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Dehydrogenative silylation of alcohols catalysed by half-sandwich iron N-heterocyclic carbene complexes

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ABSTRACT

A new series of tetramethylcyclopentadienyl-functionalised N-heterocyclic carbene complexes of iron bearing different wingtips of general type (Cp*-NHC^R)Fe(CO)I (R = ^{n}Bu, ^{i}Bu, Et, CH_2CH_2OMe, CH_2Ph) were prepared by direct reaction of $Fe_3(CO)_{12}$ and the corresponding imidazolium proligands. These new iron-NHC complexes have been found to be efficient catalysts for the dehydrogenative silylation of alcohols with silanes. Iron metal complexes bearing iso-butyl and *n*-butyl wingtips displayed slightly better catalytic performances than the related complexes (Cp*-NHC^R)Fe(CO)I (R = Et, CH_2CH_2OMe, CH_2Ph), affording quantitative yields of the corresponding silylethers in 8 h at 70 °C in acetonitrile.

Introduction

In recent years, significant efforts have been devoted to developing catalytic applications of iron N-heterocyclic carbene (NHC) complexes [1]. The low price and high abundance of iron, along with the great popularity of N-heterocyclic carbene ligands in catalysis have motivated the growing interest in this area of research [2]. Notable examples of catalytic applications of Fe–NHCs are C–C bond formation reactions [3], polymerisation [4], C–H activation and arene borylation [5], and reduction of functional groups by hydrosilylation and hydrogen transfer processes [6–12].

Recently, we disclosed a simple synthetic pathway for the preparation of iron NHC complexes by direct reaction of the corresponding imidazolium proligands with commercially available $Fe_3(CO)_{12}$. This procedure allowed us to prepare Fe–NHC complexes bearing monodentate NHCs [9] and cyclopentadienyl-functionalised NHC ligands, Cp-NHC (Cp = η^5-C_5H_4, η^5-C_5Me_4) in high yields [7]. This advance precludes the requirement for the strong bases traditionally employed in the synthesis of similar complexes [4d,13,14].

In this work, we extended our studies to the preparation of a new series of iron tetramethylcyclopentadienyl-functionalised NHCs containing different substituents in the wingtip (R) of the imidazolium ring (Fig. 1). As part of our ongoing research into the development of new catalytic applications of first-row transition metal-NHC complexes with silanes [6–9,15,16], we decided to explore the activity of the iron complexes containing the fragment "(Cp*-NHC^R)Fe" in the dehydrogenative silylation of alcohols. We found that (Cp*-NHC^R)Fe(CO)I complexes act as efficient catalysts for Si–O coupling.

Experimental

The corresponding proligands (Cp*-NHC^R)I (R = ^{n}Bu, ^{i}Bu, Et, CH_2Ph, Me) were prepared according to the method reported by us [16,17]. All other reagents were used as received from the commercial suppliers without further purification. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, and solvents were purified from appropriate drying agents. Deuterated solvents were degassed and stored over molecular sieves. NMR spectra were recorded using a Bruker Avance III 400 MHz. Elemental analyses and Electrospray mass spectra were performed in our laboratories at ITQB.

Preparation of the imidazolium salt (Cp-NHC^R)I (R = CH_2CH_2OMe)*

A procedure similar to that reported by us for the preparation of tetramethylcyclopentadienes functionalised with imidazolium salts was applied by using 1-bromo-2-methoxyethane [16].

1-Bromo-2-methoxyethane (0.80 mL, 8.5 mmol) was added to a solution of Cp*-NHC (500 mg, 1.7 mmol) in 10 mL of THF with an excess of NaI (2.5 g, 17 mmol). The mixture was stirred at 50 °C for 3

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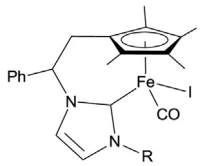

Fig. 1. Iron complexes bearing functionalised-cyclopentadienyl N-heterocyclic carbene ligands.

days. The suspension was filtered and the filtrate was evaporated to dryness to yield a yellow solid which was washed with diethyl ether and hexane. Yield: 600 mg (74%). ^{1}H NMR (400 MHz, $CDCl_3$) mixture of isomers: δ 10.40-9.92 (s, N=C*H*–*N*), 7.59-6.95 (m, C*H*$_{Phenyl}$, C*H*$_{Imid}$), 5.69–5.26 (m, C*H*$_{linker}$), 4.64–4.50 (m, NC*H*$_2$), 3.81–3.70 (m, C*H*$_{2OMe}$), 3.35, 3.33 (s, OC*H*$_3$), 3.27–3.03 (m, C*H*$_{2linker}$), 2.78–2.33 (m, C*H*$_{Cp^*}$), 1.80–1.35 (s, C*H*$_{3Cp^*}$), 1.07–0.84 (s, C*H*$_{3Cp^*}$). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.33 (N=*C*H–N), 136.47–119.54 (*C*$_{Phenyl}$, *C*$_{Imid}$), 70.35–64.29 (*C*H$_{linker}$), 59.05 (*C*H$_{Cp^*}$), 53.85–49.11 (NCH$_2$, *C*H$_{2OMe}$), 31.94–29.71 (*C*H$_{2linker}$), 14.67–10.90 (OCH$_3$, *C*H$_{3Cp^*}$). MS (ESI-TOF) *m/z* [M–I] $^+$ calcd. for $C_{23}H_{31}N_2O$: 351.24; found, 350.98 [M–I]$^+$.

*General preparation of complexes **1**–**5***

A mixture of the respective proligand (Cp*-NHC^R)I (R = ^{n}Bu, ^{i}Bu, Et, CH_2CH_2OMe, CH_2Ph) (1.38 mmol) and $Fe_3(CO)_{12}$ (0.46 mmol) was refluxed in toluene (15 mL) overnight. Filtration and removal of toluene under vacuum gave a green solid, which was washed with hexane to afford the corresponding iron complexes **1**–**5**.

Characterisation of (Cp-NHC^{nBu})Fe(CO)I (**1**)*

Yield of **1**: 86%. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.63–7.52 (m, 5H, C*H*$_{Ph}$), 7.11 (s, 1H, C*H*$_{Imid}$), 6.47 (s, 1H, C*H*$_{Imid}$), 6.06 (d, *J* = 12 Hz, 1H, C*H*Ph$_{linker}$), 4.23–4.17 (m, 2H, NC*H*$_{2Bu}$), 3.01–2.96 (m, 2H, C*H*$_{2linker}$, NC*H*$_{2Bu}$), 2.40 (s, 3H, C*H*$_{3Cp^*}$), 1.80 (s, 3H, C*H*$_{3Cp^*}$), 1.80–1.75 (m, 2H, C*H*$_{2nBu}$), 1.75 (m, 3H, C*H*$_{3Cp^*}$), 1.41–139 (m, 2H, C*H*$_3$*Bu*), 0.95 (s, 3H, C*H*$_{3Cp^*}$), 0.94 (t, *J* = 8, 3H, C*H*$_{3nBu}$). ^{13}C {^{1}H} NMR (100 MHz, acetone-d_6): δ 226.8 (*C*O), 194.9 (*C*$_{carbene-Fe}$), 138.8 (*C*$_{ipso-phenyl}$), 130.0 (*C*H$_{phenyl}$), 129.9 (*C*H$_{phenyl}$), 123.0 (*C*H$_{Imid}$), 121.0 (*C*H$_{Imid}$), 104.7 (*C*$_{Cp^*}$), 91.6 (*C*$_{Cp^*}$), 90.3 (*C*$_{Cp^*}$), 84.2 (*C*$_{Cp^*}$), 81.0 (*C*$_{Cp^*}$), 67.0 (*C*H$_{Ph-linker}$), 51.1 (NCH$_2$), 34.0 (*C*H$_{2nBu}$), 29.8 (*C*H$_{2linker}$), 20.4 (*C*H$_{2nBu}$), 14.0 (*C*H$_{3nBu}$) 13.4 (*C*H$_{3Cp^*}$), 10.4 (*C*H$_{3Cp^*}$), 9.6 (*C*H$_{3Cp^*}$), 9.5 (*C*H$_{3Cp^*}$). Selected IR data (KBr): ν(CO) 1905 vs cm^{-1}. Anal. Calcd. for $C_{25}H_{31}N_2OFeI$ (558.08): C, 53.78; H, 5.60; N, 5.02. Found: C, 53.50; H, 5.86; N, 5.23.

Characterisation of (Cp-NHC^{iBu})Fe(CO)I (**2**)*

Yield of **2**: 84%. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.64–7.54 (m, 5H, C*H*$_{Phenyl}$), 7.06 (s, 1H, C*H*$_{Imid}$), 6.48 (s, 1H, C*H*$_{Imid}$), 6.08 (d, *J* = 12 Hz, 1H, C*H*$_{linker}$), 3.97 (d, *J* = 8 Hz, 2H, NC*H*$_2$); 3.02–2.97 (m, 2H, C*H*$_{2linker}$), 2.39 (s, 3H, C*H*$_{3Cp^*}$), 2.27–2.19 (m, 1H, C*H*$_{iBu}$, 1.80 (s, 3H, C*H*$_{3Cp^*}$), 1.75 (s, 3H, C*H*$_{3Cp^*}$), 0.95 (s, 3H, C*H*$_{3Cp^*}$), 0.94 (t, *J* = 8, 3H, C*H*$_{3nBu}$). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ 226.8 (*C*O), 195.2 (Fe-*C*$_{carbene}$), 138.8 (*C*$_{ipsoPhenyl}$), 130.8 (*C*H$_{Phenyl}$), 129.9 (*C*H$_{Phenyl}$), 128.8 (*C*H$_{Phenyl}$), 128.3 (*C*H$_{Phenyl}$), 127.6 (*C*H$_{Phenyl}$), 124.0 (*C*H$_{Imid}$), 121.7 (*C*H$_{Imid}$), 104.7 (*C*$_{Cp^*}$), 91.6 (*C*$_{Cp^*}$), 90.4 (*C*$_{Cp^*}$), 84.3 (*C*$_{Cp^*}$), 81.0 (*C*$_{Cp^*}$), 67.1 (*C*H$_{linker}$), 58.3 (NCH$_2$), 29.8 (*C*H$_{linker}$), 29.1 (*C*H$_{iBu}$), 20.0 (*C*H$_{3iBu}$), 19.8 (*C*H$_{3iBu}$), 13.4 (*C*H$_{3Cp^*}$), 10.4 (*C*H$_{3Cp^*}$), 9.6 (*C*H$_{3Cp^*}$), 9.5 (*C*H$_{3Cp^*}$). Anal. Calcd. for $C_{25}H_{31}N_2OFeI$ (558.26): C, 53.78; H, 5.60; N, 5.02. Found: C, 53.40; H, 5.50; N, 4.87. Selected IR data (KBr): ν(CO) 1905 vs cm^{-1}. MS (ESI-TOF) *m/z* [M–I]$^+$ calcd for $C_{25}H_{31}N_2OFe$: 431.17; found 430.96 [M–I]$^+$.

Characterisation of (Cp-NHC^{Et})Fe(CO)I (**3**)*

Yield of **3**: 81%. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.63–7.53 (m, 5H, C*H*$_{Phenyl}$), 7.13 (s, 1H, C*H*$_{Imid}$), 6.48 (s, 1H, C*H*$_{Imid}$), 6.06 (d, *J* = 12 Hz, 1H, C*H*$_{linker}$), 4.35–4.23 (m, 2H, C*H*$_{2Et}$), 3.05–2.92 (m, 2H, C*H*$_{2linker}$), 2.40 (s, 3H, C*H*$_{3Cp^*}$), 1.81 (s, 3H, C*H*$_{3Cp^*}$), 1.76 (s, 3H, C*H*$_{3Cp^*}$), 1.35 (t, *J* = 8 Hz, 3H, C*H*$_{3Et}$). 0.96 (s, 3H, C*H*$_{3Cp^*}$). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ 226.8 (CO), 194.8 (Fe-*C*$_{carbene}$), 138.8 (*C*$_{iPhenyl}$), 130.1 (*C*H$_{Phenyl}$), 130.0 (*C*H$_{Phenyl}$), 129.9 (*C*H$_{Phenyl}$), 122.3 (*C*H$_{Imid}$), 121.3 (*C*H$_{Imid}$), 104.7 (*C*$_{Cp^*}$), 91.7 (*C*$_{Cp^*}$), 90.4 (*C*$_{Cp^*}$), 84.1 (*C*$_{Cp^*}$), 81.3 (*C*$_{Cp^*}$), 67.1 (*C*H$_{linker}$), 46.1 (NCH$_2$), 28.9 (*C*H$_{2linker}$), 16.9 (*C*H$_{3Et}$), 13.4 (*C*H$_{3Cp^*}$), 10.4 (*C*H$_{3Cp^*}$), 9.7 (*C*H$_{3Cp^*}$), 9.5 (*C*H$_{3Cp^*}$). Anal. Calcd. for $C_{23}H_{27}N_2OFeI$ (530.05): C, 52.10; H, 5.13; N, 5.28. Found: C; 52.30H, 5.29; N, 4.91. Selected IR data (KBr): ν(CO) 1904 vs cm^{-1}. MS (ESI-TOF) *m/z* [M–CO–I]$^+$ calcd. for $C_{22}H_{27}N_2Fe$: 375.15; found 375.09 [M–CO–I]$^+$.

Characterisation of (Cp-NHC^{CH2CH2OMe})Fe(CO)I (**4**)*

Yield of **4**: 76%. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.64–7.56 (m, 5H, Ph), 7.05 (s, 1H, C*H*$_{Imid}$), 6.45 (s, 1H, C*H*$_{Imid}$), 6.05 (d, *J* = 12, 1H, C*H*$_{Ph-linker}$), 4.48–4.29 (m, 2H, NC*H*$_2$), 3.69–3.67 (m, 2H, C*H*$_{2OMe}$), 3.25 (s, 3H, OC*H*$_3$), 3.02–2.97 (m, 2H, C*H*$_{2linker}$), 2.40 (s, 3H, C*H*$_{3Cp^*}$), 1.81 (s, 3H, C*H*$_{3Cp^*}$), 1.75 (s, 3H, C*H*$_{3Cp^*}$), 0.97 (s, 3H, C*H*$_{3Cp^*}$). ^{13}C {^{1}H} NMR (100 MHz, acetone-d_6): δ 227.0 (*C*O), 195.3 (*C*$_{carbene-Fe}$), 138.9 (*C*$_{ipso-phenyl}$), 130.3 (*C*H$_{phenyl}$), 129.0 (*C*H$_{phenyl}$), 127.2 (*C*H$_{phenyl}$), 124.3 (*C*H$_{Imid}$), 120.9 (*C*H$_{Imid}$), 104.9 (*C*$_{Cp^*}$), 92.0 (*C*$_{Cp^*}$), 90.7 (*C*$_{Cp^*}$), 84.3 (*C*$_{Cp^*}$), 81.5 (*C*$_{Cp^*}$), 72.7 (*C*H$_{2OMe}$), 67.3 (*C*H$_{linker}$), 58.9 (OCH$_3$), 51.2 (NCH$_2$), 29.40 (*C*H$_{2linker}$), 13.5 (*C*H$_{3Cp^*}$), 10.5 (*C*H$_{3Cp^*}$), 9.8 (*C*H$_{3Cp^*}$), 9.6 (*C*H$_{3Cp^*}$). Anal. Calcd. for $C_{24}H_{29}N_2O_2FeI$ (560.06): C, 51.45; H, 5.22; N, 5.00. Found: C, 51.20; H, 5.31; N, 4.97. Selected IR data (KBr): ν(CO) 1902 vs cm^{-1}. MS (ESI-TOF) *m/z* [M–I]$^+$ calcd. for $C_{24}H_{29}N_2O_2Fe$: 433.16; found, 432.89 [M–I]$^+$.

Characterisation of Cp-NHC^{CH2Ph})Fe(CO)I (**5**)*

Yield of **5**: 74%. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.65–7.51 (m, 5H, C*H*$_{Phenyl}$), 7.37–7.27 (m, 5H, C*H*$_{CH2Ph}$), 7.06 (s, 1H, C*H*$_{Imid}$), 6.54 (s, 1H, C*H*$_{Imid}$), 6.17 (d, *J* = 1 2 Hz, 1H, C*H*$_{linker}$), 5.51 (dd, *J* = 14 Hz, 2H, NC*H*$_2$), 3.07–2.93 (m, 2H, C*H*$_{2linker}$), 2.42 (s, 3H, C*H*$_{3Cp^*}$), 1.76 (s, 3H, C*H*$_{3Cp^*}$), 1.71 (s, 3H, C*H*$_{3Cp^*}$), 0.86 (s, 3H, C*H*$_{3Cp^*}$). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ 226.6 (*C*O), 197.1 (Fe-*C*$_{carbene}$), 138.9 (*C*$_{iPh}$), 130.2 (*C*H$_{Phenyl}$), 130.0 (*C*H$_{Phenyl}$), 129.3 (*C*H$_{Phenyl}$), 129.0 (*C*H$_{Phenyl}$), 128.4 (*C*H$_{Phenyl}$), 122.9 (*C*H$_{Imid}$), 122.1 (*C*H$_{Imid}$), 104.8 (*C*$_{Cp^*}$), 91.7 (*C*$_{Cp^*}$), 90.1 (*C*$_{Cp^*}$), 84.8 (*C*$_{Cp^*}$), 81.7 (*C*$_{Cp^*}$), 69.2 (*C*H$_{linker}$), 54.4 (NCH$_2$Ph), 28.9 (*C*H$_{2linker}$), 13.5 (*C*H$_{3Cp^*}$), 10.4 (*C*H$_{3Cp^*}$), 9.7 (*C*H$_{3Cp^*}$), 9.6 (*C*H$_{3Cp^*}$). Anal. Calc. for $C_{28}H_{29}N_2OFeI$ (592.06): C, 56.78; H, 4.94; N, 4.74. Found: C, 56.47; H, 5.08; N, 4.52. Selected IR data (KBr): ν(CO) 1904 vs cm^{-1}. MS (ESI-TOF): *m/z* [M–I]$^+$ calcd. for $C_{28}H_{29}N_2OFe$: 465.16; found 464.91 [M–I]$^+$.

Catalytic dehydrogenative silylation of alcohols

Acetonitrile (1 mL), (Cp*-NHC^R)Fe(CO)I (1 mol%), alcohol (3 mmol), silane (1 mmol) were charged in a vial. The vial was tightly closed under a nitrogen atmosphere, and the mixture was heated at 70 °C for 8–16 h depending on the silane and the alcohol. All volatiles were evaporated under vacuum, the residue was dissolved in $CDCl_3$, and Ph_2CH_2 (1 mmol) was added to the mixture as an internal standard. The ^{1}H NMR was measured at room temperature and the amount of the corresponding silylether produced was evaluated by the relative intensity of the signals of the product and internal standard. Isolation of the silylethers was carried out by removing all the volatiles under vacuum. The residue was diluted with hexanes (ca. 2 mL), loaded directly on to a silica gel column and chromatographed using hexane-acetone (10:1) as eluent to give the corresponding silylethers. The silylethers produced were identified by comparison of the NMR data with the reported data:

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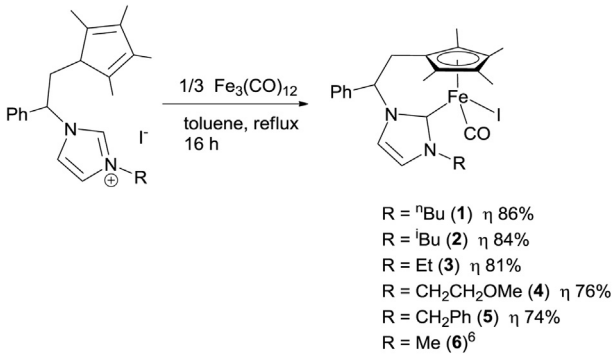

Scheme 1. Synthesis of iron complexes **1**–**6**.

$PhSi(OEt)_3$, $PhSi(O^iPr)_3$ [18], $Ph_2Si(OEt)_2$ [19], $PhSiH[OCH(Me)Ph]_2$ [20]. The obtained silylether $Si(OEt)_4$ was compared with an authenticate sample (commercially available).

Results and discussion

Compounds **1**–**5** were prepared by an extension of a method recently reported by us [7]. Direct reaction of the iron cluster $Fe_3(CO)_{12}$ with the respective proligand (Cp^*-NHC^R)I (R = ^{n}Bu, ^{i}Bu, Et, CH_2CH_2OMe, CH_2Ph) in refluxing toluene afforded complexes **1**–**5** in high yields (Scheme 1). Complexes **1**–**5** were isolated as air stable green crystalline solids. The identity of all compounds was established by analytical and spectroscopic methods. The successful metallation is confirmed by the appearance of the characteristic carbene signal at 195 ppm (for complexes **1**–**4**) and 197 ppm (for **5**) in the ^{13}C NMR, which is the region of previously reported half-sandwich Fe–NHC complexes [6,10a,10h,13,21]. The length of the alkyl substituents of the wingtip has no detectable impact on the $Fe-C_{carbene}$ resonance frequency. Introduction of a benzyl group at the wingtip decreases the upfield shift by 2 ppm. The formation of the new complexes is further verified by the carbonyl signal at 227 ppm in the ^{13}C NMR.

The infrared spectra of **1**–**5** display the expected strong carbonyl band in the region 1905–1902 cm^{-1}. The similar stretching band frequency for all complexes **1**–**5** is indicative of similar donor capacity of the N-heterocyclic carbene ligands which is not influenced by the wingtip substituents.

With these complexes in our hands, we decided to explore their catalytic activity in the dehydrogenative silylation of alcohols. Silylether formation is a fundamental process in the synthesis of functional organosilicon compounds and polymer chemistry [22]. Moreover, silylethers are widely used as protecting groups for the hydroxyl functionality in organic synthesis [23]. The catalytic dehydrogenative silylation of alcohols is a very convenient method for the preparation of silylethers from an atom economy point of view, with H_2 as the only by-product formed in the coupling reaction. Metal-catalysed dehydrogenative coupling of silanes with alcohols has been described in the literature [24]. However, to the best of our knowledge, iron-NHC complexes have not been successfully employed in this coupling reaction. Dehydrogenative coupling of thiols with hydrosilanes catalysed by CpFe(CO)Me was recently disclosed by Nakazawa [25].

The half-sandwich iron-NHC complexes **1**–**7** (Fig. 2) were applied as catalysts for the dehydrogenative silylation of alcohols. Their catalytic activity was initially explored using ethanol and $PhSiH_3$ as model substrates. The reaction was carried out in acetonitrile at 70 °C in the presence of 1 mol% of catalyst (Scheme 2). All complexes **1**–**7** were active catalysts in the dehydrogenative silylation of ethanol with $PhSiH_3$, affording high yields (91–99%) of triethoxyphenylsilane in 16 h (Table 1, entries 1–7). Complexes **1** and **2**, bearing the ^{n}Bu and ^{i}Bu wingtips respectively, displayed slightly higher activities affording quantitative yields of the silylether in 8 h (Table 1, entries 1 and 2, respectively), while longer reaction times (12–16 h) were needed for complexes **3**–**6** to afford similar yields (Table 1, entries 3–6). Interestingly, the different substitution on the cyclopentadienyl ring (Cp *vs* Cp^*) does not seem to affect the catalytic performance in the dehydrogenative silylation of alcohols (Table 1, entries 6 and 7). For all catalysts, the reaction was selective to the formation of triethoxyphenylsilane, and no other coupling products were formed in the reaction. It seems that variation of the wingtip substituents at R (Fig. 1) does not affect the catalytic performance.

We investigate the scope of the dehydrogenative silylation of alcohols, using catalyst **1**, EtOH and different silanes. In each case, reactions were performed under optimised conditions heating at 70 °C in MeCN. As shown in Table 1, phenylsilane, diphenylsilane, and triethoxysilane were all very efficient substrates when reacted with ethanol, giving high yields (85–99%) of the corresponding silylethers in 8 h (Table 1, entries 1, 8, and 9, respectively). When the reaction was performed with *tert*-butyldiphenylsilane, a 70%

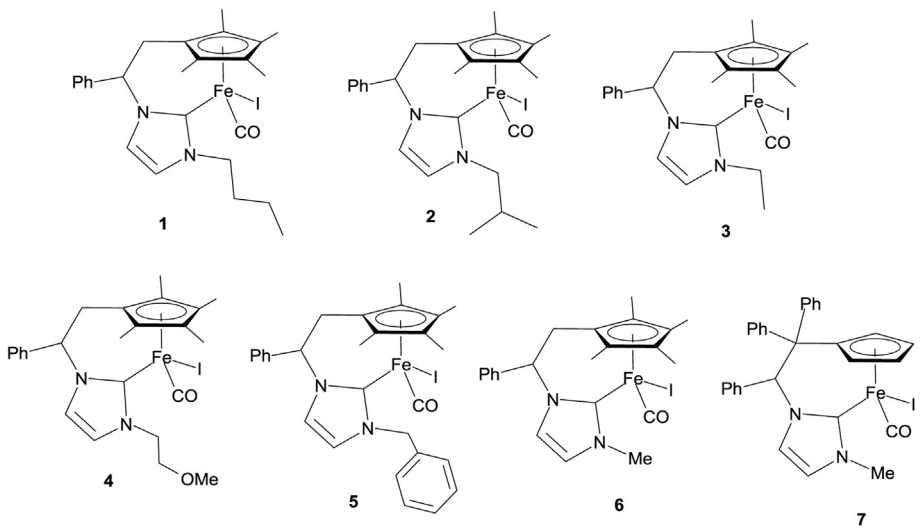

Fig. 2. Iron complexes applied in the catalytic dehydrogenative silylation of alcohols with silanes.

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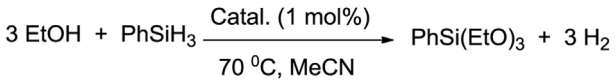

Scheme 2. Catalytic dehydrogenative silylation of ethanol with phenylsilane.

Table 1
Dehydrogenative silylation of alcohols with silanes using iron complexes **1**–**7** as catalysts.[a]

Entry	Catalyst	Silane	Alcohol	Product	Time	Yield[b] (%)
1	**1**	$PhSiH_3$	EtOH	$PhSi(OEt)_3$	8	99 (92)
2	**2**	$PhSiH_3$	EtOH	$PhSi(OEt)_3$	8	91 (87)
3	**3**	$PhSiH_3$	EtOH	$PhSi(OEt)_3$	12	99 (93)
4	**4**	$PhSiH_3$	EtOH	$PhSi(OEt)_3$	12	99 (91)
5	**5**	$PhSiH_3$	EtOH	$PhSi(OEt)_3$	16	95 (87)
6	**6**	$PhSiH_3$	EtOH	$PhSi(OEt)_3$	16	96 (87)
7	7	$PhSiH_3$	EtOH	$PhSi(OEt)_3$	16	84 (79)
8	**1**	Ph_2SiH_2	EtOH	$Ph_2Si(OEt)_2$	8	82 (77)
9	**1**	$(EtO)_3SiH$	EtOH	$Si(OEt)_4$	8	98 (91)
10	**1**	$^tBuPh_2SiH$	EtOH	$^tBuPh_2Si(OEt)$	16	70 (58)
11	**1**	$PhMe_2SiH$	EtOH	–	16	0
12	**1**	Ph_3SiH	EtOH	–	16	0
13	**1**	Et_3SiH	EtOH	–	16	0
14	**1**	$^tBu_2SiH_2$	EtOH	–	16	0
15	**1**	$PhSiH_3$	^iPrOH	$PhSi(O^iPr)_3$	8	66 (62)
16	**1**	$PhSiH_3$	$Bu^tCH(Me)OH$	$PhSiH[OCH(Me)Bu^t]_2$	16	69 (60)
17	**1**	$PhSiH_3$	PhCH(Me)OH	$PhSiH[OCH(Me)Ph]_2$	16	71 (65)

[a] Reaction conditions: EtOH (3 mmol), silane (1 mmol), catalyst (1 mol%) in MeCN at 70 °C.
[b] Yield determined by ^1H NMR spectroscopy using Ph_2CH_2 as internal standard. Isolated yields in parentheses.

yield of the corresponding silylether was obtained (Table 1, entry 10). In all cases, the reaction led to conversion of all Si–H groups to tetra-, tri-, bis-, and mono-alkoxyl silanes. The coupling reaction did not occur when dimethylphenylsilane, triphenylsilane, triethylsilane and di-*tert*-butylsilane were used as substrates in their reaction with ethanol (Table 1, entries 11–14).

The dehydrogenative silylation of bulkier alcohols such as 2-propanol, 3,3-dimethyl-butan-2-ol, and 1-phenylethanol in the presence of catalyst **1**, and under similar reaction conditions afforded the corresponding tri(alkoxy)silane and bis(alkoxy)silanes, respectively in moderate yields (Table 1, entries 15–17). We have also explored the catalytic performance of catalyst **1** in the reaction of phenylsilane with water. Treatment of phenylsilane with water in acetonitrile at 70 °C in the presence of catalyst **1** (1 mol%) afforded an intractable mixture of compounds; formation of the corresponding silanol was not detected.

Conclusion

A series of new (Cp^*-NHC^R)Fe(CO)I complexes bearing different wingtips have been prepared and fully characterised. We have demonstrated that these half-sandwich iron-NHC complexes are efficient catalysts for the dehydrogenative coupling of alcohols with silanes. Complexes bearing the ^{n}Bu and ^{i}Bu wingtips, required shorter times (8 h) to afford quantitative yields of triethoxyphenylsilane. The different substitution on the wingtips, and the replacement of the tetramethylcyclopentadienyl ring, Cp^*, by the unsubstituted Cp do not have a substantial effect on the activity of the catalysts. This is the first report of well-defined iron(II) complexes catalysing the coupling of alcohols with hydrosilanes.

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Appendix A. Supplementary material

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.06.005.

References

[1] a D. Bézier, J.-B. Sortais, C. Darcel, Adv. Synth. Catal. 355 (2013) 19–33.
[2] (a) K. Riener, S. Haslinger, A. Raba, M.P. Högerl, M. Cokoja, W.A. Herrmann, F.E. Kühn, Chem. Rev. (2014), http://dx.doi.org/10.1021/cr4006439;
(b) M.J. Ingleson, R.A. Layfield, Chem. Commun. 48 (2012) 3579–3589;
(c) F. Glorius, N-Heterocyclic carbenes in transition-metal catalysis, in: Topics in Organometallic Chemistry, vol. 21, Springer, Berlin, Germany, 2007;
(d) F.E. Hahn, M.C. Jahnke, Angew. Chem. Int. Ed. 47 (2008) 3122–3172;
(e) M.C. Jahnke, F.E. Hahn, Top. Organomet. Chem. 30 (2010) 95.
[3] (a) H.-H. Gao, C.-H. Yan, X.-P. Tao, Y. Xia, H.-M. Sun, Q. Shen, Y. Zhang, Organometallics 29 (2010) 4189–4192;
(b) S. Meyer, C.M. Orben, S. Demeshko, S. Dechert, F. Meyer, Organometallics 30 (2011) 6692–6702;
(c) J. Wu, W. Dai, J.H. Farnaby, N. Hazari, J.J. Le Roy, V. Mereacre, M. Murugesu, A.K. Powell, M.K. Takase, Dalton Trans. 42 (2013) 7404–7413.
[4] (a) J. Louie, R.H. Grubbs, Chem. Commun. (2000) 1479–1480;
(b) D.S. McGuinness, V.C. Gibson, J.W. Steed, Organometallics 23 (2004) 6288–6292;
(c) M.-Z. Chen, H.-M. Sun, W.-F. Li, Z.-G. Wang, Q. Shen, Y. Zhang, J. Organomet. Chem. 691 (2006) 2489–2494;
(d) V. Lavallo, R.H. Grubbs, Science 326 (2009) 559–562;
(e) L. Xiang, J. Xiao, L. Deng, Organometallics 30 (2011), 2018–2015;
(f) H. Gao, C. Yan, X. Tao, Y. Xia, H. Sun, Q. Shen, Y. Zhang, Organometallics 29 (2010) 4189–4192.
[5] (a) Y. Ohki, T. Hatanaka, K. Tatsumi, J. Am. Chem. Soc. 130 (2008) 17174–17186;
(b) T. Hatanaka, Y. Ohki, K. Tatsumi, Chem. Asian J. 5 (2010) 1657–1666.
[6] V.V.K.M. Kandepi, J.M.S. Cardoso, E. Peris, B. Royo, Organometallics 29 (2010) 2777–2782.
[7] J.M.S. Cardoso, B. Royo, Chem. Commun. 48 (2012) 4944–4946.
[8] R. Lopes, J.M.S. Cardoso, L. Postigo, B. Royo, Catal. Lett. 143 (2013) 1061–1066.
[9] S. Warratz, L. Postigo, B. Royo, Organometallics 32 (2013) 893–897.
[10] (a) V. César, L.C. Mistral Castro, T. Dombray, J.-B. Sortais, C. Darcel, S. Labat, K. Miqueu, J.-M. Sotiropoulos, R. Brousses, N. Lugan, G. Lavigne, Organometallics 32 (2013) 4643;
(b) H. Li, L.C. Mistral Castro, J. Zheng, T. Roisnel, V. Dorcet, J.-B. Sortais, C. Darcel, Angew. Chem. Int. Ed. 52 (2013) 1–6;
(c) L.C. Mistral Castro, D. Bézier, J.-B. Sortais, C. Darcel, Adv. Synth. Catal. 353 (2011) 1279–1284;
(d) D. Bézier, F. Jiang, T. Roisnel, J.-B. Sortais, C. Darcel, Eur. J. Inorg. Chem. (2012) 1333–1337;
(e) D. Bézie, G.T. Venkanna, L.C. Mistral Castro, J. Zheng, T. Roisnel, J.-B. Sortais, C. Darcel, Adv. Synth. Catal. 354 (2012) 1879–1884;
(f) L.C. Mistral Castro, J.-B. Sortais, C. Darcel, Chem. Commun. 48 (2012) 151–153;
(g) D. Bézier, G.T. Venkanna, J.-B. Sortais, C. Darcel, ChemCatChem 3 (2011) 1747–1750;
(h) S. Demir, Y. Gökçe, N. Kaloğlu, J.-B. Sortais, C. Darcel, İ Özdemir, Appl. Organomet. Chem. 27 (2013) 459–464;
(i) B. Blom, G. Tan, S. Enthaler, S. Inoue, J.D. Epping, M. Driess, J. Am. Chem. Soc. 135 (2013) 18108–18120.
[11] (a) C. Grohmann, T. Hashimoto, R. Frohlich, Y. Ohki, K. Tatsumi, F. Glorius, Organometallics 31 (2012) 8047–8050;
(b) T. Hashimoto, S. Urban, R. Hoshino, Y. Ohki, K. Tatsumi, F. Glorius, Organometallics 31 (2012) 4474–4479.
[12] (a) E. Buitrago, L. Zani, H. Adolfsson, Appl. Organomet. Chem. 25 (2011) 748–752;
(b) E. Buitrago, F. Tinnis, H. Adolfsson, Adv. Synth. Catal. 354 (2012) 217–222.
[13] P. Buchgraber, L. Toupet, V. Guerchais, Organometallics 22 (2003) 5144–5147.
[14] Selected references: (a) D.S. McGuinness, V.C. Gibson, J.W. Steed, Organometallics 23 (2004) 6288–6292;
(b) J.A. Przyojski, H.D. Arman, Z.J. Tonzetich, Organometallics 31 (2012) 3264–3271;
(c) S.A. Cramer, D.M. Jenkins, J. Am. Chem. Soc. 133 (2011) 19342–19345.
[15] L. Postigo, B. Royo, Adv. Synth. Catal. 354 (2012) 2613–2618. Similar work appeared simultaneously in the literature: L.P Bheeter, M. Henrion, L. Brelot,

C. Darcel, M.J. Chetcuti, J.-B. Sortais, V. Ritleng, Adv. Synth. Catal.. 354(2012) 2619–2624.
[16] L. Postigo, R. Lopes, B. Royo, Dalton Trans. 43 (2014) 853–858.
[17] A.P. da Costa, M. Viciano, M. Sanaú, S. Merino, J. Tejeda, E. . Peris, B. . Royo, Organometallics 27 (2008) 1305–1309.
[18] W. Sattler, G. Parkin, J. Am. Chem. Soc. 134 (2012) 17462–17465.
[19] J.Y. Corey, C.S. John, M.C. Ohmsted, L.H.S. Chang, J. Organomet. Chem. 304 (1986) 93–105.
[20] A.Y. Khalimon, S.K. Ignatov, R. Simionescu, L.G. Kuzmina, J.A.K. Howard, G.I. Nikonov, Inorg. Chem. 51 (2012) 754–756.
[21] L. Mercs, G. Labat, A. Neels, A. Ehlers, M. Albrecht, Organometallics 25 (2006) 5648–5656.
[22] G.W. Parshall, S.D. Itell, Homogeneous Catalysts: The Applications and Chemistry by Soluble Transition Metal Complexes, Wiley, New York, 1992.
[23] P.J. Kocienski, Protecting Groups, Springer, Stuttgart, 1994.
[24] For recent references, see: (a) A. Krüger, M. Albrecht, Chem. Eur. J. 18 (2012) 652–658;
(b) D. Mukherjee, R.R. Thompson, A. Ellern, A.D. Sadow, ACS Catal. 1 (2011) 698–702;
(c) A. Weickgenannt, M. Mewald, T.W.T. Muesmann, M. Oestreich, Angew. Chem. Int. Ed. 49 (2010) 223–2226;
(d) R.A. Corbin, E.A. Ison, M.M. Abu-Omar, Dalton Trans. 15 (2009) 2850–2855;
(e) H. Ito, A. Watanabe, M. Sawamura, Org. Lett. 7 (2005) 1869–1871;
(f) P.M. Reis, B. Royo, Catal. Commun. 8 (2007) 1057–1059;
(g) D. Gao, C. Cui, Chem. Eur. J. 19 (2013) 11143–11147;
(h) C.K. Toh, H.T. Poh, C.S. Lim, W.Y. Fan, J. Organomet. Chem. 717 (2012) 9–13.
[25] K. Fukumoto, M. Kasa, T. Oya, M. Itazaki, H. Nakazawa, Organometallics 30 (2011) 3461–3463.

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