

Synthesis of new thiophenolato hydrido iron(II) complexes and their substitution reactions with alkynes

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ABSTRACT

The novel thiophenolato hydrido iron(II) complexes [*cis*-Fe(H)(SAr)(PMe₃)₄] (**4–6**) (Ar = *p*-BrC₆H₄ (**4**), *p*-MeOC₆H₄ (**5**) and *o*-MeC₆H₄ (**6**)) were prepared through the reaction of Fe(PMe₃)₄ with thiophenols ArSH (**1–3**). Reaction of **6** with trimethylsilylacetylene and phenylacetylene afforded bisalkynyl iron(II) complexes [Fe(PMe₃)₄(C≡CSiMe₃)₂] (**7**) and [Fe(PMe₃)₄(C≡CPh)₂] (**9**) through elimination of dihydrogen and the formation of thiophenol. The reaction of **5** with 2-methyl-3-butyn-2-ol gave [Fe(PMe₃)₄(C≡CCMe₂OH)₂] (**10**). The crystal structures of complexes **4**, **7** and **10** were determined by X-ray diffraction. A mechanism for the formation of **7** is proposed.

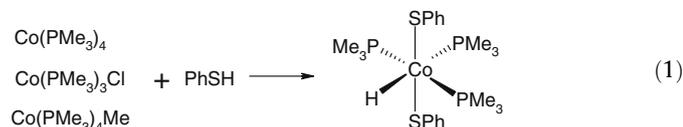
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1. Introduction

Hydrido compounds of transition metals are not only important materials in many stoichiometric reactions, but also decisive intermediates in catalytic processes. Therefore, they play an important role in synthetic and industrial chemistry. Literature reports on transition metal hydrides are mainly concentrated on precious metals such as Ru, Rh, Ir, Pt, Pd [1–13]. For their lighter congeners Fe, Co and Ni, there are rather few reports with regard to catalytic properties of their metal hydrides, which would be of great significance from the perspective of economic practicality.

A [M–H] moiety in hydrido compounds of transition metals can react with alkenes or alkynes giving rise to σ -alkyl or σ -alkenyl metal compounds. It has been demonstrated that hydrides of cobalt and nickel afforded the expected products, while the family iron hydrides has received less attention [14,15].

More recently, vinyl sulfides have shown great potential in organic synthesis with the useful feature of a unique selectivity control. They are easily obtained by reaction of thiols with alkynes [16–18], and it was recognized that the addition of thiol to alkyne in the presence of a metal catalyst occurs with high regioselectivity and good yields [19,20].



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We have reported on the S–H bond activation of thiophenols at cobalt(0) and cobalt(I) centres [21]. A novel thiophenolato hydrido cobalt(III) complex was obtained (Eq. (1)). As continuation of this work we here report on progress in the S–H bond activation by iron(0). The novel hydrido iron complexes (**4–6**) formed by oxidative addition of S–H moieties were isolated and characterized. Reaction of the hydrido iron complexes with alkynes invariably resulted in bisalkynyl iron(II) complexes. No insertion products have been observed that dominated reactions of hydrido cobalt [22] and hydrido nickel [15] complexes.

2. Experimental

2.1. General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. The literature method was used in the preparation of tetrakis(trimethylphosphane)iron(0) [23]. Other chemicals were used as purchased. Infrared spectra (4000–400 cm^{−1}), as obtained from Nujol mulls between KBr disks, were recorded on a Nicolet 5700. ¹H, ¹³C, and ³¹P NMR (300, 75, and 121 MHz, respectively) spectra were recorded on a Bruker Avance 300 spectrometer. ¹³C and ³¹P NMR resonances were obtained with broadband proton decoupling. X-ray crystallography was performed with a Bruker Smart 1000 diffractometer.

2.2. Synthesis of the complexes

2.2.1. Synthesis of **4**

To a solution of 1.10 g (3.05 mmol) of Fe(PMe₃)₄ in 50 mL of pentane was slowly injected 0.58 g (3.07 mmol) of *p*-bromothiophenol

1 at $-80\text{ }^{\circ}\text{C}$. The reaction started immediately with formation of a yellow solid. The mixture was allowed to warm to ambient temperature. During this period the color turned yellow-brown. After stirring at room temperature for 16 h a dark brown solution was obtained. After a slight turbidity had been filtered off, the red filtrate at $4\text{ }^{\circ}\text{C}$ gave red crystals of **4** suitable for X-ray diffraction. Yield: 0.28 g (17%). *Anal. Calc.* for $\text{C}_{18}\text{H}_{41}\text{BrFeP}_4\text{S}$ (549.21 g/mol): C, 39.36; H, 7.52. Found: C, 39.02; H, 8.01%. IR (Nujol, cm^{-1}): 1866 $\nu(\text{Fe-H})$, 1580 $\nu(\text{C}=\text{C})$, 939 $\nu(\text{PMe}_3)$. ^1H NMR (300 MHz, C_6D_6 , 296 K, ppm): δ 0.99 (m, 36H, PCH_3), 7.16–8.09 (m, 4H, Ar-H), -10.31 (m, 1H, Fe-H); ^{31}P NMR (121 MHz, C_6D_6 , 300 K, ppm): δ 10.1 (m, 1P), 16.6 (m, 2P), 27.6 (m, 1P).

2.2.2. Synthesis of **5**

To a solution of 1.24 g (3.44 mmol) of $\text{Fe}(\text{PMe}_3)_4$ in 50 mL of pentane was slowly injected 0.48 g (3.44 mmol) of *p*-methoxythiophenol **2** at $-80\text{ }^{\circ}\text{C}$. The reaction started immediately with formation of a yellow solid. The reaction mixture was allowed to warm to ambient temperature. During this period the color turned yellow-brown. After stirring at room temperature for 16 h a dark brown solution was obtained. A slight turbidity was filtered off, and from the red filtrate at $4\text{ }^{\circ}\text{C}$ red crystals of **5** were obtained. Yield: 0.43 g (25%). *Anal. Calc.* for $\text{C}_{19}\text{H}_{44}\text{FeOP}_4\text{S}$ (500.36 g/mol): C, 45.61; H, 8.86. Found: C, 45.46; H, 9.00%. IR (Nujol, cm^{-1}): 1818 $\nu(\text{Fe-H})$, 1591 $\nu(\text{C}=\text{C})$, 942 $\nu(\text{PMe}_3)$. ^1H NMR (300 MHz, C_6D_6 , 296 K, ppm): δ 1.12 (m, 36H, PCH_3), 3.40 (s, 3H, OCH_3), 7.15–8.22 (m, 4H, Ar-H), -14.20 (m, 1H, Fe-H); ^{31}P NMR (121 MHz, C_6D_6 , 300 K, ppm): δ 10.8 (m, 1P), 16.5 (m, 2P), 24.2 (m, 1P).

2.2.3. Synthesis of **6**

To a solution of 1.37 g (3.80 mmol) of $\text{Fe}(\text{PMe}_3)_4$ in 50 mL of pentane were slowly injected 0.47 g (3.79 mmol) of *o*-methylthiophenol **3** at $-80\text{ }^{\circ}\text{C}$. The reaction started immediately with formation of a yellow solid. The reaction mixture was allowed to warm to ambient temperature. During this period the color turned yellow-brown. After stirring at room temperature for 16 h a dark brown solution was obtained. A slight turbidity was filtered off, and from the red filtrate at $4\text{ }^{\circ}\text{C}$ red crystals of **6** were obtained. Yield: 0.51 g (28%). *Anal. Calc.* for $\text{C}_{19}\text{H}_{44}\text{FeP}_4\text{S}$ (484.36 g/mol): C, 47.12; H, 9.16. Found: C, 46.80; H, 8.88%. IR (Nujol, cm^{-1}): 1834 $\nu(\text{Fe-H})$, 1580 $\nu(\text{C}=\text{C})$, 937 $\nu(\text{PMe}_3)$. ^1H NMR (300 MHz, C_6D_6 , 296 K, ppm): δ 1.13 (m, 36H, PCH_3), 2.87 (s, 3H, CH_3), 7.16–8.66 (m, 4H, Ar-H), -9.99 (m, 1H, Fe-H); ^{31}P NMR (121 MHz, C_6D_6 , 300 K, ppm): δ 10.4 (m, 1P), 16.4 (m, 2P), 27.5 (m, 1P); ^{13}C NMR (75 MHz, C_6H_6 , 297 K, ppm): δ 24.5 (m, PCH_3), 30.5 (s, Ar-C), 119.3 (s, Ar-C), 125.0 (s, Ar-C), 131.3 (s, Ar-C).

2.2.4. Synthesis of **7**

To a solution of 0.50 g (1.03 mmol) of complex **6** in 50 mL of pentane were slowly injected 0.21 g (2.14 mmol) of trimethylsilylacetylene at $-80\text{ }^{\circ}\text{C}$. After stirring at room temperature for 18 h a dark brown solution was obtained. A slight turbidity was filtered off, and from the brown filtrate at $4\text{ }^{\circ}\text{C}$ yellow cubic crystals of **7** were obtained. Yield: 0.17 g (30%). *Anal. Calc.* for $\text{C}_{22}\text{H}_{54}\text{FeP}_4\text{Si}_2$ (554.55 g/mol): C, 47.65; H, 9.81. Found: C, 47.86; H, 10.01%. IR (Nujol, cm^{-1}): 1968 $\nu(\text{C}=\text{C})$, 939 $\nu(\text{PMe}_3)$. ^1H NMR (300 MHz, C_6D_6 , 296 K, ppm): δ 1.42 (m, 36H, PCH_3), 0.11 (d, 6H, CH_3); ^{31}P NMR (121 MHz, C_6D_6 , 300 K, ppm): δ 20.0 (s, PCH_3).

2.2.5. Synthesis of **9**

To a solution of 0.80 g (1.65 mmol) of complex **6** in 50 mL of pentane were slowly injected 0.34 g (3.33 mmol) of phenylethyne at $-80\text{ }^{\circ}\text{C}$. After stirring at room temperature for 18 h a dark brown solution was obtained. A slight turbidity was fil-

tered off, and from the brown filtrate at $4\text{ }^{\circ}\text{C}$ yellow cubic crystals of **9** were obtained. Yield: 0.23 g (25%). *Anal. Calc.* for $\text{C}_{28}\text{H}_{46}\text{FeP}_4$ (562.41 g/mol): C, 59.80; H, 8.24. Found: C, 59.90; H, 8.01%. IR (Nujol, cm^{-1}): 2037 $\nu(\text{C}=\text{C})$, 1589 $\nu(\text{C}=\text{C})$, 936 $\nu(\text{PMe}_3)$. ^1H NMR (300 MHz, C_6D_6 , 296 K, ppm): δ 1.41 (m, 36H, PCH_3), 6.96–7.41 (m, 10H, Ar-H); ^{31}P NMR (121 MHz, C_6D_6 , 300 K, ppm): δ 20.9 (s, PCH_3).

2.2.6. Synthesis of **10**

To a solution of 0.82 g (1.64 mmol) of complex **5** in 50 mL of pentane at $-80\text{ }^{\circ}\text{C}$ were slowly injected 0.28 g (3.33 mmol) of 2-methyl-3-butyn-2-ol. The reaction mixture was allowed to warm to ambient temperature. After stirring at room temperature for 16 h the color of the solution changed to yellow-brown. A slight turbidity was filtered off, and from the yellow filtrate at $4\text{ }^{\circ}\text{C}$ yellow cubic crystals of **10** were obtained. Yield: 0.43 g (25%). *Anal. Calc.* for $\text{C}_{22}\text{H}_{50}\text{FeO}_2\text{P}_4$ (526.38 g/mol): C, 50.20; H, 9.57. Found: C, 50.50; H, 9.55%. IR (Nujol, cm^{-1}): 1922 $\nu(\text{C}=\text{C})$, 938 $\nu(\text{PMe}_3)$. ^1H NMR (300 MHz, C_6D_6 , 296 K, ppm): δ 1.22 (m, 36H, PCH_3), 5.00 (s br, 1H, OH); ^{31}P NMR (121 MHz, C_6D_6 , 300 K, ppm): δ 20.8 (s, PCH_3).

2.3. X-ray structure determinations

Intensity data were collected on a Bruker SMART diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Crystallographic data for complexes **4**, **7**, and **10** are summarized in Table 1. The structures were solved by direct methods and refined with full matrix least-squares on all F^2 (*shelxl-97*) with non-hydrogen atoms anisotropic.

3. Results and discussion

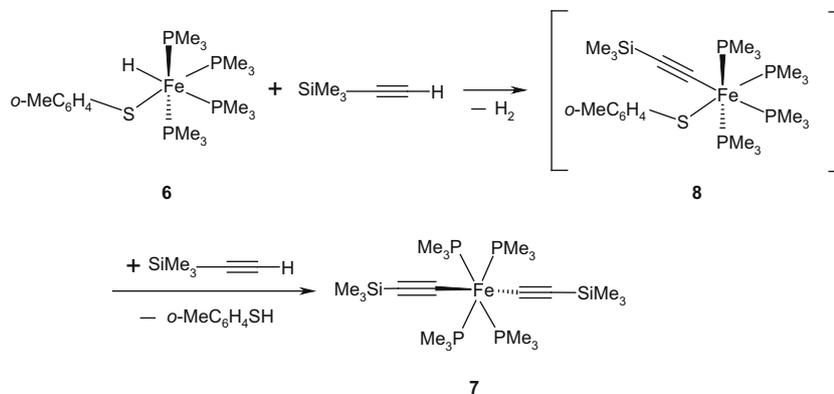
3.1. Synthesis of hydrido phenylthiolato iron(II) complexes

Reaction of $\text{Fe}(\text{PMe}_3)_4$ with thiophenols **1–3** to gave rise to the hydrido iron complexes **4–6** (Eq. (2)) via an oxidative addition of the S–H bond.

At $-27\text{ }^{\circ}\text{C}$ crystalline solids were obtained with yields of 17–28%. In the solid state complexes **4–6** rapidly decompose when exposed to air.

Table 1
Crystallographic data for complexes **4**, **7** and **10**.

Complex	4	7	10 × 2
Empirical formula	$\text{C}_{18}\text{H}_{41}\text{BrFeP}_4\text{S}$	$\text{C}_{22}\text{H}_{54}\text{FeP}_4\text{Si}_2$	$\text{C}_{44}\text{H}_{100}\text{Fe}_2\text{O}_4\text{P}_8$
Formula weight	549.21	554.55	1052.70
<i>T</i> (K)	100(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
<i>a</i> (Å)	13.8039(7)	16.024	24.009
<i>b</i> (Å)	28.913(2)	10.587	19.446
<i>c</i> (Å)	12.8157(7)	20.696	17.018
α (°)	90	90	90
β (°)	90.327(4)	112.05	134.38
γ (°)	90	90	90
<i>V</i> (Å ³)	5114.8(5)	3254.2	5678.6
<i>Z</i>	8	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.426	1.132	1.231
Reflections measured	24688	17323	12078
Unique reflections	8974	6821	4880
<i>R</i> _{int}	0.2316	0.0916	0.0349
θ _{max} (°)	25.00	27.04	25.00
<i>R</i> ₁ (<i>I</i> > 2σ (<i>I</i>))	0.0830	0.0563	0.0919
<i>wR</i> ₂ (all data)	0.1321	0.1709	0.2435

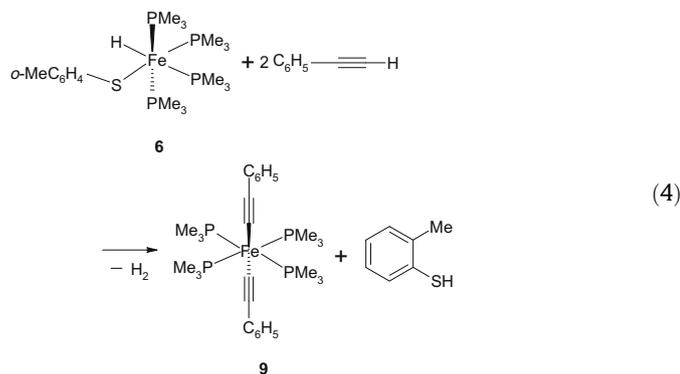


Scheme 1. Proposed mechanism of reaction (3).

iron hydrides reactivity is turned towards substituted products. A possible reaction mechanism is proposed in Scheme 1. In the first step, trimethylsilylacetylene reacts with a [Fe–H] function by elimination of dihydrogen yielding intermediate **8** which can react with another trimethylsilylacetylene molecule through elimination of thiophenol to give the bisalkynyl iron(II) complex **7** as end product.

3.3. Reaction of **6** with phenylacetylene

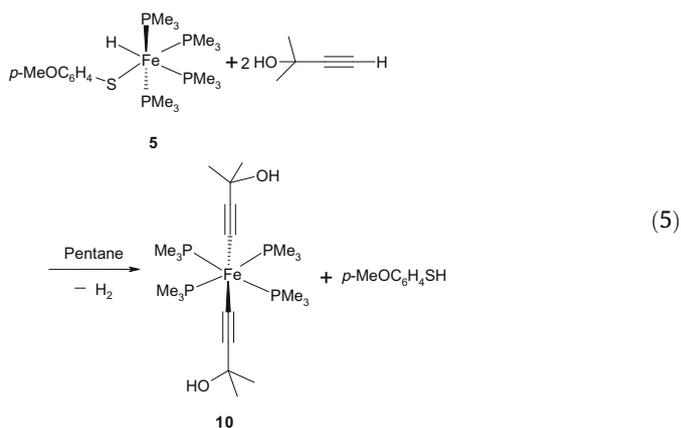
When phenylethyne was used in the reaction of complex **6**, complex **9** was directly obtained from pentane as yellow cubic crystals (Eq. (4)). Complex **9** is stable in the air for several hours at room temperature.



In the IR spectrum of complex **9** the characteristic $\nu(\text{C}\equiv\text{C})$ band is registered at 2037 cm^{-1} . The PMe_3 protons resonate at 1.41 ppm. In the ^{31}P NMR spectrum a singlet for the PMe_3 ligands was found at 20.9 ppm. The spectroscopic data are compatible with an octahedral configuration around the iron atom.

3.4. Reaction of **5** with 2-methyl-3-butyne-2-ol

By reaction of complex **5** with 2-methyl-3-butyne-2-ol under similar conditions complex **10** was obtained as yellow cubic crystals (Eq. (5)). In the IR spectrum of **10** the typical $\nu(\text{C}\equiv\text{C})$ absorption appears at 1922 cm^{-1} , and the $\nu(\text{O}-\text{H})$ band is registered at 3442 cm^{-1} . The ^1H NMR spectrum shows PMe_3 protons as multiplet at 1.22 ppm. In the ^{31}P NMR spectrum a singlet was found at 20.8 ppm for the PMe_3 ligands. The spectroscopic data are compatible with an octahedral configuration around the iron atom consisting of a C–Fe–C axis and equatorial coordination of P1, P2, P3, and P4 donor atoms. The molecular structure of complex **10** was confirmed by X-ray diffraction analysis.



The molecular structure of complex **10** is shown in Fig. 3, which is similar with complex **7**. The bending of [C=C–C]-chain away from 180° and some differences in Fe–P distances in complex **7** and **10** should be attributable to packing effects in the crystal structures.

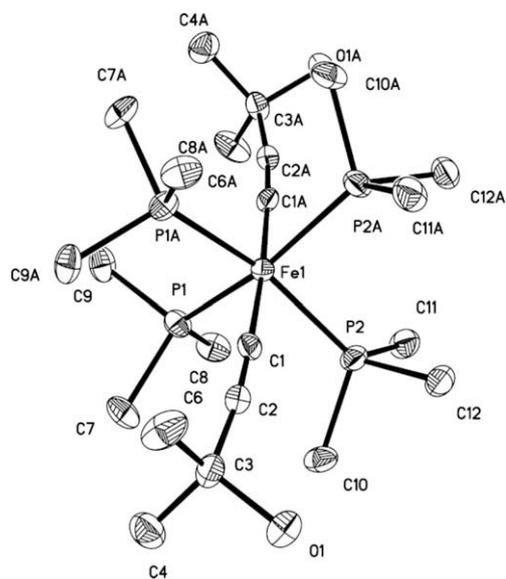


Fig. 3. Molecular structure of **10** and selected bond distances (Å) and angles ($^\circ$): Fe1–C1 1.955(8), Fe1–C1A 1.955(8), Fe1–P1 2.224(2), Fe1–P1A 2.224(2), Fe1–P2A 2.232(2), Fe1–P2 2.232(2), P1–C9 1.820(9), P1–C8 1.834(9), P1–C7 1.848(9), P2–C10 1.833(9), P2–C11 1.840(9), P2–C12 1.855(10); C1–Fe1–C1A 176.5(4), C1–Fe1–P1 98.2(2) C1A–Fe1–P1 79.4(2), C1–Fe1–P1A 79.4(2), C1A–Fe1–P1A 98.2(2), P1–Fe1–P1A 92.1(1), C1–Fe1–P2A 101.6(2), C1A–Fe1–P2A 80.9(2), P1–Fe1–P2A 160.3(1), P1A–Fe1–P2A 91.6(1), C1–Fe1–P2 80.9(2), C1A–Fe1–P2 101.6(2), P1–Fe1–P2 91.6(1), P1A–Fe1–P2 160.3(1), P2A–Fe1–P2 91.5(1).

4. Conclusion

The novel hydrido iron complexes **4–6** are formed by oxidative addition of S–H bond of the thiophenols. The structures of these hydrido iron complexes as derived from solution spectroscopy were confirmed for the solid state by single crystal X-ray diffraction. The reaction of the hydrido iron complexes with alkynes resulted in bisalkynyl iron(II) complexes. No products arising from an expected insertion reaction have been observed.

Supplementary data

CCDC 711798, 711796, and 711797 contain the supplementary crystallographic data for **4**, **7** and **10**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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