Metallocycle synthesis accelerated by high pressure

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Abstract

Reaction of cis-[FeH$_2$(dmpe)$_2$] (1) with diphenylbutadiyne results in an insertion into both of the iron–hydride bonds to form an iron metallocycle. Spectroscopic and crystallographic data of [Fe(PhHCC$_2$CHPh)(dmpe)$_2$] (3) show 1,4-diphenylbutatriene is symmetrically bound to the metal via the central double bond. The reaction to form the metallocyclic complex is greatly accelerated by application of external pressure. A 41% yield of (3) is isolated after two days at atmospheric pressure or after approximately 75 min at 800 MPa. © 1997 Elsevier Science S.A.

Keywords: Metallocycle; Transition metals

1. Introduction

Complexes of transition metals with alkynes form a diverse group of compounds. When σ-bound, metal acetylides are potential non-linear optical [1], conducting [2] or liquid crystalline [3] materials, and when π-bound they may result in metallocyclic compounds [4] and cyclotrimerisation [5] products. Metal complexes of cumulenes are closely allied to metal acetylides and may form complexes with allylidene links between metal centres [6] or occur as a range of π-bound complexes [7–10].

High pressure techniques are well known in the synthesis of organic compounds [11] and have been used in combination with transition metal catalysts [12] or main group organometallic reagents [13] but have rarely been applied to the synthesis of organometallic compounds [14]. As part of a program of synthesis of acetylide complexes of iron and ruthenium [15] we have investigated the influence of high reaction pressures on the reaction of [FeH$_2$(dmpe)$_2$] (1) (dmpe Me$_2$PCH$_2$CH$_2$PMe$_2$) with substituted butadiynes. In this paper we report that high pressure facilitates the synthesis of a novel metallocycle, [Fe(PhHCC$_2$CHPh)(dmpe)$_2$] (3), on reaction between [FeH$_2$(dmpe)$_2$] (1) and diphenylbutadiyne.

2. Results and discussion

Reaction of excess diphenylbutadiyne with [FeH$_2$(dmpe)$_2$] (1) in tetrahydrofuran solution produced metallocycle (3) after two days at room temperature and pressure in approximately 41% yield (Scheme 1).

The reaction proceeded via an intermediate tentatively assigned to structure (2), observed by ^{31}P, ^{13}C and ^{1}H NMR. The concentration of (2) rose initially before decreasing as the final product (3) formed. The compound (2) displayed a singlet resonance in the ^{31}P{^{1}H} spectrum which splits into a doublet in the proton coupled phosphorus spectrum, indicating a complex of *trans* geometry containing an iron bound hydride ligand (δ 74 ppm, $^2J_{PH}$ = 49 Hz). This structure is supported by the ^{1}H spectrum which showed a quintet at high field (δ −20.5 ppm) typical of a metal bound hydride coupled to four phosphorus atoms. The ^{13}C{^{1}H} spectrum contained a resonance associated with the metal bound carbon (δ 167.5 ppm) and the two acetylenic carbon atoms (δ 105.5 and 110.0 ppm).

The ^{31}P{^{1}H} NMR spectrum of (3) exhibits a distinctive pair of apparent triplet resonances at δ 57.8 and 71.7 ppm which confirms a *cis* arrangement of phosphine ligands. Moreover, the triplet-like ^{31}P resonances indicate that the two remaining coordination sites are substituted by identical ligands. The ^{1}H spectrum displayed a singlet resonance at δ 6.5 ppm assigned to the vinylic proton. The ^{13}C{^{1}H} NMR spectrum of (3)

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Scheme 1.

revealed that, upon complexation, the C_4 fragment of the diyne was symmetrically coordinated to the metal centre, with a phosphorus-coupled resonance typical of a metal bound carbon atom at δ 169.1 ppm and a vinylic carbon atom at $\delta \sim$ 120 ppm. The resonance of the vinylic carbon atoms is close to that of the carbon in the *para* position of the aromatic rings (119.5 and 121.9 ppm) and individual assignment cannot be made with confidence. There are two possible structures consistent with the NMR data. The metal could be bound to the 1,4-positions of the butadiyne to form a five-membered metallocycle or to the 2,3-positions to form a three-membered metallocycle. The structure of (3) was confirmed by X-ray crystallography. A summary of crystallographic data is given in Table 1, representative bond lengths and angles are given in Table 2 and atom coordinates in Table 3.

The iron atom is symmetrically coordinated to C(2) and C(3) of the butadiyne ligand in the complex (3) (Fig. 1). The C(1)–C(2) and C(2)–C(3) bond lengths

Table 1
Summary of crystallographic data for [Fe(dmpe)$_2$(PhCHCCCHPh)] (3)

Molecular formula	$C_{28}H_{44}FeP_4$
Molecular weight	560.4
Crystal system	Monoclinic
Space group	$P2_{1/n}$ (No. 14)
Cell dimensions	$a = 9.892(2)$, $b = 23.664(5)$,
	$c = 12.881(5)$ Å
	$\beta = 99.76(2)°$
Volume	2972(1) Å^3
Z	4
D_{calc}	1.25 g cm^{-3}
Crystal dimensions	$0.45 \times 0.25 \times 0.1$ mm^3
Wavelength	0.71069 Å
Abs. (min, max)	0.84, 0.93
μ(Mo Kα)	7.37 cm^{-1}
$2\theta_{max}$	50.0°
hkl Range	$-11 \to 11$, $0 \to 28$, $0 \to 15$
Residual peaks	-0.32, 0.45
Data collected	5618
Unique data	5413
R_{merge}	6.5%
Data with $I > 2.5\sigma(I)$	2213
Number of variables	306
R	0.049
R_w	0.049
Solution method	Direct
Solution program	SHELX86

Table 2
Summary of representative bond lengths (Å) and angles (°) for [Fe(dmpe)$_2$(PhCHCCCHPh)] (3)

Fe(1)–P(1)	2.190(3)	C(3)–C(4)	1.35(1)
Fe(1)–P(2)	2.184(3)	C(4)–C(5)	1.47(1)
Fe(1)–P(3)	2.203(3)	C(5)–C(6)	1.39(1)
Fe(1)–P(4)	2.189(3)	C(5)–C(10)	1.40(1)
Fe(1)–C(2)	1.939(8)	C(6)–C(7)	1.36(1)
Fe(1)–C(3)	1.940(8)	C(7)–C(8)	1.38(1)
C(1)–C(2)	1.36(1)	C(8)–C(9)	1.39(1)
C(1)–C(11)	1.46(1)	C(9)–C(10)	1.37(1)
C(2)–C(3)	1.375(8)		
P(1)–Fe(1)–P(2)	84.5(1)	Fe(1)–C(2)–C(1)	145.3(7)
P(1)–Fe(1)–P(3)	177.3(1)	C(2)–C(1)–C(11)	128.7(8)
P(1)–Fe(1)–P(4)	94.3(1)	C(1)–C(2)–C(3)	142.7(8)
P(1)–Fe(1)–C(2)	84.9(2)	C(2)–C(3)–C(4)	143.0(8)
P(1)–Fe(1)–C(3)	97.1(2)	C(3)–C(4)–C(5)	127.1(7)
C(2)–Fe(1)–C(3)	41.5(2)	C(4)–C(5)–C(6)	121.0(8)
Fe(1)–C(2)–C(3)	69.3(5)	C(4)–C(5)–C(10)	122.2(7)

are 1.36(1) and 1.375(8) Å respectively, slightly longer than a simple alkene (1.34 Å) and considerably longer than the central bond of butatriene (1.26 Å) [16]. The

Table 3
Positional parameters for [Fe(dmpe)$_2$(PhCHCCCHPh)] (3) with estimated standard deviations in parentheses

Atom	x	y	z
Fe	0.4320(1)	0.17348(4)	0.8570(1)
P(1)	0.3789(2)	0.1720(1)	1.0153(2)
P(2)	0.6022(2)	0.1190(1)	0.9256(2)
P(3)	0.4852(2)	0.1706(1)	0.6978(2)
P(4)	0.2580(2)	0.1208(1)	0.7876(2)
C(1)	0.2570(8)	0.2845(4)	0.8626(7)
C(2)	0.3647(8)	0.2506(3)	0.8520(6)
C(3)	0.5054(8)	0.2497(3)	0.8632(6)
C(4)	0.6154(8)	0.2816(3)	0.8520(7)
C(5)	0.6149(8)	0.3406(3)	0.8157(6)
C(6)	0.7331(8)	0.3732(4)	0.8345(6)
C(7)	0.735(1)	0.4277(4)	0.8009(8)
C(8)	0.618(1)	0.4524(4)	0.7450(8)
C(9)	0.499(1)	0.4203(4)	0.7224(7)
C(10)	0.4980(8)	0.3657(3)	0.7566(7)
C(11)	0.2586(8)	0.3428(3)	0.8990(6)
C(12)	0.1391(8)	0.3753(4)	0.8806(7)
C(13)	0.138(1)	0.4305(4)	0.9194(8)
C(14)	0.254(1)	0.4539(4)	0.9753(8)
C(15)	0.371(1)	0.4226(5)	0.9948(7)
C(16)	0.375(1)	0.3685(4)	0.9582(7)
C(17)	0.450(1)	0.2285(4)	1.1040(7)
C(18)	0.2022(9)	0.1704(5)	1.0403(7)
C(19)	0.450(1)	0.1096(4)	1.0877(7)
C(20)	0.591(1)	0.1028(5)	1.0662(8)
C(21)	0.7790(9)	0.1466(4)	0.9465(8)
C(22)	0.631(1)	0.0487(4)	0.8765(9)
C(23)	0.416(1)	0.2271(4)	0.6100(7)
C(24)	0.6617(9)	0.1680(4)	0.6735(7)
C(25)	0.408(1)	0.1083(4)	0.6254(7)
C(26)	0.263(1)	0.1062(5)	0.6445(8)
C(27)	0.0825(8)	0.1485(4)	0.7676(8)
C(28)	0.227(1)	0.0499(4)	0.832(1)

C(1)–C(2) and C(2)–C(3) bond lengths suggest that there is a degree of electron delocalisation across the fragment and this extends to the phenyl substituents, the bond length between C(1) and C(11), for example, being 1.46(1) Å. However, the bond angle C(1)–C(2)–C(3) is 142.7(8)°, which indicates considerable deviation from the ideal angle of 180° expected for a cumulene. The complexed butadiyne is not planar, the C(1)–C(2)–C(3)–C(4) torsion angle being 36(2)° and the distance between C(10) and C(16) of the two phenyl rings being 3.05(1) Å.

There is one previous report of a crystal structure of iron symmetrically bound to tetraphenylbutatriene to form the three-membered metallocycle [Fe(CO)$_4$(Ph$_2$C$_4$Ph$_2$)] [7]. In this case, the distances between C(1)–C(2) (1.33 Å) and C(2)–C(3) (1.35 Å) are slightly shorter than the comparable distances in (3) while the Fe–C(butatriene) distance in [Fe(CO)$_4$(Ph$_2$C$_4$Ph$_2$)] is longer (2.04 Å) than Fe–C(2) in (3) (1.94 Å). The C(butatriene)–Fe–C(butatriene) bond angles of [Fe(CO)$_4$(Ph$_2$C$_4$Ph$_2$)] and (3) are 38.4° and 41.5° respectively. There are several reports of rhodium chloride bisphosphine complexes with C$_4$ and C$_6$ ligands and in all cases the metal–ligand distance is longer and C–Rh–C angle smaller than in (3) [9,10].

The influence of pressure on the formation of (2) and (3) over a period of 75 min was studied (Table 4). The application of pressure had a dramatic effect on the reaction, accelerating the formation of both (2) and (3). At pressures above 600 MPa, quantitative formation of (2) was observed within 5 min. Over a period of 1 h at this pressure, the concentration of (2) decayed as the
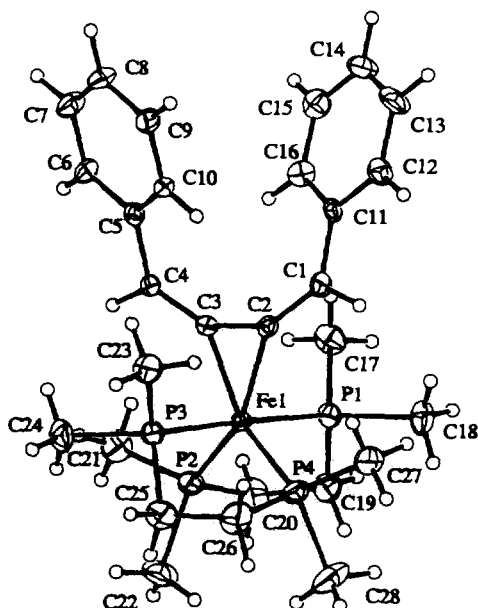
Table 4
The effect of pressure and time on the reaction of [FeH$_2$(dmpe)$_2$] (1) with diphenylbutadiyne in THF solvent at 25 °C to yield (2) and (3)

	0.1 MPa	200 MPa	400 MPa	600 MPa	800 MPa
5 min (2)	0	5%	12%	100%	a
(3)	0	0	0	0	a
10 min (2)	a	a	a	a	76%
(3)	a	a	a	a	24%
15 min (2)	2%	9%	25%	91%	a
(3)	0	0	0	9%	a
45 min (2)	2%	10%	39%	79%	a
(3)	0	0	0	21%	a
65 min (2)	a	a	a	a	66%
(3)	a	a	a	a	34%
75 min (2)	2%	14%	32%	70%	33%[b]
(3)	0	0	16%	30%	67%[b]

[a] Not recorded.
[b] Yields recorded after 130 min.

metallocycle formed. A 92% isolated yield of (3) was obtained after 4 h at 800 MPa at room temperature.

Associative reactions and reactions involving an increase in charge separation in the transition state are accelerated by pressure [11]. The formation of (2) appears to be particularly sensitive to pressure. The reaction must involve several steps, probably including de-coordination of a phosphine ligand, binding of the butadiyne in a π fashion, migration of a hydride from the metal to the bound acetylene and recoordination of the phosphine ligand. Each step will contribute to the volume profile of the reaction but the dominant process will be the coordination of the butadiyne to the metal which will be associated with a volume decrease [17]. The intramolecular rearrangement of (2) to (3) involves smaller volume changes and would be expected to be less pressure sensitive.

When diphenylbutadiyne was reacted with [FeH$_2$(dmpe)$_2$] (1) for a prolonged period at high pressure, an additional complex (4) was observed. The same complex was formed in approximately 10% yield when a THF solution of (3) was pressurised at 800 MPa for five days. The ^{31}P NMR spectrum possessed four distinct phosphorus resonances (δ 45, 51, 61, 69 ppm) indicative of an unsymmetrically substituted cis complex. There is precedent for a complex with a symmetrically bound cumulene to isomerise to a thermodynamically more stable complex in which the cumulene is unsymmetrically bound [10]. It seems likely that a similar situation occurs in this case to give complex (4), however this product has not been fully characterised.

Fig. 1. ORTEP of Fe(dmpe)$_2$(PhCHCCCHPh) (3) showing the atom numbering used and thermal ellipsoids plotted at the 25% level.

(4)
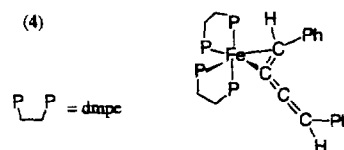
3. Conclusions

High yields of $[Fe(PhHCC_2CHPh)(dmpe)_2]$ (3) have been obtained from the reaction of $[FeH_2(dmpe)_2]$ (1) with diphenylbutadiyne at room temperature and a pressure of 800 MPa. The reaction is slow at atmospheric pressure and temperature. A crystal study shows the butadiyne is bound to the metal through C(2) and C(3), forming a three-membered metallocycle. Bond lengths indicate the bound organic fragment has some cumulene character.

4. Experimental section

The high pressure equipment has been described before [14]. 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.

$[FeH_2(dmpe)_2]$ (1) [18] (60 mg, 0.17 mmol) and diphenylbutadiyne [19] (100 mg, 0.50 mmol) were dissolved in THF (2 ml) and the solution pressurised to 800 MPa. After 4 h at room temperature, the solvent was removed under vacuum and solid residue washed with hexane (3 × 5 ml). The residue was recrystallised from a THF/hexane mixture to give $[Fe(PhHCC_2CHPh)(dmpe)_2]$ (3) as a red–brown solid (87 mg, 92%).

$[Fe(PhHCC_2CHPh)(dmpe)_2]$ (3): m.p. decomposed at temperatures above 245 °C. $^{31}P\{^1H\}$ NMR δ (THF-d_8) 57.8 (apparent triplet, 2P), 71.7 (apparent triplet, 2P). $^1H\{^{31}P\}$ NMR δ (THF-d_8) 0.68 (s, 6H, CH$_3$), 1.32 (s, 6H, CH$_3$), 1.41 (s, 6H, CH$_3$), 1.68 (s, 6H, CH$_3$), 1.5–1.8 (m, 8H, CH$_2$), 6.45 (s, 2H, =CH), 6.6–6.8 (m, 10H, ArH). $^{13}C\{^1H,^{31}P\}$ NMR δ (THF-d_8) 15.64 (CH$_3$), 18.48 (CH$_3$), 22.44 (CH$_3$), 24.31 (CH$_3$), 31.61 (CH$_2$), 33.26 (CH$_2$), 119.46 (=CH or ArCH), 121.93 (=CH or ArCH), 127.28 (CH), 128.12 (CH), 143.29 (C), 169.07 (FeC). M.s. $m/z = 561$ (M + 1$^+$, 30%), 411 (23), 211 (20), 183 (100), 167 (20), 151 (26).

In a typical experiment to study the effect of pressure on the reaction, $[FeH_2(dmpe)_2]$ (1) (40 mg, 0.11 mmol) and diphenylbutadiyne (50 mg, 0.25 mmol) were dissolved in THF (4 ml). A portion was kept at room pressure while the remainder was pressurised to 600 MPa; both samples were maintained at ambient temperature. Aliquots of the reaction solution were removed from the pressure vessel after 5, 15, 45 and 75 min and examined by ^{31}P NMR spectroscopy.

An orange blade-like crystal was attached to a thin glass fibre with cyanoacrylate resin and mounted on an Enraf–Nonius CAD 4 diffractometer employing graphite monochromated Mo Kα radiation. Primitive mono-

clinic cell constants were obtained from a least-squares refinement against the setting angles of 16 reflections in the range $19.12° < 2\theta < 24.14°$. Data were collected at a temperature of 21 ± 1 °C with ω–1.33θ scans to a maximum 2θ value of 50.0°. The intensities of three representative reflections measured every 60 min decreased by 17.4% during the data collection.

A linear correction factor was accordingly applied to the data. The crystal faces were indexed and an analytical absorption correction was applied to the data. The data were also corrected for Lorentz and polarisation effects.

All calculations were performed using the teXsan [20] crystallographic software package. The structure was solved in the space group $P2_1/n$ (No. 14) by direct methods [21] and expanded using Fourier techniques [22]. Neutral atom scattering factors were taken from Cromer and Waber [23]. Anomalous dispersion effects were included in the structure factor calculation [24], and the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [25]. The values for the mass attenuation coefficients are those of Creagh and Hubbell [26]. The non-hydrogen atom parameters were refined anisotropically and the H(1) and H(4) proton sites were located and refined with isotropic displacement parameters. The remaining hydrogen atoms were included in the full-matrix least-squares refinement at calculated positions with group temperature factors. An ORTEP depiction of the molecule is given in Fig. 1 [27].

Acknowledgements

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