAr); $\lambda_{max}$ (THF, log $\varepsilon$) 222 (3.95), 284 (4.17), and 413 (4.17) nm; $\nu_{C\equiv C}$ (Nujol) 2037 and 2016 $cm^{-1}$; satisfactory elemental analyses were obtained.

*trans*-$[Fe\{C{\equiv}CC_6H_3(C{\equiv}CH)_2\}_2(dmpe)_2]$ (**6**): $^{31}P\{^1H\}$ NMR ([$^2H_8$]tetrahydrofuran) $\delta$ 66.5; $^1H$ NMR ([$^2H_8$]tetrahydrofuran) $\delta$ 1.62 (br.s, 24H, $CH_3$), 1.89 (br.s, 8H, $CH_2$), 3.51 (s, 4H, $C{\equiv}CH$), 7.08 (m, 4H, CH), and 7.38 (m, 2H, CH); $^{13}C\{^1H; ^{31}P\}$ NMR ([$^2H_8$]tetrahydrofuran) $\delta$ 17.4 ($CH_3$), 32.5 ($CH_2$), 79.5 (ArC≡*C*H), 85.1 (Ar*C*≡CH), 115.7 (FeC≡C*C*), 124.5 (*C*C≡CH), 130.7 (CH), 133.0 (FeC≡*C*Ar), 135.4 (CH), and 146.9 (Fe*C*≡CAr); $\lambda_{max}$ (THF, log $\varepsilon$) 250 (4.10) and 405 (3.72) nm; $\nu_{C\equiv C}$ (Nujol) 2033 $cm^{-1}$; satisfactory elemental analyses were obtained.



**(5)**



**(6)**

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