The Reactions of $[FeH(H_2)(Me_2PCH_2CH_2PMe_2)_2][BPh_4]$ with Allenes and Acetylenes, and the Reduction of Cyclopropene by Molybdenum Nitrogenases

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The reduction of cyclopropenes by metal hydrides shows significant parallels with their reduction by *Klebsiella pneumoniae* nitrogenase; intermediates isolated from the reduction of the isomeric allenes and acetylenes by $[FeH(H_2)(Me_2PCH_2CH_2PMe_2)_2][BPh_4]$ show novel features of much wider implication.

Molybdenum nitrogenase reduces cyclopropene to cyclopropane and propene in the ratio 1 : 2 under normal electron flux. If deuteriated solvent is used, the products are *cis*-1,2-dideuteriocyclopropane and *cis*- and *trans*-1,3-dideuteriopropene as well as some 2,3-dideuteriopropene.[1] An explanation of how all these species arise would help us understand how nitrogenase functions. We have undertaken a programme involving both enzyme and model studies to achieve this,[2] and have extended the work to include reactions of allenes and acetylenes, because allene and propyne are more stable isomers of C_3H_4 than cyclopropene,[3] and isomerization might well occur during cyclopropene reduction. In fact, isomerization to allene has already been suggested as a minor pathway for cyclopropene reduction, though no evidence was adduced for isomerization to propyne.[1]

We have found that the reactions of cyclopropene with hydrides such as $[MoH_4(Ph_2PCH_2CH_2PPh_2)_2]$[4] occur only in the presence of protons, and the products are cyclopropane and propene with proportionately more propene than produced by the enzyme under normal electron flux. The proportions vary to some degree with the acid employed. Cyclopropane alone was obtained upon treating $[Pt(C_3H_4)(PPh_3)_2]$[5] with acid. Cyclopropene reacts with $[FeH(H_2)(dmpe)_2][BPh_4]$[6] (dmpe = $Me_2PCH_2CH_2PMe_2$) to yield dihydrogen and cyclopropane, but no propene or identifiable complex. No acid is required. 3,3-Dimethylcyclopropene, in contrast, yields 3-methylbut-2-ene and dimethylcyclopropane in the ratio 10 : 1. The quantitative aspects of these reactions are currently being amplified.

We next turned our attention to allene and 3,3-dimethylallene, the isomers of cyclopropene and 3,3-dimethylcyclopropene, respectively. These react with $[FeH(H_2)(dmpe)_2][BPh_4]$ in tetrahydrofuran or acetone to yield solid products of similar structure, as indicated by ^1H and ^{31}P NMR spectroscopy, and no volatile hydrocarbons. The crystal structure of the dimethylallene product was determined (Fig. 1).†

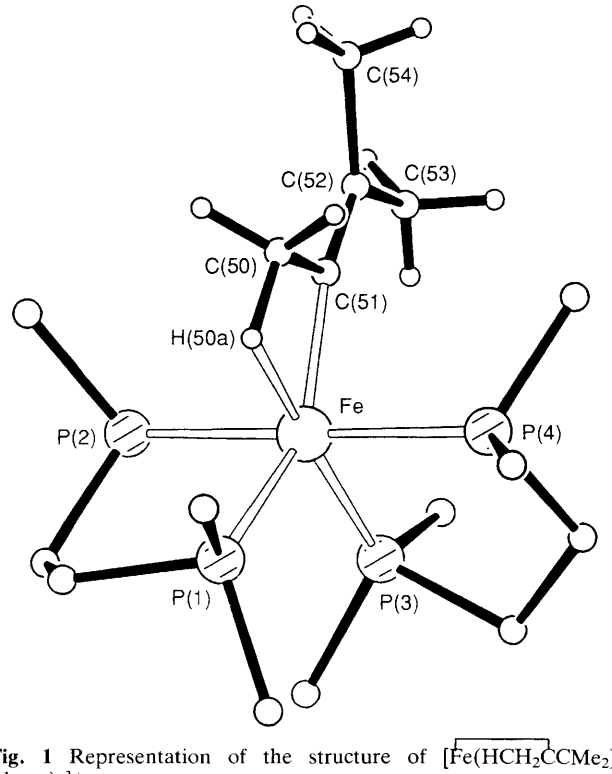

Fig. 1 Representation of the structure of $[\overline{Fe(HCH_2CCMe_2)}(dmpe)_2]^+$

† X-Ray crystal structure analyses: (*a*) $[\overline{Fe(HCH_2CCMe_2)}(dmpe)_2][BPh_4]\cdot Me_2CO$. *Crystal data*: $C_{44}H_{67}BFeOP_4$, M = 802.6. Monoclinic, space group $P2_1/n$ (equiv. to no 14), a = 15.373(1), b = 14.723(1), c = 19.733(2) Å, β = 91.653(7)°, V = 4464.6(6) Å^3, Z = 4, D_c = 1.194 g cm^{-3}, $F(000)$ = 1720, μ(Mo-Kα) = 5.1 cm^{-1}, λ(Mo-K$\bar{\alpha}$) = 0.71069 Å.

Crystals are chunky, translucent, orange rhombs. One was mounted in a glass capillary, examined photographically, then put on an Enraf-Nonius CAD4 diffractometer (with monochromated radiation). Accurate cell parameters from goniometer settings of 25 reflections, θ *ca.* 10.5°, each centred in four orientations; diffraction intensities measured to θ_{max} = 20°. 4166 Unique data corrected for deterioration, Lorentz–polarisation effects and to ensure no negative nett intensities. In the SHELX program,[13] structure determined by the heavy-atom method. All non-hydrogen atoms allowed anisotropic thermal parameters. Hydrogen atoms of the 2-methylbut-2-en-3-yl ligand located in a difference Fourier map and refined independently; all other H atoms included in idealised positions with free isotropic thermal parameters. Refinement, by full-matrix least-squares methods, concluded with R = 0.077, R_w = 0.053[13] for all 4166 data, weighted $w = \sigma_F^{-2}$. No significant features in final difference map.

(*b*) $[\overline{Fe\{C(CHPh)C{\equiv}CPh\}}(dmpe)_2][BPh_4]\cdot Me_2CO$. *Crystal data*: $C_{55}H_{69}BFeOP_4$, M = 936.7. Triclinic, space group P$\bar{1}$ (no. 2), a = 12.954(2), b = 13.283(1), c = 17.081(2) Å, α = 90.704(9), β = 96.796(10), γ = 61.238(8)°, V = 2554.9 Å^3, Z = 2, D_c = 1.217 g cm^{-3}, $F(000)$ = 996, μ(Mo-Kα) = 4.5 cm^{-1}.

Crystals are red, thick plates, slightly air-sensitive. One, *ca.* 0.20 × 0.25 × 0.25 mm, was mounted on a glass fibre in air and coated with silicone grease. Diffractometry as above; 6679 unique data (to θ_{max} = 22.5°) corrected for Lorentz–polarisation effects, absorption and to ensure no negative intensities. Structure determined principally by direct methods in SHELXS.[14] Refinement indicated disorder in the phosphine ligands, with the major conformation as shown in Fig. 3; minor component has dmpe ligands spanning P(1)–C–C–P(4) and P(2)–C–C–P(3). P(4) is split into two distinct sites; the other P atoms refined anisotropically and satisfactorily. Some Fe···C and C···C geometrical constraints applied.

Hydrogen atoms on the phenyl rings of the acetylene ligand and anion were included in idealised positions; H atom on C(50b) was located and refined well. The atoms of the solvent molecule (acetone) are not fully resolved. Currently, R = 0.072, R_w = 0.078[13] for 3865 reflections (those with $I \geq 2\sigma_I$), weighted $w = (\sigma_F^2 + 0.0036F^2)^{-1}$. No features of significance remain in difference map.

For both structures, scattering factors taken from ref. 15. Computer programs noted above and in ref. 16, and run on the MicroVAXII machine in our Laboratory.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

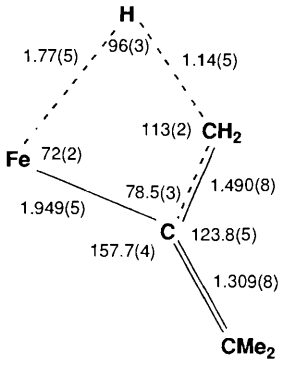

Fig. 2 Selected distances (in Å) and angles (in °) in $[Fe(HCH_2CCMe_2)(dmpe)_2]$

The structure of this complex is remarkable in that it clearly shows the presence of an agostic hydrogen between the methylene of the original dimethylallene and the iron. The structure represents an intermediate in the insertion of an alkene into a metal–hydrogen bond, and is one of very few examples detected by X-ray structural analysis and the first ever identified in the reactions of a cumulene.[7] The protonated allene (2-methylbut-2-en-3-yl) is acting as an η^2, (1−) ligand, and the agostic hydrogen is detected as a broad resonance in the ^1H NMR spectrum {and also in the ^2H spectrum of the product derived from $[Fe^2H(^2H_2)(dmpe)_2]^+$} at −4.56 ppm. The pendant dimethylmethylene forms an essentially double bond with its carbon (Fig. 2).‡

Treatment of this complex with $HBF_4{\cdot}OEt_2$ yields 2-methylbut-2-ene, with the additional hydrogen atom attaching itself at the central carbon atom of the allene skeleton. McKenna *et al.*[1] showed that allene is reduced by nitrogenase in D_2O to give the 2,3-dideuteriopropene, and our data are fully consonant with this. Isomerization is a feasible way to deuterium labelling at position 2 of allene, as observed in the enzymic reduction of cyclopropene. These observations also demonstrate that the reduction of allenes by metal hydrides does not invariably follow a free radical pathway, as has been suggested.[8]

Reactions of acetylenes with iron complexes have given a variety of complexes, including $[FeCl(CCPh)(dmpe)_2]$[6] and $[Fe(CCPh)_2(dmpe)_2]$.[9] We have been able to obtain a range of compounds depending upon the acetylene, but generally all contain two acetylene residues. We have determined the structure of one product from $[FeH(H_2)(dmpe)_2][BPh_4]$ and PhC≡CH, and this is shown in Fig. 3, with bond lengths and angles being given in Fig. 4.§ The acetylenes have joined at the

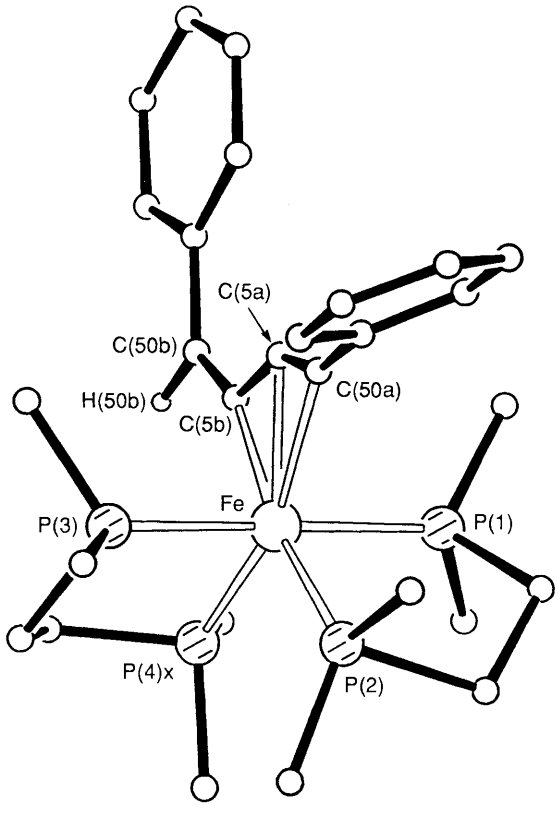

Fig. 3 Representation of the structure of $[Fe\{C(CHPh)C{\equiv}CPh\}(dmpe)_2]^+$

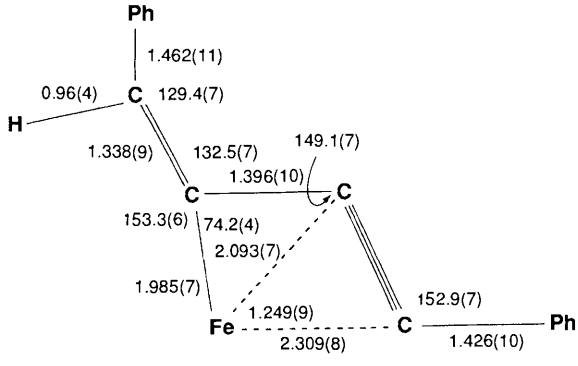

Fig. 4 Selected distances (in Å) and angles (in °) in $[Fe\{C(CHPh)C{\equiv}CPh\}(dmpe)_2]^+$

‡ NMR spectra (δ values) of the new compounds: (*a*) $[Fe(HCH_2CCMe_2)(dmpe)_2][BPh_4]$; (*b*) $[Fe(PhC_3CHPh)(dmpe)_2][BPh_4]$: $^{13}C\{^1H\}$, solvent CD_2Cl_2, (*a*) PCH_3: 11.2(m), 12.8(m), 19.7(2×m), 20.2(m), 22.2(m), 23.6(m), 25.9(m); PCH_2: 27.8(m), 31.6(2×m), 34.6(m), Fe–H–CH_2: 31.4(s); $C(CH_3)_2$: 23.5(s), 27.1(s); $C(CH_3)_2$: 146(3); $CH_2C{=}CMe_2$: 232(s). (*b*) PCH_3: 9.8(m), 10.5(m), 16.5(m), 18.1(m), 19.9(m), 20.3(m), 20.4(m), 21.4(m); PCH_2: 27.3(m), 28.8(m), 32.5(m), 34.7(m); *C*≡*C*: 51(s), 106(s); *C*HPh, 133.5(s); PhC*H*C: 153(s).

^1H, (*a*) (CD_2Cl_2), PCH_3: 0.88, 1.02, 1.21, 1.48, 1.51, 1.63, 1.67, 1.73 (all d, 3H, $^2J_{PH}$ 5–8 Hz); PCH_2: 1.98 (broad quintet, 8H); Fe–*H*–CH_2: −4.6(br, s, 1H); $C(CH_3)_2$: 2.15(s, 6H); HCH_2C: 1.28 (s,2H). (*b*) (CD_3COCD_3), PCH_3: 0.80(3H), 0.91(3H), 1.38(6H), 1.53(6H), 1.71(6H) (all d, $^2J_{PH}$ 7–9 Hz); PCH_2: obscured; C*H*Ph: 2.81(s); aromatic protons: 6.76(t), 6.91(t), 7.19(t), 7.32(s), 7.34(t), 7.47(s), 7.78(d) (30H in all, CPh + BPh_4).

§ This compound has now also been isolated from the reaction of $[FeCl_2(dmpe)_2]$ with an excess of PhC≡CH. Its structure was inferred (correctly) from NMR data (L. D. Field, A. V. George and T. W. Hambley, *Inorg. Chem.*, 1990, **29**, 4565).

hydrogen-bearing carbon atoms and a hydrogen atom has migrated to an adjacent carbon. The ligand so generated is probably best described as an η^3,(1−) ligand, a 1,4-diphenyl-1-yn-3-en-3-yl, although nothing is adequate to name it entirely satisfactorily.‡ There are precedents for this structure in $[Ru(CCPh)(\eta^3\text{-}PhC_3CHPh)\{PhP[CH_2CH_2CH_2P(cyclo\text{-}C_6H_{11})_2]_2\}]$[10] and $[Os(PMe_3)_4(\eta^3\text{-}PhC_3CHPh)][PF_6]$,[11] but this is the first in iron chemistry.

We have yet to detect coupled products in the reduction of cyclopropene by nitrogenases, neither was 1,2-dideuteriopropene identified in reactions in deuteriated solvents. The ready formation of coupled products in the presence of polyhydrides[12] makes it highly unlikely that isomerization to propyne is involved in nitrogenase reductions, but clearly we have strong circumstantial evidence that nitrogenase can catalyse the isomerization of cyclopropene to allene.

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