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Iron piano-stool phosphine complexes for catalytic hydrosilylation reaction

Jianxia Zheng [a], Luis C. Misal Castro [a], Thierry Roisnel [b], Christophe Darcel [a], Jean-Baptiste Sortais [a,*]

[a] UMR 6226 CNRS, Université de Rennes 1, "Sciences Chimiques de Rennes" (Catalysis and Organometallics), Campus de Beaulieu, Bat 10C, 263 avenue du Général Leclerc, 35042 Rennes Cedex, France
[b] UMR 6226 CNRS, Université de Rennes 1, "Sciences Chimiques de Rennes"(Centre de Diffractométrie X), Campus de Beaulieu, Bat 10B, 263 avenue du Général Leclerc, 35042 Rennes Cedex, France

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ABSTRACT

A family of six cyclopentadienyl–iron carbonyl complexes bearing phosphine ligands (PPh_3, PMe_2Ph and PCy_3) with iodide or PF_6 as a counter-anion were prepared and used as catalysts for the hydrosilylation of carbonyl derivatives. Aldehydes were reduced at 30 °C, using PMHS as the silane, whereas ketones were reduced at 70 °C using $PhSiH_3$.

1. Introduction

The decrease in non-renewable natural resources has become a global concern for the future, and it is usually the main issue associated with fossil fuel feedstock. However, precious transition metals, such as palladium, rhodium or ruthenium which are extensively used for catalytic processes in the chemical industry are also limited, and their costs have already increased tremendously over the last decade. New directions for homogeneous catalysis should not only address energy issues by developing highly reactive catalysts, but should also favour the use of earth-abundant materials as the catalysts. Iron, in terms of its abundance, low cost and low toxicity is especially attractive surrogate for precious transition metals. During the last decade, the use of iron as an efficient catalyst has dramatically increased and efficient processes are now able to compete with other transition metals [1–7]. In the field of reduction, important breakthroughs have recently been achieved, mainly in hydrogenation, hydrogen transfer reaction and hydrosilylation reactions [8–10]. Since the pioneering report from Brunner [11,12], important contributions have been made using either a combination of iron salts and ligands to generate in situ catalysts [13–21] or well-defined complexes as pre-catalysts [22–31]. As part of our research on iron-catalysed transformations [32,33], we have recently described the use of well-defined iron complexes, neutral or cationic, bearing *N*-heterocyclic carbene as ligands for the reduction of carbonyl derivatives [34–37].

Building on our work on piano-stool iron complexes, we describe in the present study the synthesis, characterisation and catalytic activity of a family of iron complexes bearing phosphine ligands with two different counter-anions iodide and PF_6 (Scheme 1). These complexes are the phosphorus analogs of the previously studied complex $[CpFe(CO)_2(IMes)]I$.

2. Experimental

2.1. General considerations

All reagents were obtained from commercial sources and used as received, excepted liquid aldehydes which were distilled prior to use. Toluene was distilled following conventional methods (sodium/benzophenone) and stored under an argon atmosphere. All reactions were carried out under argon atmosphere. Technical grade petroleum ether (40–60 °C bp) and ethyl acetate were used for column chromatography. ^1H NMR spectra were recorded in $CDCl_3$ at ambient temperature on Bruker DPX-200, AVANCE I 300 spectrometers at 200.1, and 300.1 MHz, respectively, using the solvent as an internal standard (7.26 ppm). ^{13}C NMR spectra were obtained at 50 or 75 MHz and referenced to the internal solvent signals (central peak is 77.1 ppm). Chemical shift (δ) and coupling constants (J) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad). GC analysis were per-

* Corresponding author. Tel.: +33 2 23 23 62 88; fax: +33 2 23 23 69 39.
E-mail address: jean-baptiste.sortais@univ-rennes1.fr (J.-B. Sortais).

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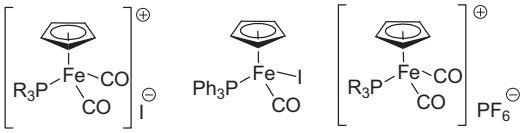


1 : $PR_3 = PMe_2Ph$
2 : $PR_3 = PCy_3$

3

4 : $PR_3 = PMe_2Ph$
5 : $PR_3 = PCy_3$
6 : $PR_3 = PPh_3$

Scheme 1. Structure of the complexes **1**–**6**.

formed with GC-2014 (Shimadzu) 2010 equipped with a 30-m capillary column (Supelco, SPBTM-20, fused silica capillary column, 30 M × 0.25 mm × 0.25 mm film thickness), which was used with N_2/air as the vector gas. The following GC conditions were used: initial temperature 80 °C for 2 min, then heating rate 10 °C/min up to 225 °C then 225 °C for 15 min. [CpFe(CO)$_2$I] [38], [Cp$_2$Fe]PF$_6$ [39], and [CpFe(CO)$_2$(THF)]PF$_6$ [40] were prepared according to the published procedures. HR–MS spectra were carried out by the corresponding facilities at the CRMPO (Centre Régional de Mesure Physiques de l'Ouest), University Rennes 1. FTIR spectra were recorded at room temperature in solution between KBr plates on an IR Affinity-1 Shimadzu apparatus.

2.2. Syntheses and characterisations of complexes *1*–*6*

Complexes **1** and **2** were prepared according to modified published procedures [41,42]: [CpFe(CO)$_2$I] (1.22 g, 4.0 mmol) and phosphine (4.8 mmol) were stirred overnight at room temperature in toluene (10 mL). The supernatant was removed by cannula transfer, the yellow solid was then washed with toluene and recrystallized with CH_2Cl_2 and diethyl ether.

[CpFe(CO)$_2$(PMe$_2$Ph)]I (Complex **1**). 63% yield. IR (CH_2Cl_2, cm^{-1}): 2006, 2049. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74–7.41 (m, 5H, Ph), 5.47 (s, 5H, Cp), 2.24 (d, J = 10.7, 6H, CH_3). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 37.0. ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.0 (d, J = 25.0), 134.4 (d, J = 52.9), 131.6 (d, J = 3.0), 129.7 (d, J = 10.9), 128.9 (d, J = 9.5), 87.9 (s), 20.2 (d, J = 34.7). HRMS (ESI): *m/z* calcd for $C_{15}H_{16}O_2P^{56}Fe$ [M−I]$^+$ 315.0237; found 315.0236.

[CpFe(CO)$_2$(PCy$_3$)]I (Complex **2**). 60% yield. IR (CH_2Cl_2, cm^{-1}): 2004, 2048. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.63 (s, 5H), 2.29–1.13 (m, 33H). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 80.4. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 211.1 (d, J = 22.2), 87.0 (s), 38.5 (d, J = 20.4), 30.6 (d, J = 2.4), 27.2 (d, J = 10.4), 25.8 (s). HRMS (ESI): *m/z* calcd for $C_{25}H_{38}O_2P^{56}Fe$ [M−I]$^+$ 457.1959; found 457.1960.

The complex **3** was prepared according to the published procedure [43].

[CpFe(CO)(PPh$_3$)I] (Complex **3**). 58% yield. IR (CH_2Cl_2, cm^{-1}): 1952. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.63–7.52 (m, 6H), 7.44–7.33 (m, 9H) 4.48 (d, J = 1.1, 5H). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 68.6. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 136.2 (d, J = 44.8), 134.0 (d, J = 9.3), 130.5 (d, J = 1.8), 128.5 (d, J = 9.6), 83.3 (s). HRMS: *m/z* calcd for $C_{24}H_{20}OINaP^{56}Fe$ [M+Na]$^+$ 560.9543; found 560.9541.[1]

Complexes **4** and **5** were prepared according to the modified published procedure [40]:

[CpFe(CO)$_2$(THF)]PF$_6$ (197 mg, 0.5 mmol), phosphine (0.60 mmol) were stirred in 10 mL of CH_2Cl_2 for 30 min at room temperature. After filtration, the solution was concentrated under vacuum, the complexes were obtained after recrystallization by CH_2Cl_2 and Et$_2$O.

[CpFe(CO)$_2$(PMe$_2$Ph)]PF$_6$ (Complex **4**). 90% yield. IR (CH_2Cl_2, cm^{-1}): 2009, 2054. ^{1}H NMR (200 MHz, acetone-d_6): δ 7.88–7.61 (m, 5H), 5.59 (d, J = 1.2 Hz, 5H), 2.25 (d, J = 11.2, 6H). ^{31}P{^{1}H} NMR (81 MHz, acetone-d_6): δ 38.4 (s), −142.9 (sept, J = 707). ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ 209.7 (d, J = 24.8), 135.3 (d, J = 53.0), 131.5 (d, J = 2.6), 129.4 (d, J = 9.0), 129.3 (d, J = 7.4), 87.9 (s), 18.0 (d, J = 35.4). HRMS (ESI): *m/z* calcd for $C_{15}H_{16}O_2P^{56}Fe$ [M−PF$_6$]$^+$ 315.0237; found 315.0236.

[CpFe(CO)$_2$(PCy$_3$)]PF$_6$ (Complex **5**). 93% yield. IR (CH_2Cl_2, cm^{-1}): 2005, 2048. ^{1}H NMR (300 MHz, acetone-d_6): δ 5.80 (s, 5H), 2.83–1.40 (m, 33H). ^{31}P{^{1}H} NMR (81 MHz, acetone-d_6): δ 79.5 (s), −143.0 (sept, J = 707). ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 212.8 (d, J = 22.6), 88.2 (s), 39.2 (d, J = 21.4), 31.1 (d, J = 2.8), 27.9 (d, J = 10.8), 26.5 (d, J = 1.5). HRMS (ESI): *m/z* calcd for $C_{25}H_{38}O_2P^{56}Fe$ [M−PF$_6$]$^+$ 457.1959; found 457.1958.

The complex **6** was prepared according to the modified published procedures [44,45]: [CpFe(CO)$_2$]$_2$ (0.18 g, 0.5 mmol), ferricenium salt [Cp$_2$Fe]PF$_6$ (0.33 g, 1.0 mmol) and PPh$_3$ (0.29 g, 1.1 mmol) were added into 10 mL CH_2Cl_2 solution and stirred for 30 min. The colour of reaction mixture turned from dark brown to orange. After removing the solvent under vacuum, the complex was further purified by recrystallization from CH_2Cl_2 and Et$_2$O.

[CpFe(CO)$_2$(PPh$_3$)]PF$_6$ (Complex **6**). 80% yield. IR (CH_2Cl_2, cm^{-1}): 2017, 2058. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.75–7.51 (m, 15H), 5.63 (d, J = 1.4 Hz, 5H). ^{31}P{^{1}H} NMR (121 MHz, acetone-d_6): δ 61.5 (s), −144.2 (sept, J = 707). ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 210.9 (d, J = 24.3), 133.8 (d, J = 10.4), 133.1 (d, J = 2.8), 132.2 (d, J = 52.2), 130.5 (d, J = 11.0), 89.8 (s). HRMS (ESI): *m/z* calcd for $C_{25}H_{20}O_2P^{56}Fe$ [M−PF$_6$]$^+$ 439.0550; found 439.0551.

2.3. X-ray structure determinations

Suitable crystals (obtained by slow diffusion of Et$_2$O in CH_2Cl_2 solution of the complexes) were collected on an APEXII, Bruker-AXS diffractometer equipped with a CCD detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at T = 150(2) K. The structure was solved by direct methods using the SIR97 program [46], and then refined with full-matrix least-square methods based on F^2 (SHELX-97) [47] with the help of the WINGX [48] program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. For the complex **1**, the contribution of the disordered solvents to the calculated structure factors was estimated following the BYPASS algorithm [49], implemented as the SQUEEZE option in PLATON [50]. A new data set, free of solvent contribution, was then used in the final refinement. The Refinement of the Flack parameter, for the complex **3**, lead to a value of 0.53(5). Due to the presence of anomalous atoms (I and Fe) in the complex and a suitable data collection (high redundancy and high completeness), accuracy on this refined Flack parameter is quite large, leading to an unambiguous meaning of this parameter. Thus, the value of the Flack parameter is the signature of the presence of racemic twin (two enantiomer molecules in identical quantity) in the crystal. Crystal data and collection parameters as well as the selected bond distances and angles are collected in Tables 1 and 2, respectively.

2.4. Procedure for hydrosilylation of aldehydes

A 10 mL oven dried Schlenk tube containing a stirring bar, was loaded with [CpFe(CO)$_2$(PPh$_3$)]PF$_6$ (0.015 g, 0.025 mmol), THF (0.5 mL) was then added followed by aldehyde (0.5 mmol) and PMHS (119 μL, 2.0 mmol). The reaction mixture was stirred in a preheated oil bath at 30 °C for 24 h under visible light irradiation (24 Watt compact fluorescent lamp). Then 1 mL of MeOH was added followed by 1 mL of 2 M NaOH aqueous solution with vigorous stirring. The reaction mixture was further stirred for 1 h at room temperature and extracted with diethyl ether

[1] The ^{13}C{^{1}H} NMR signal for the carbonyl ligands were not detected.

Table 1
Crystal data and data collection parameters.

Complex	1	2	3	4	5
Formula	$C_{15}H_{16}FeO_2PI$	$C_{25}H_{38}FeO_2PI$	$C_{24}H_{20}FeIOP$	$C_{15}H_{16}F_6FeO_2P_2$	$2(C_{25}H_{20}F_6FeO_2P_2)$
Formula weight	442.01	584.27	538.12	460.07	1204.69
Crystal system	triclinic	triclinic	orthorhombic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$Pc2_1n$	$P2_1/n$	$P\bar{1}$
a (Å)	9.6568 (10)	9.5701 (4)	8.7065 (3)	10.8531 (8)	11.3616 (8)
b (Å)	10.1855 (11)	11.6070 (4)	13.7633 (5)	13.6501 (11)	14.6952 (12)
c (Å)	11.0017 (12)	11.6957 (5)	17.2369 (6)	12.0929 (9)	16.5388 (12)
α (°)	88.056 (7)	89.6710 (10)	90	90	97.930 (3)
β (°)	65.179 (6)	82.8080 (10)	90	90.108 (4)	93.846 (3)
γ (°)	89.511 (6)	80.9860 (10)	90	90	90.079 (3)
V (Å^3)	981.57 (18)	1272.89 (9)	2065.50 (13)	1791.5 (2)	2728.6 (4)
Z	2	2	4	4	2
ρ_{calcd} (g cm^{-3})	1.495	1.524	1.73	1.706	1.466
μ (mm^{-1})	2.420	1.886	2.314	1.087	0.732
$F(000)$	432	596	1064	928	1256
Crystal size (mm^3)	0.32 × 0.27 × 0.24	0.34 × 0.13 × 0.08	0.14 × 0.12 × 0.08	0.38 × 0.27 × 0.05	0.38 × 0.29 × 0.1
θ range (°)	3.06–27.5	3.51–27.4	2.62–27.49	1.49–27.47	2.97–27.48
Index ranges	$-12 \leqslant h \leqslant 12$	$-12 \leqslant h \leqslant 10$	$-9 \leqslant h \leqslant 11$	$-14 \leqslant h \leqslant 11$	$-14 \leqslant h \leqslant 14$
	$-13 \leqslant k \leqslant 13$	$-14 \leqslant k \leqslant 15$	$-17 \leqslant k \leqslant 15$	$-15 \leqslant k \leqslant 17$	$-19 \leqslant k \leqslant 19$
	$-14 \leqslant l \leqslant 13$	$-15 \leqslant l \leqslant 15$	$-16 \leqslant l \leqslant 22$	$-15 \leqslant l \leqslant 12$	$-21 \leqslant l \leqslant 20$
No. of reflections collected	11267	20643	10307	8529	35921
No. of independent reflections collected (R_{int})	4397/0.0345	5764/0.0316	4535/0.0319	3931/0.0494	12380/0.047
Completeness to δ_{max} (%)	97.1	99.3	99.9	95.7	98.9
No. of refined parameters	183	271	140	238	649
GOF (F^2)	1.088	1.051	1.056	0.783	1.039
R1(F) ($I > 2\delta(I)$)	0.0564	0.0192	0.0507	0.0354	0.0413
wR2(F^2) ($I > 2\delta(I)$)	0.1506	0.0511	0.116	0.0909	0.0985
Absolute structural parameters			0.53 (5)		
Largest diff peak/hole (e Å^{-3})	3.535/−1.065	0.789/−0.523	1.75/−0.857	0.373/−0.429	0.845/−0.686

(2 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The conversion was determined by ^{1}H NMR. The residue was then purified by silica gel column chromatography using a petroleum ether–ethyl acetate mixture (10–40%) to achieve the desired product. ^{1}H and ^{13}C NMR of the products were in accordance with those described in the literature.

2.5. Procedure for hydrosilylation of ketones

A 10 mL oven-dried Schlenk tube containing a stirring bar, was loaded with [CpFe(CO)PPh_3I] (0.014 g, 0.025 mmol). The ketone (0.5 mmol) was added followed by $PhSiH_3$ (74 μL, 0.6 mmol). The reaction mixture was stirred in a preheated oil bath at 70 °C for 30 h. Then 1 mL of MeOH was added followed by 1 mL of 2 M NaOH aqueous solution with vigorous stirring. The reaction mixture was further stirred for 1 h at room temperature and was extracted with diethyl ether (2 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Conversion was determined by ^{1}H NMR. The residue was purified by silica gel column chromatography using a petroleum ether–ethyl acetate mixture (10–20%) to achieve the desired product. ^{1}H and ^{13}C NMR of the products were in accordance with those described in the literature.

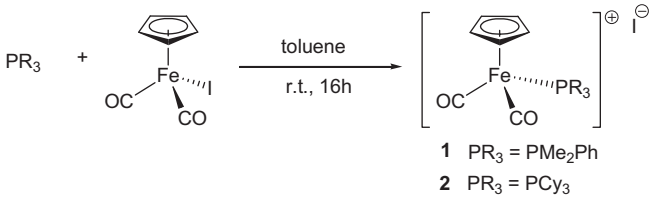
3. Results and discussion

3.1. Synthesis of the catalysts

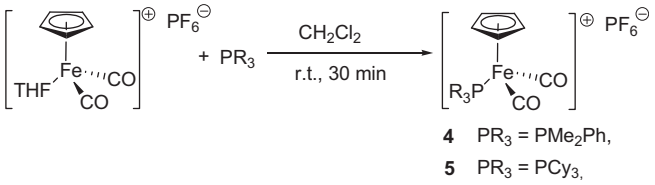
Cyclopentadienyl iron carbonyl complexes have been studied extensively as models in coordination chemistry [51] to investigate, for example, the properties of phosphines [42] or NHC-carbene ligands [52,53] and the chirality at the metal center [54]. To start our investigation on iron–phosphine complexes as potential catalysts for hydrosilylation, we selected three phosphine ligands for their steric and electronic properties: PPh_3, PMe_2Ph, and PCy_3. Various iron derivatives were prepared according to established pathways. For the first family, which uses iodide as a counter-anion, complexes **1** and **2**, respectively with PMe_2Ph and PCy_3,

Table 2
Selection of bonds and distances of the complexes **1**–**5**.

Complex	1	2	3	4	5
Distances (Å)					
Fe–P	2.2183 (16)	2.2675 (4)	2.2275 (15)	2.2234 (8)	2.2646 (6)
Fe–Cp	1.722	1.725	1.686	1.725	1.729
Fe–CO	1.789 (6)	1.7892 (16)	1.847 (11)	1.782 (3)	1.785 (2)
Fe–CO	1.777 (6)	1.7799 (16)	–	1.785 (3)	1.782 (2)
Fe–I	–	–	2.6298 (8)	–	–
Angles (°)					
P–Fe–CO	92.6 (2)	93.44 (5)	92.7 (3)	91.61 (10)	94.05 (7)
P–Fe–CO	90.2 (2)	93.88 (5)	–	91.45 (11)	91.60 (7)
OC–Fe–CO	93.6 (3)	96.11 (7)	–	92.56 (13)	95.34 (10)
P–Fe–I	–	–	97.62 (4)	–	
I–Fe–CO	–	–	87.5 (3)	–	–



Scheme 2. Synthesis of the complexes **1** and **2**.



Scheme 3. Synthesis of the complexes **4** and **5**.

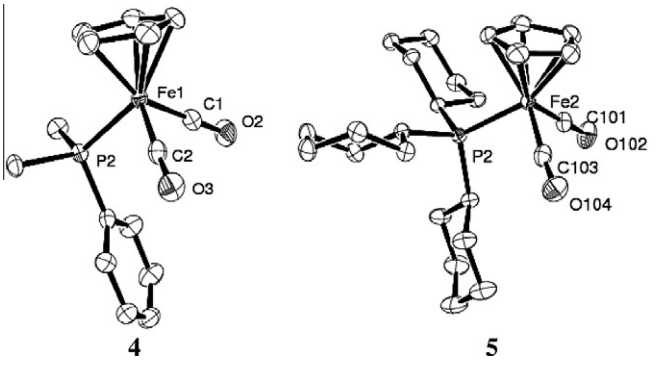
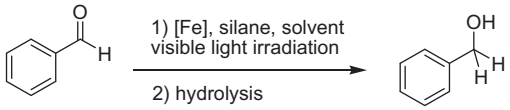


Fig. 2. ORTEP view of the complexes **4**–**5**, drawn at 50% of probability. Hydrogen atoms and PF_6 moities were omitted for clarity.



Scheme 4. Hydrosilylation of benzaldehyde catalyzed by the iron complexes **1**–**6**.

respectively, were obtained in moderate yields (60%) by direct reaction of the phosphine with the iron precursor $[CpFe(CO)_2I]$ in toluene at rt [41,42] (Scheme 2). When the same conditions were applied to PPh_3 as the phosphine, a mixture of the desired cationic compound $[CpFe(CO)_2PPh_3]I$ (<20%) and the neutral complex **3**, $[CpFe(CO)(PPh_3)I]$ was obtained [55]. Thus, the neutral complex **3** selectively was prepared from $[CpFe(CO)_2I]$ and triphenylphosphine according to Coville [56,57] and Aime's [43] procedures using $[CpFe(CO)_2]_2$ dimer as a catalyst to favour the substitution of the carbonyl ligand.

In order to study the effect of the nature of the counter-anion in the course of the catalytic reaction, the analogous complexes with PF_6 as non-coordinative anion were prepared following the methodology described by Schumann [40]. Complexes **4** and **5** were obtained in one step by reaction of the corresponding phosphine with the precursor $[CpFe(CO)_2(THF)]PF_6$ in CH_2Cl_2 (Scheme 3). Although the same conditions could be applied for the preparation of the complex **6**, this compound was obtained by the direct oxidation of $[CpFe(CO)_2]_2$ by $[Cp_2Fe]PF_6$ in the presence of PPh_3 in CH_2Cl_2 at rt [45,58].

All complexes have been characterized by ^1H, ^{13}C and ^{31}P NMR, IR, HR–MS and X-ray diffraction studies. To the best of our knowledge, only the crystallographic structure of **6** has been described [59]. Singles crystals suitable for X-ray diffraction studies were obtained for all the other complexes. Representative molecular structures are displayed in Figs. 1 and 2 for complexes **1**–**3** and **4**–**5**, respectively. Typical piano-stool geometries were observed for this family of catalysts (See Table 2) and no significant structural difference was observed between the iodide and PF_6 series. With those complexes in hand, we then started to investigate their catalytic properties.

3.2. Catalytic hydrosilylation reaction

We performed studies of the catalytic activities of [CpFe(phosphine)] complexes to explore their potential in the hydrosilylation reaction of aldehydes (Scheme 4).

The optimization of the hydrosilylation reaction was carried out with benzaldehyde as the model substrate. As illustrated in Table 3, the preliminary survey was carried out using 5 mol.% of $[CpFe(CO)_2(PMe_2Ph)]I$ **1** as the catalyst, and 1.2 equiv. of diphenylsilane as the reducing agent, under exposure to visible light in toluene. After a 16 h reaction at 70 °C, 53% conversion was observed after basic cleavage of the silyl ether intermediate (Table 3, entry 1). When the reaction was performed with phenylsilane as the hydride source, the conversion increased to 80% (Table 3, entry 2). Interestingly, the conversion was improved to 98% when THF was chosen as the reaction solvent (Table 3, entry 4). When the reaction temperature was decreased to 30 °C and the concentration of the catalyst increased, 92% conversion was observed (Table 3, entry 5). However, with 2 mol.% of the catalyst under neat

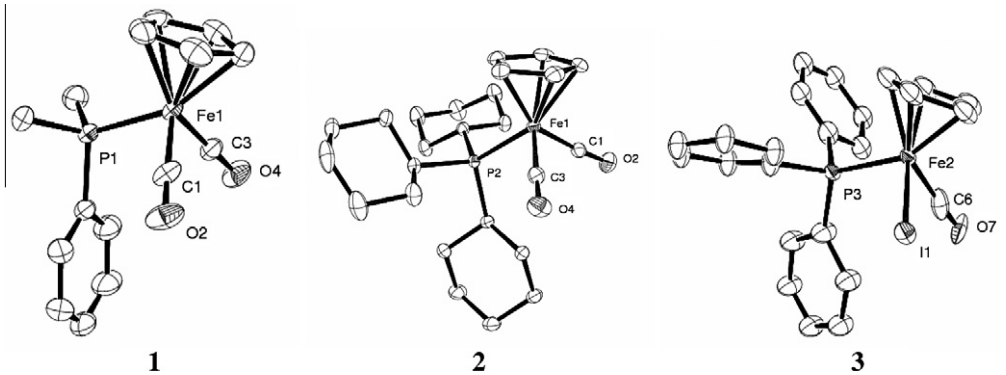


Fig. 1. ORTEP view of the complexes **1**–**3**, drawn at 50% of probability. Hydrogen atoms and iodide atom for **1** and **2** were omitted for clarity.

Table 3
Optimisation of the hydrosilylation of benzaldehyde with catalyst **1**. Typical conditions: benzaldehyde (0.5 mmol), silane and catalyst were stirred under visible light irradiation, conversions were determined by GC after methanolysis (MeOH, NaOH 2 M).

Entry	Catalyst loading (mol.%)	Silane (equiv.)	Solvent	Temp. (°C)	Time (h)	Conversion (%)
1	5	Ph_2SiH_2 (1.2)	Toluene[a]	70	16	53
2	5	$PhSiH_3$ (1.2)	Toluene[a]	70	16	80
3	5	Ph_2SiH_2 (1.2)	THF[a]	70	16	70
4	5	$PhSiH_3$ (1.2)	THF[a]	70	16	98
5	5	$PhSiH_3$ (1.2)	THF[b]	30	16	92
6	2	$PhSiH_3$ (1.2)	THF[b]	30	16	83
7	5	$PhSiH_3$ (1.2)	CH_2Cl_2[b]	30	16	87
8	5	PMHS (4)	THF[b]	30	16	68
9	5	PMHS (4)	THF[c]	30	24	>98
10	5	Ph_2SiH_2 (1.2)	Neat	30	16	96
11	5	$PhSiH_3$ (1.2)	Neat	30	16	98

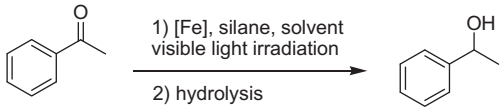
[a] 2 mL.
[b] 1 mL.
[c] 0.5 mL.

Table 4
Comparison of the different catalysts **1**–**6** for the reduction of benzaldehyde. Typical conditions: benzaldehyde (0.5 mmol), catalyst (5 mol%), silane ($PhSiH_3$, 0.6 mmol or PMHS 2 mmol) and solvent were stirred at 30 °C under visible light irradiation for 16 h. Conversions were determined by GC after methanolysis (MeOH, 2 M NaOH).

Entry	Catalyst	$PhSiH_3$		PMHS
		THF	Neat	THF
1	**1**	92	96	68
2	**2**	95	92	42
3	**3**	>98	91	85
4	**4**	94	97	95
5	**5**	95	97	95
6	**6**	95	91	88

condition, the reaction slowed down, and only 83% conversion was obtained (Table 3, entry 6). Replacing the solvent by CH_2Cl_2 also reduced the conversion to 87% (Table 3, entry 7). Therefore, THF was employed as the solvent for all following reactions. It is noteworthy that the cheap and convenient silane PMHS could be employed as the silane at 30 °C in THF, since the reaction reached the completion after 24 h (Table 3, entries 8–9). These results show the potential advantage of this family of catalysts over similar systems which usually require higher temperature with PMHS [16,32]. Notably, the reactions could also be performed in neat condition with diphenylsilane or phenylsilane (Table 3, entries 10–11) without decomposition of the catalyst.

Further screening of the catalysts **1**–**6** using the optimized conditions (catalyst loading 5%, THF or neat conditions, phenylsilane or PMHS as the hydride source, Table 4) revealed that for the reactions performed with PMHS catalysts with PF_6 as the counter anion usually worked better than catalysts with iodide as the counter



Scheme 5. Hydrosilylation of acetophenone catalyzed by the iron complexes **1**–**6**.

Table 5
Optimisation of the hydrosilylation of acetophenone with catalyst **1**. Typical conditions: acetophenone (0.5 mmol), silane (1.2 equiv.), THF (2 mL) or neat, under visible light irradiation, conversion determined by GC after methanolysis (MeOH, NaOH 2 M).

Entry	Catalyst loading (mol.%)	Silane	Solvent	Temp. (°C)	Time (h)	Conversion (%)
1	5	Ph_2SiH_2	THF	70	16	1
2	5	$PhSiH_3$	THF	70	16	2
3	5	$PhSiH_3$	Neat	70	16	66
4	5	$PhSiH_3$	Neat	70	30	73
5	2	$PhSiH_3$	Neat	50	16	41

Table 6
Comparison of the different catalysts **1**–**6** for the reduction of acetophenone. 5 mol.% of catalyst, 0.5 mmol of acetophenone, 1.2 equiv. of $PhSiH_3$, no solvent, 70 °C, 30 h, conversion determined by GC.

Entry	Catalyst	Conversion (%)
1	**1**	73
2	**2**	69
3	**3**	88
4	**4**	43
5	**5**	50
6	**6**	87

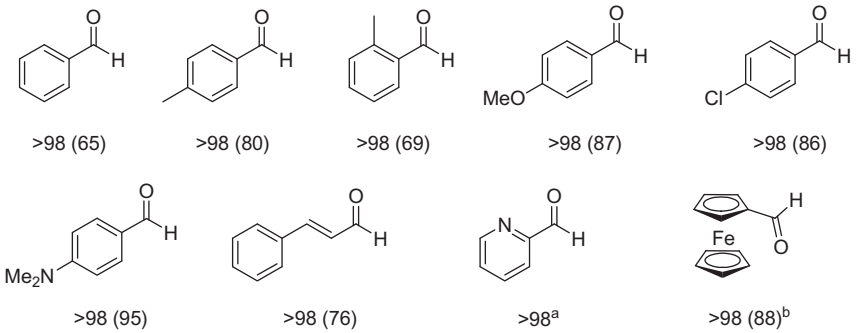


Fig. 3. Scope of iron-catalysed hydrosilylation of aldehydes using $[CpFe(CO)_2PPh_3]PF_6$ as the catalyst. Conversions are determined by ^1H NMR and isolated yields are given in parentheses. (a) Conversion determined by GC. (b) At 70 °C.

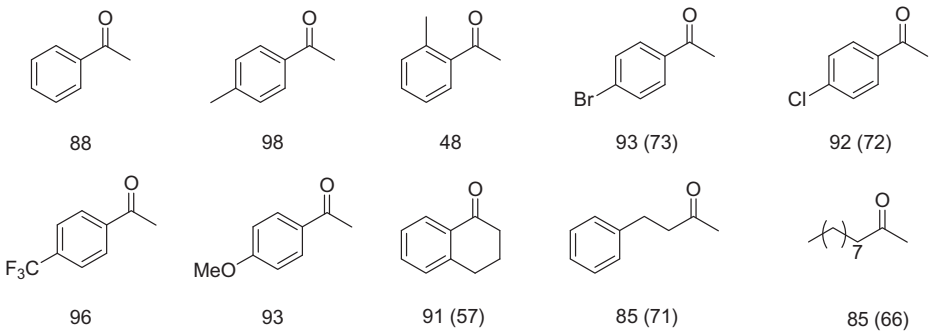


Fig. 4. Scope of iron-catalysed hydrosilylation of ketones using [CpFe(CO)(PPh_3)I] as the catalyst. Conversions are determined by ^{1}H NMR and isolated yields are given in parentheses.

anion. Since PPh_3 is economical and easy to handle, the catalyst **6** [$CpFe(CO)_2(PPh_3)]PF_6$ was chosen as the catalyst for the scope of aldehydes, albeit the conversion is slightly lower than when with PMe_2Ph and PCy_3 are used as ligands (Table 4, entries 6, versus 4 and 5).

To investigate the scope of the reaction, a variety of aldehydes were then tested using the optimized mild conditions (PMHS, THF, 24 h at 30 °C, 5 mol.% of **6**, under visible light irradiation). Several aldehydes were reduced with good to excellent yields (Fig. 3). The electronic effects on the reactivity were limited. Electron-deficient as well as electron-donating groups on the aryl ring did not show any significant influence on the activity of the iron catalyst. Interestingly, functional groups such as chloride remained unchanged under such reaction conditions. The chemoselectivity of the hydrosilylation of aldehyde versus alkene was also demonstrated: the catalyzed hydrosilylation of enal derivatives such as cinnamaldehyde led exclusively to the corresponding allyl alcohol resulting in an exclusive 1,2-addition with no GC-detectable amounts of 1,4-addition products and the isolated yield was up to 76%. Extension of the procedure to heterocyclic aromatic aldehydes, such as 2-pyridinecarboxaldehyde, was also possible. Interestingly, ferrocenecarboxaldehyde could also be reduced using this catalyst (at 70 °C, 24 h) and the corresponding alcohol was obtained with a good isolated yield (88%).

Based on the promising results obtained with [CpFe(phosphine)] complexes as catalysts for the hydrosilylation of aldehydes, we also tested these compounds with ketones which are usually more difficult to reduce (Scheme 5).

The optimisation was carried out using catalyst **1** as the model catalyst and acetophenone as the model substrate (Table 5). When reactions were performed in THF, after 16 h under irradiation, no conversion was observed for either types of hydride source, diphenylsilane or phenylsilane (Table 5, entries 1 and 2). Under solvent-free conditions, the conversion could reach 73% at 70 °C after 30 h (Table 5, entries 3 and 4).

The different catalysts were tested using the best conditions for the reduction of acetophenone (5 mol.% of catalyst, 1.2 equiv. of $PhSiH_3$, no solvent, 70 °C, 30 h, under irradiation). (Table 6) By contrast with the results obtained for the reduction of benzaldehyde, the complexes bearing a non-coordinative counter-anion were not found to be more efficient than the ones with iodide as the counter-ion (Table 6, entries 1,2 versus 4–6). Only complexes **3** and **6**, derived from PPh_3, gave satisfactory conversion rates above 85% (Table 6, entries 3 and 6). Following these encouraging results, we performed reactions in the absence of light. The reaction only worked well with the neutral complex **3**, whereas no conversion was observed for complex **6**.

Given the cheapness of phosphine (PPh_3), the easy preparation of the catalyst and the fact that no irradiation was needed, complex **3** was selected as the catalyst for the scope of the reaction. Several ketones were subjected to the best reaction conditions optimized for the scope of this reaction (Fig. 4). It turned out that this iron-catalyzed hydrosilylation could adapt to various ketones. In contrast to aldehydes, aryl methyl ketones bearing substituents in the ortho-position of the aryl ring led to the corresponding alcohols in 48% conversion, which probably means that ortho-hindered substituents can hamper the reaction. The hydrosilylation reaction was suitable to both electron-rich and electron-poor substituted (Me, OMe, Cl, and Br) aromatic methyl ketones, and the reaction resulted in corresponding alcohols with good to excellent yields. The principle of this iron-catalyzed transformation can also be extended to alkyl methyl ketones such as 4-phenyl-2-butanone and 2-undecanone. In the case of the cyclic ketone, α-tetralone, the reaction led to the corresponding 1,2,3,4-tetrahydro-1-naphthol with moderate yield (57%).

4. Conclusion

In conclusion, we have demonstrated that cationic and neutral cyclopentadienyl iron carbonyl complexes bearing a phosphine as the ligand could be successfully used as catalysts for the hydrosilylation of aldehydes and ketones. Interestingly, we observed that compared to complexes bearing a NHC-carbene as the ligand, phosphine analogs proceeded more slowly (5 mol.% were required instead of 1 mol.%), but PMHS could be used as the silane for the reduction of aldehydes at 30 °C. We also showed that simple PPh_3 could be a good ligand for this family of catalysts. More detailed studies directed towards a precise mechanism are currently under investigation in our group.

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Appendix A. Supplementary material

Crystallographic data for complexes **1**–**5** are summarised in Table 1. CCDC-836108 (for **1**), -836109 (for **2**), -836110 (for **3**), -836111 (for **4**) and -836112 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.10.048.

References

[1] C. Bolm, J. Legros, J. Le Paih, L. Zani, Chem. Rev. 104 (2004) 6217.
[2] B. Plietker (Ed.), Iron Catalysis in Organic Chemistry, Wiley VCH Verlag, Weinheim, 2008.
[3] S. Enthaler, K. Junge, M. Beller, Angew. Chem., Int. Ed. 47 (2008) 3317.
[4] A. Correa, O. Garcia Mancheño, C. Bolm, Chem. Soc. Rev. 37 (2008) 1108.
[5] B.D. Sherry, A. Fürstner, Acc. Chem. Res. 41 (2008) 1500.
[6] W.M. Czaplik, M. Mayer, J. Cvengros, A. Jacobi Von Wangelin, ChemSusChem 2 (2009) 396.
[7] C.-L. Sun, B.-J. Li, Z.-J. Shi, Chem. Rev. 111 (2011) 1293.
[8] R.H. Morris, Chem. Soc. Rev. 38 (2009) 2282.
[9] M. Zhang, A. Zhang, Appl. Organometal. Chem. 24 (2010) 751.
[10] K. Junge, K. Schorder, M. Beller, Chem. Commun. 47 (2011) 4849.
[11] H. Brunner, K. Fisch, Angew. Chem., Int. Ed., Engl. 29 (1990) 1131.
[12] H. Brunner, K. Fisch, J. Organomet. Chem. 412 (1991) C11.
[13] H. Nishiyama, A. Furuta, Chem. Commun. (2007) 760.
[14] A. Furuta, H. Nishiyama, Tetrahedron Lett. 49 (2008) 110.
[15] N.S. Shaikh, K. Junge, M. Beller, Org. Lett. 9 (2007) 5429.
[16] N.S. Shaikh, S. Enthaler, K. Junge, M. Beller, Angew. Chem., Int. Ed. 27 (2008) 2497.
[17] S. Zhou, K. Junge, D. Addis, S. Das, M. Beller, Angew. Chem., Int. Ed. 48 (2009) 9507.
[18] D. Addis, N. Shaikh, S. Zhou, S. Das, K. Junge, M. Beller, Chem. Asian J. 5 (2010) 1687.
[19] T. Inagaki, L.T. Phong, A. Furuta, J. Ito, H. Nishiyama, Chem. Eur. J. 16 (2010) 3090.
[20] Y. Sunada, H. Kawakami, Y. Motoyama, H. Nagashima, Angew. Chem., Int. Ed. 48 (2009) 9511.
[21] K. Muller, A. Schubert, T. Jozak, A. Ahrens-Botzong, V. Schünemann, W.R. Thiel, ChemCatChem 3 (2011) 887.
[22] S. Zhou, D. Addis, S. Das, K. Junge, M. Beller, Chem. Commun. 1 (2009) 4883.
[23] A.M. Tondreau, E. Lobkovsky, P.J. Chirik, Org. Lett. 10 (2008) 2789.
[24] D.V. Gutsulyak, L.G. Kuzmina, J.A.K. Howard, S.F. Vyboishchikov, G.I. Nikonov, J. Am. Chem. Soc. 130 (2008) 3732.
[25] B.K. Langlotz, H. Wadepohl, L.H. Gade, Angew. Chem., Int. Ed. 47 (2008) 4670.
[26] A.M. Tondreau, J.M. Darmon, B.M. Wile, S.K. Floyd, E. Lobkovsky, P.J. Chirik, Organometallics 28 (2009) 3928.
[27] J. Yang, T.D. Tilley, Angew. Chem., Int. Ed. 49 (2010) 10186.
[28] V.V.K.M. Kandepi, J.M.S. Cardoso, E. Peris, B. Royo, Organometallics 29 (2010) 2777.
[29] T. Muraoka, Y. Shimizu, H. Kobayashi, K. Ueno, H. Ogino, Organometallics 29 (2010) 5423.
[30] S. Hosokawa, J. Ito, H. Nishiyama, Organometallics 29 (2010) 5773.
[31] L.C. Misal Castro, D. Bézier, J.-B. Sortais, C. Darcel, Adv. Synth. Catal. 353 (2011) 1279.
[32] X.-F. Wu, C. Darcel, Eur. J. Org. Chem. 1 (2009) 1144.
[33] X.-F. Wu, D. Bezier, C. Darcel, Adv. Synth. Catal. 351 (2009) 367.
[34] F. Jiang, D. Bézier, J.-B. Sortais, C. Darcel, Adv. Synth. Catal. 353 (2011) 239.
[35] D. Bézier, G.T. Venkanna, J.-B. Sortais, C. Darcel, ChemCatChem (2011) doi:10.1002/cctc.201100202.
[36] D. Bézier, F. Jiang, T. Roisnel, J.-B. Sortais, C. Darcel, Eur. J. Inorg. Chem. (2011) doi:10.1002/ejic.201100762.
[37] L.C. Misal Castro, J.-B. Sortais, C. Darcel, Chem. Commun. (2011). doi:10.139/C1CC14403K.
[38] S. Yasuda, H. Yorimitsu, K.O. Yasuda, H. Yorimitsu, K. Oshima, Organometallics 27 (2008) 4025.
[39] T.C. Lehman, C. Thorpe, Biochemistry 29 (1990) 10594.
[40] H. Schumann, J. Organomet. Chem. 304 (1986) 341.
[41] P.M. Treichel, R.L. Shublin, K.W. Barnett, D. Reichard, Inorg. Chem. 5 (1966) 1177.
[42] N.J. Coville, E.A. Darling, A.W. Hearn, P. Johnston, J. Organomet. Chem. 328 (1987) 375.
[43] S. Aime, M. Botta, R. Gobetto, D. Osella, Organometallics 4 (1985) 1476.
[44] D.L. Reger, C. Coleman, J. Organomet. Chem. 131 (1977) 153.
[45] D. Catheline, D. Astruc, J. Organomet. Chem. 266 (1984) C11.
[46] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Cryst. 32 (1999) 115.
[47] G.M. Sheldrick, Acta Crystallogr., Sect. A64 (2008) 112.
[48] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837.
[49] P.V.D. Sluis, A.L. Spek, Acta Crystallogr., Sect. A46 (1990) 194.
[50] A.L. Spek, J. Appl. Cryst. 36 (2003) 7.
[51] V. Guerchais, Eur. J. Inorg. Chem. (2002) 783.
[52] P. Buchgraber, L. Toupet, V. Guerchais, Organometallics 22 (2003) 5144.
[53] L. Mercs, G. Labat, A. Neels, A. Ehlers, M. Albrecht, Organometallics 25 (2006) 5648.
[54] H. Brunner, H. Ike, M. Muschiol, T. Tsuno, N. Umegaki, M. Zabel, Organometallics 30 (2011) 414.
[55] V.N. Pandey, Inorg. Chim. Acta 22 (1977) L39.
[56] N.J. Coville, M.O. Albers, E. Singleton, J. Chem. Soc., Dalton Trans. (1983) 947.
[57] N.J. Coville, M.O. Albers, E. Singleton, J. Organomet. Chem. 232 (1982) 261.
[58] B.D. Dombek, R.J. Angelici, Inorg. Chim. Acta 7 (1973) 345.
[59] T.S. Janik, L.M. Krajkowski, M.R. Churchill, J. Chem. Crystallogr. 25 (1995) 751.