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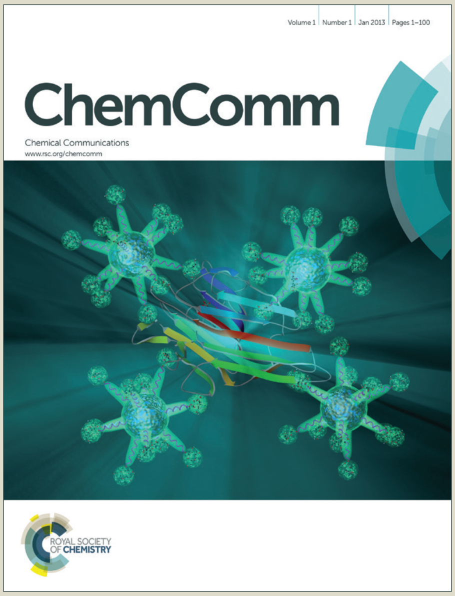

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**ARTICLE TYPE**

# A novel iron complex for highly efficient catalytic hydrogen generation from the hydrolysis of organosilanes†

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**Hydrolytic oxidation of organosilanes based on an iron catalyst is described for the first time. The novel iron complex, [Fe($C_6H_5N_2O$)(CO)(MeCN)$_3$][$PF_6$], exhibits excellent mediating power in the catalytic hydrolysis of organosilanes to produce dihydrogen and organosilanols with turnover numbers approaching $10^4$ and turnover frequencies in excess of $10^2$ min$^{-1}$ under ambient conditions.**

In line with the prospects of a future hydrogen economy,[1] increasing attention is being paid to the possibility of replacing fossil fuels with hydrogen as an alternative energy source.[2] Fuel cells are attractive because it produces energy with water as the only by-products. To realize the full potential of fuel cells, key issues with regard to hydrogen sources and storage, such as the need to replace currently used large and heavy gas cylinders, must be addressed.[3] Cost-effective and highly efficient chemical methods used to provide hydrogen on demand are, therefore, desirable.[4] Organosilanes are attractive and promising candidates for several reasons: (i) Si–H bond is relatively weak and can undergo protolytic cleavage with water to generate dihydrogen; (ii) most organosilanes are storable liquid under ambient conditions and hence eliminates the daunting problem of transportation; (iii) organosilanes rich in Si–H groups such as $C(SiH_3)_4$ and cyclo-$(CH_2SiH_2)_3$ satisfy the revised U.S. Department of Energy (DOE) 2015 system target of 5.5 wt% hydrogen.[5,6] and (iv) organosilanols, the by-products of organosilanes hydrolysis, serve as useful building blocks for polymeric and other organic materials.[7,8] Unfortunately, the hydrolysis of Si–H bonds is slow, even though it is thermodynamically favorable.[9] To overcome this drawback, catalytic systems, based on noble metals such as gold,[10] rhodium,[11] iridium,[12] rhenium,[13] and ruthenium,[14] have been reported. While these catalytic systems often exhibited good mediating capabilities, the heavy price tag of these expensive and earth precious metals will significantly increase the cost for real applications. For any sustainable and economically viable future application, catalysts should be made of cheap and earth abundant elements with minimal compromise on its catalytic efficiencies. Iron is one such candidate and to the best of our knowledge, there are no reports of hydrolysis of organosilanes based on iron complexes. Herein, we wish to report the synthesis of an iron complex for the hydrolytic oxidation of organosilanes to produce dihydrogen and organosilanols.

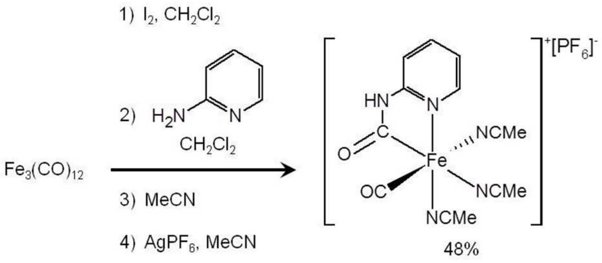


**Fig. 1** Synthesis of [Fe($C_6H_5N_2O$)(CO)(MeCN)$_3$][$PF_6$].

Reaction of [$Fe_3(CO)_{12}$] with iodine in dichloromethane rapidly produced dark violet [$Fe(CO)_4I_2$] (Fig. 1, see ESI† for experimental procedures). Subsequent addition of 2-aminopyridine yielded a dark green precipitate accompanied by evolution of carbon monoxide as a result of a reaction between the pendant amino group of the pyridine and a metal-bound carbonyl ligand which formed a coordinated carbamoyl unit. The precipitate was then dissolved in acetonitrile resulting in further evolution of gas bubbles. We believe that acetonitrile had substituted one of the carbonyl ligands since a similar structure based on its bromide analogue had been reported.[15] Silver hexafluorophosphate was then added to give an orange supernatant liquid and a grey residue which was found to be silver iodide. Gas effervescence was again observed. It is evident that the second iodide ligand was extracted by silver ions and replaced by acetonitrile to give a cationic iron complex.

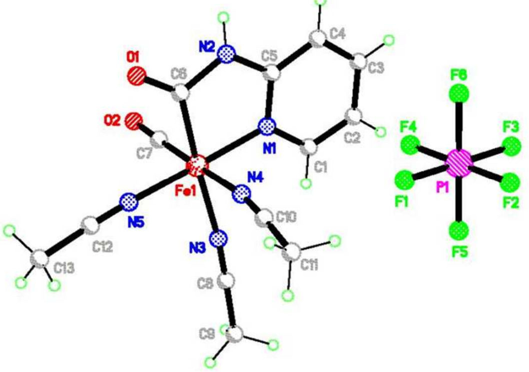


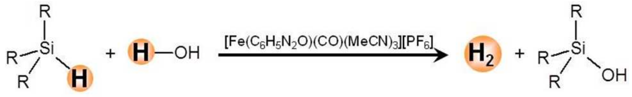
**Fig. 2** ORTEP view of solid-state structure of [Fe($C_6H_5N_2O$)(CO)(MeCN)$_3$][$PF_6$]. Pertinent bond distances (Å): Fe1-N1, 1.966(4); Fe1-N3, 2.025(4); Fe1-N4, 1.979(5); Fe1-N5, 1.931(5); Fe1-C6, 1.930(5); Fe1-N3, 1.761(6).

Spectroscopic evidence provided the first hint of a successful cationic iron complex synthesis. In acetonitrile, the carbonyl stretching blue-shifted by 31 cm$^{-1}$ (from 2046 cm$^{-1}$ to 2077 cm$^{-1}$) to higher energy when silver hexafluorophosphate was added to give the cationic iron complex. This is not surprising since a decreased electron density on the cationic metal center will give rise to less π-backbonding to the carbonyl ligand which in turn leads to a stronger carbonyl bond as a result of the decrease in electron density in its formally empty carbonyl π* orbital. The exact same shift in carbonyl stretching was also observed when silver nitrate was added in place of silver hexafluorophosphate.

Upon slow cooling in diethyl ether, homogeneous X-ray quality crystals of $[Fe(C_6H_5N_2O)(CO)(MeCN)_3][PF_6]\bullet½(Et_2O)$ (Fig. 2, see ESI† for crystal structure report) were obtained and sent for X-ray crystallography structural determination. $[Fe(C_6H_5N_2O)(CO)(MeCN)_3][PF_6]$ crystallizes in the monoclinic space group $P\ 1\ 2_1/c\ 1$, with unit cell dimensions $a$ = 14.3610(14) Å, $b$ = 8.1428(7) Å, $c$ = 18.0294(17) Å, and $\beta$ = 91.916(3)°. The cationic iron complex adopts a facial configuration since each of the three acetonitrile ligands occupies one face of the octahedron surrounding the iron centre. Nevertheless, the difference in their bond lengths indicates that each of these acetonitrile ligands binds to the metal centre with slightly different strengths. The acetonitrile ligand which is *trans* to the carbonyl ligand of the CONH– group in amide is likely to be the most labile ligand (2.025(4) Å). Two carbonyl ligands are retained with relative *cis* geometry: one is a typical C≡O carbonyl ligand and the second is a C=O ligand which is part of the CONH– group in amide. The bond length of the former was determined to be 1.141(6) Å and shorter than that of the latter (1.225(6) Å). The 5-membered ring containing the coordinated carbamoyl unit lies on a near perfect plane.

In addition, the iron complex was found to be paramagnetic as measured by a Gouy balance. In addition, when the iron complex was cooled using liquid nitrogen, a color change from orange to dark green was observed, hence indicating the possibility of the iron complex undergoing spin crossing.

**Table 1** Hydrolysis of various organosilanes catalyzed by $[Fe(C_6H_5N_2O)(CO)(MeCN)_3][PF_6]$.[a]



| Entry | Silane | Silanol | Solvent | Time (min) | $H_2$ (%)[b] | Yield (%5)[c] |
|---|---|---|---|---|---|---|
| 1 | $Et_3SiH$ | $Et_3SiOH$ | THF | 15 | 99 | > 99 |
| 2[d] | $Et_3SiH$ | $Et_3SiOH$ | THF | 20 | < 1 | < 1 |
| 3 | $i$-$Pr_3SiH$ | $i$-$Pr_3SiOH$ | THF | 20 | 96 | 93 |
| 4 | $PhMe_2SiH$ | $PhMe_2SiOH$ | THF | 30 | 95 | 94 |
| 5 | $Ph_2MeSiH$ | $Ph_2MeSiOH$ | THF | 30 | 96 | 96 |
| 6 | $Ph_3SiH$ | $Ph_3SiOH$ | THF | 40 | 50 | 46 |
| 7 | $Et_3SiH$ | $Et_3SiOH$ | $CHCl_3$ | 60 | 22 | 18[e] |

[a] Catalytic runs involved 2 mmol of organosilane and 20 mmol of $H_2O$ with 0.01% catalytic loading at 25 °C. [b] Total $H_2$ yields derived from a calibration curve obtained from a known amount of $H_2$. [c] $^1H$ NMR organosilanol yield calculated with respect to organosilane, using toluene or $n$-hexane as internal standard. [d] Without addition of water. [e] Organic product obtained was siloxane.

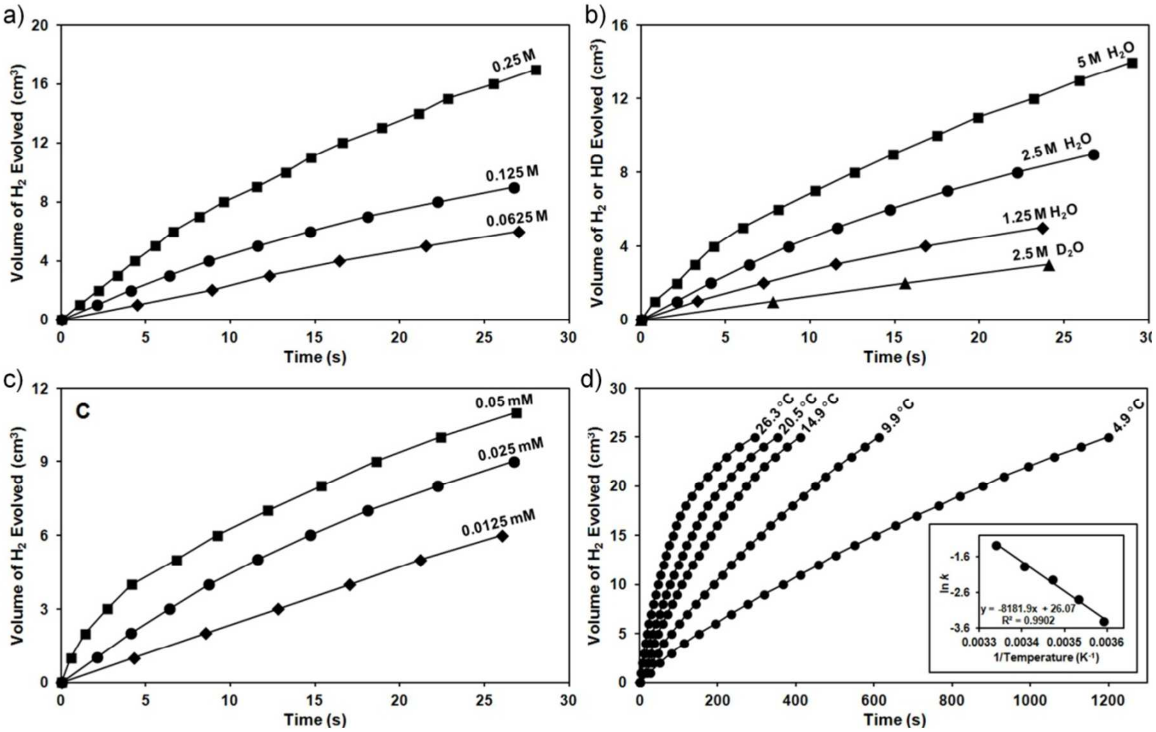


**Fig. 3** The effect of (a) triethylsilane, (b) water, (c) catalyst, and (d) temperature on the hydrogen evolution for the hydrolysis of triethylsilane catalyzed by $[Fe(C_6H_5N_2O)(CO)(MeCN)_3][PF_6]$. Conditions: (a) $c(H_2O)$ = 2.5 M and $c$(catalyst) = 0.025 mM; (b) $c$(organosilane) = 0.125 M and $c$(catalyst) = 0.025 mM; (c) $c$(organosilane) = 0.125 M and $c(H_2O)$ = 2.5 M; (d) $c$(organosilane) = 0.125 M, $c(H_2O)$ = 2.5 M, and $c$(catalyst) = 0.025 mM.

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The excellent mediating capability of the iron complex catalyst was demonstrated by the strong effervescence which was immediately observed when triethylsilane was added into a solution containing the catalyst and excess water (entry 1, Table 1). An intense signal at *m/z* 2, which corresponded to the evolution of $H_2$, was observed when the headspace of the reaction vessel was analyzed by a mass spectrometer. A carefully repeated experiment using $D_2O$ resulted in an intense signal at *m/z* 3 (HD) and a diminished signal at *m/z* 2. This indicates that water was one of the substrates in the reaction. To verify this hypothesis, the experiment was repeated without the addition of water (entry 2). Indeed, less than 1% $H_2$ yield was obtained. Furthermore, no $H_2$ evolution was detected when anhydrous tetrahydrofuran (distilled from sodium benzophenone ketyl) was used, or when either triethylsilane or the catalyst was removed. As such, there was sufficient experimental evidence to suggest that dihydrogen was formed as a result of both organosilane and water supplying one H atom each. This was similar to a previous work reported by our group.[14b]

The catalytic efficiency of the iron complex was then studied for a series of aliphatic and aromatic organosilanes (entries 3 to 6). All hydrolysis can be carried out in air and after each of these experiments, the catalyst was carefully removed and upon evaporation of the solvent, a colorless liquid was obtained and found to be its corresponding organosilanols, based on $^1H$ and $^{13}C$ NMR analyses. Turnover numbers approaching $10^4$ with turnover frequencies in excess of $10^2$ $min^{-1}$ were obtained for most of the organosilanes. Generally, a decrease in the hydrolysis rate was observed when the steric bulk on the organosilane molecule was increased. It was also noticed that a polar solvent, i.e. tetrahydrofuran, played an important role in ensuring good miscibility of the organosilanes with water. When the reaction was performed in a solvent of low dielectric constant such as chloroform (entry 7), the major organic product obtained was found to be its corresponding siloxane instead. It is worth mentioning that this newly developed iron complex exhibits prominent catalytic performance for hydrogen evolution as compared to its expensive metal counterparts (see ESI†). The durability and long term storage potential of the iron complex was also examined. By dissolving and storing the iron complex in acetonitrile solution, it was found to be air stable and practically no activity loss was observed within 1 month of storage.

A kinetic study was carried out to further understand the reaction pathway for the hydrolytic oxidation of organosilanes. This was achieved via the monitoring of the initial rate of hydrogen evolution, through the displacement of water from an inverted measuring cylinder, for triethylsilane hydrolysis. When the concentration of organosilane was doubled successively, the initial rates of hydrolysis were found to increase from $1.27 \times 10^{-3}$ $s^{-1}$ to $2.39 \times 10^{-3}$ $s^{-1}$ and from $2.39 \times 10^{-3}$ $s^{-1}$ to $4.84 \times 10^{-3}$ $s^{-1}$ (Fig. 3a). This represents an average of $1.95 \pm 0.09$ times increase in the initial rates of hydrolysis when the concentration of organosilane was doubled successively. Similar trends were also observed when the concentrations of water (Fig. 3b) and catalyst (Fig. 3c) were doubled successively to give an average increase of $1.98 \pm 0.07$ and $2.03 \pm 0.11$ times in its initial rates respectively. Given that the observed rate constants $k_{obs}$ were independent of the concentrations (at the same temperature), two important deductions can be drawn from these experimental findings. Firstly, the experimental data strongly suggest the first order dependence on organosilane, water, and catalyst respectively. Secondly, the rate dependence implied that each of these species was involved in the rate determining step(s). This was further confirmed by the kinetic isotope effect study, where the initial rate of hydrolysis [$k_D/k_H = (1.38 \times 10^{-3}\ s^{-1})/(5.21 \times 10^{-3}\ s^{-1})$] was slowed down by 3.78 times, hence giving a kinetic isotopic effect value of 3.78 when $H_2O$ was substituted by $D_2O$ (Fig. 3b). The activation parameters for the hydrolysis, obtained from the Arrhenius plot by means of measuring $k_{obs}$ over the temperature range 278-299 K, were determined to be $\Delta H^{‡} = 68.0$ kJ $mol^{-1}$, $\Delta S^{‡} = -220$ J $K^{-1}$ $mol^{-1}$, and $\Delta G^{‡}(298K) = 134$ kJ $mol^{-1}$ (Fig. 3d).

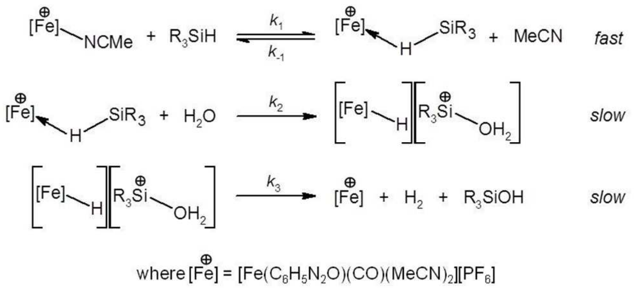

**Fig. 4** Proposed pathway for the hydrolysis of organosilanes catalyzed by $[Fe(C_6H_5N_2O)(CO)(MeCN)_3][PF_6]$.

Based on the above experimental data, a reaction pathway which was consistent with the observed kinetic experiments is given in Fig. 4. Upon replacing one of the acetonitrile ligands in the iron complex with organosilane, $[[Fe]–H][R_3Si–OH_2]^+$ is formed upon hydride abstraction of the coordinated organosilane. Similar interactions have been proposed for iridium complex[16] and were thought to be a plausible mechanism for the organosilane hydrolysis based on a ruthenium complex.[14b] Dihydrogen and the respective organosilanol were then generated when the solvated $R_3Si\text{-}OH_2^+$ species reacts with the iron hydride intermediate. The second and third steps are expected to be endothermic as they involve bond breaking, hence contributing to most of the activation barrier. By applying steady-state approximation on $[[Fe]–H][R_3Si–OH_2]^+$ and making the reasonable assumption that $k_{-1} >> k_2$, the rate law immediately simplifies to (1), which is consistent with the results from our kinetic studies:

$$\text{rate} = \frac{d[H_2]}{dt} = k_{obs}[\text{organosilane}][\text{water}][\text{catalyst}] \qquad (1)$$

where $k_{obs} = \dfrac{k_1 k_2}{k_{-1}[\text{MeCN}]}$.

Further experiments were performed to study the effect of acetonitrile on the rate of hydrolysis. Indeed, it was found that when the concentration of acetonitrile was doubled successively, the initial rate decreased by an average of 2.00 ± 0.08 times. This confirmed the inverse first order dependence on acetonitrile, which is in accordance with our derived $k_{obs}$.

In conclusion, we have shown that the hydrolytic oxidation of organosilanes to produce dihydrogen and organosilanols can be performed by an iron-based catalyst which is air-stable and exhibits excellent mediating power with turnover numbers approaching $10^4$ and turnover frequencies in excess of $10^2$ $min^{-1}$ for most of the organosilanes. A mechanism, consistent with our experimental data, had been proposed to further our current understanding of the catalytic organosilane hydrolysis reaction. The attractive characteristics of this iron complex may open new opportunities in the development of hydrogen storage materials derived from organosilanes for simple and cost-effective hydrogen on-demand generation strategies.

## Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental details and crystal structure report]. See DOI: 10.1039/b000000x/

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