A reductive rearrangement of iron acetylide hydride complexes

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Iron acetylide hydride complexes of the type [Fe(H)(C≡CR)(dmpe)$_2$] [dmpe = 1,2-bis(dimethylphosphino)ethane] react with anions in a methanol solution to form substituted alkenyl complexes; the crystal structure of *trans*-FeN$_3$(CH=CHPh)(dmpe)$_2$] is presented.

There is current interest in metal acetylide complexes as materials which may be used as components in non-linear optical materials,[1,2] the construction of organometallic polymers[2–4] and as new liquid crystals.[5] Metal σ-acetylide complexes have been prepared by a number of routes including ligand exchange reactions,[4,6] oxidative addition reactions[7,8] and by deprotonation of metal vinylidene complexes.[9]

Acetylide hydride complexes of iron [FeH(C≡CR)L$_4$] have been formed by reaction of a terminal acetylene with a coordinatively unsaturated iron complex [FeL$_4$] (L is usually a phosphine).[8,10] The acetylide hydride complexes of [Fe(PP)$_2$] [PP = 1,2-bis(dimethylphosphino)ethane (dmpe) or 1,2-bis(diethylphosphino)ethane] are typically reactive, air-sensitive materials but they can be handled and stored as solids under an inert atmosphere.[11] They can be converted to the more stable acetylide chloride derivatives [FeCl(C≡CR)(PP)$_2$] by treatment with dichloromethane or other alkyl halides.‡

Treatment of the iron acetylide hydride complexes with a chloride, azide or thiocyanate salt in methanol solution, resulted effectively in substitution of the hydride by Cl$^-$, N$_3{}^-$ or SCN$^-$ with partial reduction of the bound acetylene. Treatment of *trans*-[FeH(C≡CPh)(dmpe)$_2$] **1** with a methanol solution of sodium azide resulted in formation of *trans*-[FeN$_3$(CH=CHPh)(dmpe)$_2$] **2** (Scheme 1).

The conversion of **1** to **2** was clean and quantitative and the ^{31}P NMR spectrum indicated the reaction was complete within 30 min. Removal of the solvent and washing the residue with methanol produced *trans*-[FeN$_3$(CH=CHPh)(dmpe)$_2$] **2** as an orange solid. The ^{1}H NMR spectrum exhibited two alkenyl protons (at δ 7.05 and 5.73) with a coupling ($^3J_{\mathrm{HH}}$ 16.7 Hz) and this is consistent with a *trans* stereochemistry for the alkene. The vinyl resonance at δ 7.05 also showed coupling to the four equivalent phosphorus ligands ($^3J_{\mathrm{PH}}$ 6.9 Hz). An analogous reaction between **1** and chloride or thiocyanate in methanol solvent quantitatively gave *trans*-[FeCl(CH=CHPh)(dmpe)$_2$] **3** and *trans*-[FeSCN-(CH=CHPh)(dmpe)$_2$] **4** respectively.

The crystal structure of **2** (Fig. 1)† confirms that the azide and alkenyl ligands adopt a *trans* configuration about the metal centre and the stereochemistry of the double bond is (*Z*). The three nitrogen atoms of the azide group are approximately collinear (176°) and form an approximate angle of 146° with the equatorial plane containing the metal and the four phosphorus donors.

A likely reaction course for the reduction of the acetylide complexes reported here, involves initial protonation of the σ-bound acetylide ligand at the carbon β to the metal centre to form a vinylidene complex. Metal-to-carbon hydride migration in the vinylidene complex with attack by the anion (Cl$^-$, N$_3{}^-$ or SCN$^-$) leads to the neutral complexes (Scheme 2).

Protonation (or the addition of other electrophiles) at the β carbon of metal acetylide complexes is well known[12] and the intramolecular hydride migration from the metal to the α carbon

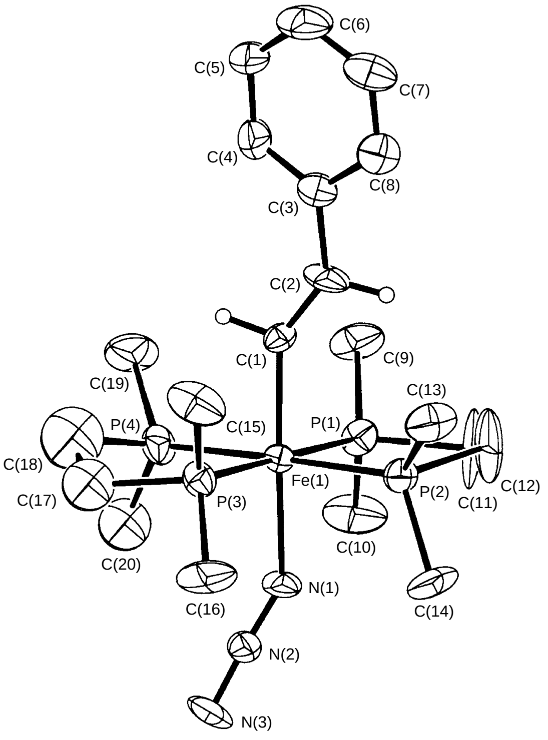
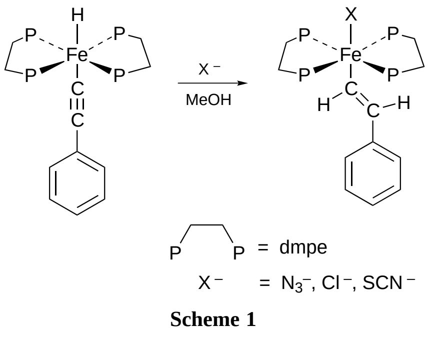
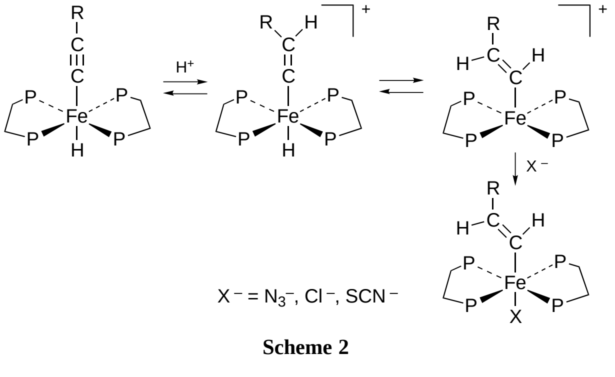


Fig. 1 ORTEP[20] plot of *trans*-[FeN$_3$(CH=CHPh)(dmpe)$_2$] **2**



Scheme 1



Scheme 2

of the vinylidene complex is analogous to the mechanism proposed for formation of η^3-butenyne complexes from metal bis(acetylide)s.[13] The complex *trans*-[FeH(C≡CC$_6$H$_4$C≡CH)(dmpe)$_2$] **5** which has both metal- and non-metal-bound acetylides reacts with a methanol solution of sodium azide, to give *trans*-[FeN$_3$(CH=CHC$_6$H$_4$C≡CH)(dmpe)$_2$] **6** as the sole product. Exclusive formation of the vinyl metal product **6** from **5** supports the proposal that an intramolecular metal-to-carbon hydride migration is a key step in the mechanism.

Treatment of analogous ruthenium acetylide hydride complexes with a methanol solution of azide or chloride produces ruthenium alkenyl complexes, presumably by a similar mechanism.[14]

The partial hydrogenation of an acetylene by metal hydride complexes has previously been reported.[15] Reaction of excess phenylacetylene with [FeH$_2$(dmpe)$_2$] in methanol solution forms a bis(acetylide) complex (*via* an acetylide hydride complex) and 2 equiv. of styrene are produced in the reaction.[16] A reasonable intermediate in the conversion of the acetylide hydride complex to the bis(acetylide) is an acetylide styryl iron complex, [Fe(C≡CPh)(CH=CHPh)(dmpe)$_2$], which would undergo substitution of the styryl group in the presence of excess phenylacetylene to form the bis(acetylide) and free styrene.

The metal-to-carbon hydride migration reported here provides a novel method of reducing metal acetylides to vinyl metal complexes in protic solvents. The reduction is stereospecific and provides an alternative approach for the introduction of the vinyl group into metal complexes.

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Footnote

† *Crystal data* for *trans*-[FeN$_3$(CH=CHPh)(dmpe)$_2$] **2**: C$_{20}$H$_{39}$N$_3$FeP$_4$, M = 501.29, monoclinic, space group $P2_1/c$, a = 23.888(3), b = 9.112(2), c = 35.680(3) Å, β = 95.568(8)°, Z = 12 (three independent complexes), R = 0.055 [3624 F, $I > 1.50\sigma(I)$]. Orange acicular crystals of *trans*-[FeN$_3$(CH=CHPh)(dmpe)$_2$] **2** suitable for X-ray diffraction studies were grown by the slow evaporation of a methanol–tetrahydrofuran solution of the complex. A crystal was mounted in a glass capillary, on a Rigaku AFC7R diffractometer equipped with a graphite monochromator. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[17] Data were reduced and Lorentz, polarisation and absorption corrections (psi scan) were applied. The structure was solved by direct methods[18] and expanded using Fourier techniques.[19]

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/303.

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