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The use of high reaction pressures in the synthesis of acetylide complexes of iron

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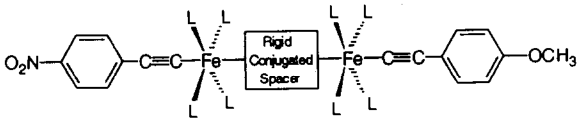
Abstract

High pressures (100–800 MPa) have been used to assist the synthesis of acetylide complexes of iron. The complex $FeH(C{\equiv}CPh)(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) was formed quantitatively in 30 min from the reaction of $FeH_2(dmpe)_2$ with phenylacetylene in toluene under a pressure of 800 MPa.

1. Introduction

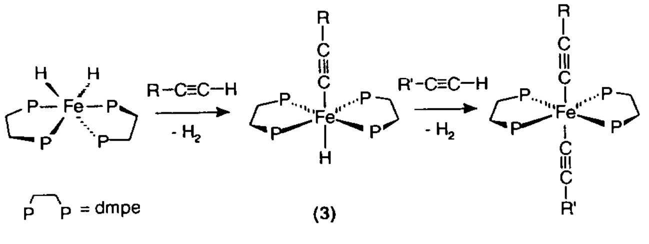
Iron(II) dihydrides of the type $FeH_2(dmpe)_2$ (**1**) (dmpe = $Me_2PCH_2CH_2PMe_2$) are protonated by weak acids to give molecular hydrogen complexes in which a molecule of dihydrogen is bound to the metal in an η^2 fashion [1]. Molecular hydrogen in the complex *trans*-$[FeH(H_2)(dmpe)_2]^+$ (**2**) is only weakly bound, and may be displaced by a variety of species including neutral ligands (*e.g.* dinitrogen, nitriles, tertiary phosphines or ethylene) [2] and anions (*e.g.* halides, thiolates, cyanide or acetylides) [3]. 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 $FeH_2(dmpe)_2$ (**1**) to form the molecular hydrogen complex, $[FeH(H_2)(dmpe)_2]^+$ (**2**), which reacts to give an acetylide hydride metal complex, $FeH(C{\equiv}CPh)(dmpe)_2$ (**3**), and eventually the metal bis(acetylide) complex, $Fe(C{\equiv}CPh)_2(dmpe)_2$ (**4**) [4].

The facile synthesis of bis(acetylide)iron complexes has already been reported [4] and the importance of this type of compound as precursors of materials with non-linear optical properties has been highlighted by several groups [5]. Most of the metal acetylides so far synthesised have been symmetrically substituted, *i.e.* two or more identical acetylides are attached to the metal centre. The synthesis of complexes with the metal centre bonded to different acetylenes, *e.g.* **5**, is more challenging. Extended complexes of this type are expected to be long, rigid, non-charged species with large dipole moments and, possibly, novel optical properties.



(**5**)

For the synthesis of bisacetylide complexes of iron, the acetylide hydride complex **3** is a useful intermediate. The acetylide hydride may be treated with a different acetylene to give a complex containing two different acetylenic ligands (Scheme 1). However the isolation of metal acetylide hydrides in pure form has been difficult.



Scheme 1.

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High pressure synthesis is now an established technique in many areas of preparative organic chemistry [6]. There is also a large body of volume of activation data for coordination compounds [7], but there has been little work on the use of high pressure techniques in the synthesis of organometallic complexes. In this paper we report the use of high pressures to control the reaction of a terminal acetylene with $FeH_2(dmpe)_2$ (**1**) in order to optimise the yield of the mono-addition product, $FeH(C{\equiv}CR)(dmpe)_2$ (**3**).

2. Results and discussion

When a ten-fold excess of phenylacetylene was mixed with a solution of $FeH_2(dmpe)_2$ (**1**) in toluene (*ca.* 15 mM) at atmospheric pressure, the yield of $FeH(C{\equiv}CPh)(dmpe)_2$ (**3**) steadily increased with time. The conversion of **1** to **3** was approximately 8% (determined by ^{31}P NMR spectroscopy) after 24 h. The reaction was not clean and several additional products were observed, by ^{31}P NMR. The major byproduct was the symmetrical bis(acetylide) complex, $Fe(C{\equiv}CPh)_2(dmpe)_2$ (**4**), formed by the secondary reaction of **3** with remaining phenylacetylene in the mixture.

In contrast, when a sample of the same reaction mixture was pressurised to 750 MPa (7500 atm) at room temperature, there was 40% conversion in to the acetylide hydride **3** after *ca.* 15 min, and the reaction was complete after 90 min (Table 1). When the reaction mixture is kept at high pressure for a longer time, the yield of $FeH(C{\equiv}CPh)(dmpe)_2$ (**3**) fell, with increase in the amount of byproducts. The principal byproduct was again the bis(acetylide) complex, $Fe(C{\equiv}CPh)_2(dmpe)_2$ (**4**).

In a separate experiment, the effect on the reaction of systematically increasing pressure was examined (Table 2). Aliquots of the same solution were maintained at various pressures for 30 min at room temperature before the reaction solutions were examined. Increase in the pressure clearly facilitated the formation of $FeH(C{\equiv}CPh)(dmpe)_2$ (**3**). An excellent yield (95%) of **3** was achieved after 30 min under a pressure of 800 MPa, and ^{31}P NMR spectroscopy indicated that **3** was the only phosphorus-containing species in solution.

TABLE 1. Effects of time and pressure on the yields of $FeH(C{\equiv}CPh)(dmpe)_2$ (**3**) and $Fe(C{\equiv}CPh)_2(dmpe)_2$ (**4**) [a]

Pressure (MPa)	Time (h)	FeH_2-(dmpe)$_2$ (**1**) yield, %	FeH(C≡CPh)-(dmpe)$_2$ (**3**) yield, %	Fe(C≡CPh)$_2$-(dmpe)$_2$ (**4**) yield, %
0.1	2	99	1	0
0.1	5	93	7	0
0.1	24	92	8	0
750	0.25	58	42	0
750	1.5	0	100	0
750	14.5	0	53	26

[a] reaction at 20°C.

TABLE 2. Effects of pressure on the yield of $FeH(C{\equiv}CPh)(dmpe)_2$, (**3**) [a]

Pressure (MPa)	$FeH_2(dmpe)_2$ (**1**) yield, %	$FeH(C{\equiv}CPh)(dmpe)_2$ (**3**) yield, %
100	89	11
400	81	19
600	35	65
800	0	95

[a] reaction at 20°C after 30 min reaction time.

The fact that pressure has a marked effect on the rate of formation of the acetylide hydride complex, $FeH(C{\equiv}CPh)(dmpe)_2$ (**3**) indicates that the volume of activation ($\Delta V^{\ddagger}$) for its formation is substantial and negative in sign. The reaction is likely to involve a multistep mechanism and almost certainly proceeds via the initial formation of a molecular hydrogen complex, $[FeH(H_2)(dmpe)_2]^+$ (**2**). A significant contribution to the volume profile of the reaction will result from the pre-equilibrium formation of $[FeH(H_2)(dmpe)_2]^+$ (**2**). This reaction is likely to possess a value of $\Delta V^{\ddagger}$ which is substantially negative in toluene solution, since the ionogenic nature of the reaction would be accompanied by a volume decrease resulting from electrostriction of the solvent. The application of pressure would increase the equilibrium concentration of the charged species.

3. Conclusions

High yields of $FeH(C{\equiv}CPh)(dmpe)_2$ (**3**) have been obtained from the reaction of $FeH_2(dmpe)_2$ (**1**) with phenylacetylene in toluene solvent after 30 min under a pressure of 800 MPa. The reaction does not proceed at an appreciable rate at atmospheric pressure and temperature, but, under high pressure conditions, it is rapid and clean, with minimal formation of byproducts.

4. Experimental section

High pressure equipment consisted of a mono-block cylindrical pressure vessel fitted with a piston powered by a 50 ton hydraulic ram, the whole apparatus being contained in a press frame. The pressures were calibrated by means of the freezing pressures of suitable liquids. Samples of up to 5 ml of the reaction mixture were encapsulated in a poly(tetrafluoroethylene) cylindrical cell closed with a sliding stopper. The reaction cell was placed within the high pressure vessel, which was filled with hydraulic fluid (ethanol) and the desired pressure applied.

In a typical experiment FeH$_2$(dmpe)$_2$ (**1**, 12 mg, 0.03 mmol) was dissolved in toluene-d_8 (2 ml) and phenylacetylene (40 mg, 0.4 mmol) added. The solution was split into five portions; one portion was retained at room temperature and pressure while the others were pressurised to 100, 400, 600 or 800 MPa. After 30 min the pressure was released and the sample cooled to -78°C prior to analysis by ^{31}P and ^{1}H NMR spectroscopy. The product complexes had identical spectra to those of authentic samples.

FeH(C≡CPh)(dmpe)$_2$, (**3**) [8]: ^{31}P{^{1}H} NMR [9*] (toluene-d_8) δ 74.3 ppm; ^{1}H NMR [9*] (toluene-d_8) δ -17.44 (quintet, 1H, FeH, $^{2}J(\mathrm{PH}) = 45$ Hz) 1.66 (s, 12H, CH$_3$), 1.35 (s, 12H, CH$_3$), 1.6 (m, 8H, CH$_2$), 6.8–7.5 (m, 5H, Ar–H) ppm. Fe(C≡CPh)$_2$(dmpe)$_2$ (**4**) [4]: ^{31}P{^{1}H} NMR (toluene-d_8) δ 68.7 ppm; ^{1}H NMR (toluene-d_8) δ 1.61 (s, 24H, CH$_3$), 1.72 (s, 8H, CH$_2$), 7.18 (m, 2H, Ar–H), 7.38 (m, 4H, Ar–H), 7.54 (m, 4H, Ar–H) ppm.

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9 ^{31}P{^{1}H} NMR spectra (162.0 MHz) were referenced to external, neat, trimethyl phosphite taken as 140.85 ppm. ^{1}H NMR spectra (400.1 MHz) were referenced to solvent resonances.

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* Reference number with an asterisk indicates a note in the list of references.