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Catalytic Disproportionation of Formic Acid to Methanol using Recyclable Silylformates

Clément Chauvier,† Arnaud Imberdis,‡ Pierre Thuéry and Thibault Cantat*[^1]

**Abstract:** A novel strategy to prepare methanol from formic acid without external reductant is presented. The overall process described herein consists in the disproportionation of silyl formates to methoxysilanes catalyzed by ruthenium complexes and the production of methanol thereof by simple hydrolysis. Aqueous solutions of MeOH (> 1 mL, > 70 % yield) were prepared in this manner. The sustainability of the reaction has been established by the recycling of the silicon-containing byproducts with cheap, readily available and environmentally-benign reagents.

The depletion of fossil fuels and their participation to the global warming increasingly calls for a paradigm shift in both the energy and chemical sectors to utilize renewable feedstocks as raw materials. Because of their highly oxidized nature, the upgrading of renewable carbon sources (incl. CO₂ and biomass wastes) into value-added chemicals or fuels requires the development of efficient reduction methods to form energy-rich C–H bonds pre-existing in fossil hydrocarbons. This endeavour is a cornerstone in the reduction of CO₂ to methanol, an important precursor to industrial chemicals, such as formaldehyde, acetic acid and light olefins, but also a promising molecule for energy storage applications.[1a–c] Notably, the so-called circular and carbon-neutral methanol economy conceptualized by Olah relies on CO₂ reduction to methanol via hydrogenation.[2] A variety of heterogeneous and homogeneous catalysts have been designed and optimized to circumvent the kinetic inertness of the apolar gases H₂ and CO₂.[3a–g] Despite these efforts, the resulting processes involve energy intensive conditions, with the need for high operating pressures (>50 bar), and/or pose selectivity problems, with CO and formate derivatives being obtained as side-products. Alternatively, CO₂ can be reduced at the methoxy level under milder conditions by using polarized hydride donors, such as sacrificial hydroxilanes[4] and hydroboranes[5]. Nevertheless, these methods are not sustainable as they produce stoichiometric amounts of non-recyclable silyl and boryl oxides as wastes.[6]

A conceptually different strategy has recently emerged to generate CH₃OH from CO₂ via the intermediary of formic acid (FA). At the onset, FA is produced by a well-studied two-electron electroreduction of CO₂ or, alternatively, through biomass reforming. The subsequent disproportionation of 3 equiv. FA produces CH₃OH, CO₂ and water, so that the net cascade reaction is equivalent to the direct electroreduction or hydrogenation of CO₂ to methanol (Scheme 1). This strategy, which does not involve any additional reductant, requires efficient catalysts able to promote both the activation and disproportionation of FA. While the first catalyst, [Cp*Ir(bpy)(OH₂)][OTf]₂ (bpy = 2,2’-bipyridine), reported by Goldberg, Miller et al., generated small quantities of CH₃OH (< 3%),[7] our group obtained significantly improved yields of up to 50 % from THF solutions of FA with a ruthenium(II) complex paired with the tripodal ligand triphos (CH₃C(CH₃PPh₂)₃).[8] Shortly thereafter, Parkin and Neary reported on the first base metal catalysts comprising molybdenum(II), which provided benzene solutions of CH₃OH with yields up to 21 %.[9]

Nonetheless, irrespective of the catalyst employed, H₂ is always produced as a side product in at least 50 % yield and this feature conveys a strong limitation of this disproportionative approach to methanol. Under standard conditions, the competitive dehydrogenation and the targeted disproportionation of FA indeed display similar overall energetics (ΔG°[D,H]₀ = – 33 kJ mol⁻¹ vs ΔG°[D,H]₀ = – 36 kJ mol⁻¹ at 298 K for one mole HCO₂H), which have, thus far, not been bypassed by establishing a genuine kinetic control of the disproportionation. Laurenzy and Himeda recently showed that an iridium(III) complex catalyzes the low-temperature disproportionation of aqueous FA, with high selectivity (96 %).[10] Only when the thermodynamic balance for the disproportionation was favored by applying a pressure of H₂ (50 bar), in the presence of excess H₂SO₄,[11]

**Electroreduction or hydrogenation of CO₂:**

CO₂ + 6H→ , or 3 H₂ + CH₃OH + H₂O

**Disproportionation and dehydrogenation of formic acid:**

3 HCO₂H[⁰] → CH₃OH[+ 2 CO₂] + H₂O[⁰]

**ΔG°° = – 108 kJ mol⁻¹**

**dehydration**

[⁰] → 3 (CO₂) + H₂O[⁰]

**ΔG° = – 99 kJ mol⁻¹**

This work: disproportionation of silyl formates

scheme 1: Routes for the disproportionation of formic acid to methanol

To overcome this intrinsic thermodynamic limitation, we have sought an alternative disproportionative route to methanol, able to suppress the competing dehydrogenation pathway. Herein we wish to report a novel strategy based on the high-yielding catalytic disproportionation of silyl formates (HCO₂SiR₃) to methoxysilanes (CH₂OSiR₃) and CO₂ followed by the release of free CH₃OH by hydrolysis. In a distinct step, the silylformate is reformed by recycling the silicon-containing byproducts generated throughout the process with formic acid (Scheme 1).

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Supporting information for this article is given via a link at the end of the document.
Silyl formates (HCO₂SiR₃) feature a formate ligand coordinated to a silicon atom and these species can mimic the behaviour of a genuine hydroxosilane (HSiR₃), in the presence of an oxidant and a suitable catalyst. As a proof-of-concept, our group has recently reported the reduction of aldehydes by transfer hydrosilylation using the ruthenium(II) complex [Ru(n²-OAc)(κ²-OAc)(κ²-triphos)] (1) as a catalyst. In 2018, Hong and coworkers showed that silyl formates can also act as oxidants in their catalytic reduction with H₂ afforded methanol and silanols in the presence of ruthenium pincer complexes. The combination of our and Hong’s results suggest that silyl formates possess an amphoteric redox behavior, able to serve both as reductants and as oxidants. The disproportionation of silyl formates to generate methoxysilanes was therefore investigated, for the first time.

At the outset, the transfer hydrosilylation catalyst 1 was envisaged, but failed to promote the disproportionation of triethylsilyl formate (Et₃SiOHCOC₂H₅) into the corresponding methoxysilane 3a under various reaction conditions (e.g., entry 1 in Table 1). In several occasions, we were able to clarify the fate of complex 1 in the reaction medium and could identify by X-Ray diffraction the known [(triphos)RuH₂(CO)] which is presumably formed by decarbonylation of 2a and is catalytically inactive. Formate esters or aldehydes are indeed known to yield carbonyl complexes, which in the case of tripodal ligands such as triphos are often inactive in reduction chemistry because of the lack of a vacant coordination site and the reduced hydricity of Ru-H intermediates. To circumvent this limitation, Kuriyama et al. introduced the so-called Ru-MACHO complex [RuCl(CO)(PN₃Ph)₂] (4) ligated by the aliphatic pincer aminodiphosphine HN(CH₂CH₂PPh₂)₂ (PN₃Ph) for the hydrogenation of esters and we thus evaluated this class of ligand for the disproportionation of 2a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Ru] (mol%)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Ru(n²-OAc)(κ²-OAc)(κ²-triphos)] (1) [3]</td>
<td>&gt; 24</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>2</td>
<td>[RuCl(CO)(PN₃Ph)₂] (4) [3]</td>
<td>21</td>
<td>79</td>
</tr>
<tr>
<td>3</td>
<td>[RuCl(CO)(PN₃Ph)₂] + KOBu [3]</td>
<td>4</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>[Ru(H₃C(CH₂)₅)₅] (5) [3]</td>
<td>5.5</td>
<td>77</td>
</tr>
<tr>
<td>5</td>
<td>[Ru(n²-OAc)(κ²-OAc)(κ²-PNP₃Ph)₃] (5) [3]</td>
<td>2</td>
<td>76</td>
</tr>
<tr>
<td>6</td>
<td>[Ru(n²-OAc)(κ²-OAc)(κ²-PNP₃Ph)₃] (5) [3]</td>
<td>5</td>
<td>70</td>
</tr>
<tr>
<td>7</td>
<td>[Ru(n²-OAc)(κ²-OAc)(κ²-PNP₃Ph)₃] (5) [3]</td>
<td>5</td>
<td>70</td>
</tr>
<tr>
<td>8</td>
<td>[Ru(n²-OAc)(κ²-OAc)(κ²-PNP₃Ph)₃] (5) [3]</td>
<td>8.5</td>
<td>71</td>
</tr>
<tr>
<td>9</td>
<td>[Ru(n²-OAc)(κ²-OAc)(κ²-PNP₃Ph)₃] (5) [3]</td>
<td>24</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>

Table 1. Optimization of the disproportionation of silyl formate 2a.

Gratifyingly, using 3 mol% of catalyst 4, the silyl formate 2a decomposed into methoxysilane 3a (δ₁ = 3.42 ppm and δ₂ = 50.8 ppm) in 79 % yield (90 % conversion) after 21 h at 110 °C in THF (entry 2). CO₂ was also detected in solution by ¹³C NMR spectroscopy (δ = 126.0 ppm), thereby establishing the disproportional nature of this new transformation of silyl formates. Although the addition of catalytic amounts of KOBu to complex 4 afforded methoxysilane in a decreased 67 % yield, it also improved the kinetics of the reaction (entry 3), suggesting that replacing the chloride ligands in 4 with oxygen donors might be beneficial. The reactivity of other ruthenium complexes was thus explored (see SI for full details of the optimization studies) and we found that the catalysis with borohydride complex [RuH₂(η²-C₅H₅)(PN₃Ph)₃] provided 3a in 77 % yield after a lower reaction time of 5.5 h at 110 °C. This borohydride ruthenium complex also displays catalytic activity for the hydrogenation of 2a as demonstrated by Hong and coworkers.

Finally, the kinetics of disproportionation could be improved with the novel ruthenium complex [Ru(n²-OAc)(κ²-OAc)(κ²-PNP₃Ph)] (5) without any additive. 5 is easily synthesized in 81 % isolated yield as a single isomer from free PN₃Ph ligand and [Ru(n²-OAc)(κ²-OAc)(κ²-cymene)] in THF (Scheme 2). 5 was fully characterized by ¹H, ¹³C and 31P NMR spectroscopy and its structure unambiguously assigned by X-ray diffraction analysis. It comprises the PN₃Ph ligand facially coordinated to the Ru⁺⁺ ion with the two acetate ligands being inequivalent at the NMR time scale (see SI).

Complex 5 enables the formation of methoxysilane 3a from 2a in 76 % and 70 % yield after 2 h and 5 h at 110 °C, with a catalyst loading of 3 and 1.5 mol%, respectively (entries 6 and 7). 5 is also active at milder temperature (90 °C), albeit at the expense of an increased reaction time (71 % yield 3a after 8.5 h; entry 8) as well as in non-polar solvents such as benzene or cyclohexane (see SI). Importantly, the NH functionality on the ligand backbone proved to be fundamental for the catalytic disproportionation of 2a, as replacing catalyst 5 with its N-methylated analogue (5M⁺, R = CH₃) on Scheme 2) led to only 10 % yield of 3a after 24 h at 110 °C.

Beyond triethylsilylformate 2a, the formates 2b-d featuring silyl groups with diverse steric and electronic properties were also readily decomposed into methanol derivatives 3b-d, in the presence of complex 5 (3 mol%) at 110 °C in THF (as well as in cyclohexane and nonane for the silyl formate 2b (Scheme 5)). In these cases, the methoxysilanes are accompanied with small amounts (< 8 %) of the corresponding silylacetals intermediates (R₂SiOCH₃OR₂Si) resulting from the exchange of formate and acetate anion at silicon.
Silyl formates comprising bulky silyl groups such as TIPS (2e) or TBDSM (2f) did not yield the corresponding methoxy silanes. With 2f, the conversion remained very low (< 10%) after more than 24 h at 110 °C in THF or benzene and 3f was barely present (< 5%). However, formate 2e behaved differently: its full conversion was observed within 6.5 h at 110 °C in THF and the corresponding silanol ([Pr3SiOH] was the major product (80% yield) detected in NMR spectroscopy along with small amounts of 3e and methyl formate. Analysis of the gaseous headspace by GC revealed the presence of carbon monoxide, thereby pointing to a competitive decarbonylation of 2f catalyzed by 5 ([Pr3SiOCHO → [Pr3SiOH + CO]).

In fact, more decarbonylation pathways are also available with less hindered silyl formates such as 2a. Monitoring the decomposition of [13C]-labelled 2a by 13C NMR spectroscopy with 3 mol% 5 indeed reveals the presence of small amounts of free [13CO] (δC = 185.3 ppm in THF), from the early stages of the reaction, along with the major products: [13CO2 and [13CH2OSiEt3 (3a). In addition, two novel hydride ruthenium complexes, 6 and 7 (Scheme 4), containing respectively one and two [13CO ligands were also identified in the catalytic medium at room temperature (6: δCO = 206.5 ppm; 7: δCO1 = 201.6 ppm & δCO2 = 193.3 ppm, δC = 3.5 Hz). Complex 6 could be independently synthesized in 65% isolated yield from 5 and an excess of 2a (4 equiv.) at 110 °C in toluene, while cationic 7 could be prepared in 54% isolated yield by exposing a toluene solution of 6 to an atmosphere of CO (1 bar) and both were characterized by NMR spectroscopy and X-Ray diffraction (see SI). Importantly, complexes 6 and 7 are competent catalysts in the disproportionation of silyl formate 2a into 3a and CO2 in 70% and 60% yield after 4 h and 5 h, respectively. This not only suggests that 6 and 7 are resting states of the catalytic system, but also clearly demonstrates that decarbonylation at ruthenium does not shut down the catalytic activity. Furthermore, the catalytic system tolerates well free CO as disproportionation catalyzed by 5 still occurs under 1 atm of CO (68% yield) in the presence of triethylsilanol (Et3SiOH).

To further demonstrate the utility of the disproportionation of silyl formates in the overall conversion of FA to methanol, the catalytic disproportionation of 2b was performed on a preparative scale (15.6 mmol, 2 mL) with a low loading of pre-catalyst 5 (0.75 mol%). Nonane was selected as solvent because its boiling point (151 °C) facilitates the isolation of the somewhat volatile trimethylsilylated products (b.p. 57 °C and 101 °C for 3b and hexamethyldisiloxane (HMDSO), respectively). Under these conditions, the desired methoxy silane 3b and the siloxane (Me2Si)3O were produced in 85% yield after ca. 50 h at 110 °C (Scheme 5). Their separation from the reaction medium was conveniently carried out by distillation (at 130 °C), leaving a suspension of the catalyst in nonane. The addition of an excess of water (ca. 10 equiv with respect to 3b) to the resulting mixture of 3b and (Me2Si)3O afforded, after 20 h at 80 °C, a biphasic solution comprising an aqueous methanol layer (3.4 M, 3.69 mmol; 71% yield from 2b) covered with a layer of the hydrophobic HMDSO (73% yield from 2b, NMR purity >95%).

The sequential catalytic disproportionation of 2b followed by the hydrolysis of methoxytrimethylsilane by:

\[
\text{Me}_2\text{SiOOSiMe}_3 + \text{H}_2\text{O} \rightarrow \text{Me}_2\text{SiOH} + \text{Me}_2\text{SiOSiMe}_3
\]

The net reaction balance:

\[
3 \text{Na}_2\text{SO}_4 + 1.5 \text{H}_2\text{SO}_4 \rightarrow \text{CH}_2\text{OH} + 2 \text{CO}_2 + \text{H}_2\text{O} + 1.5 \text{Na}_2\text{SO}_4
\]
product of the process. Although disiloxanes are generally considered as terminal wastes in hydrosilylation reactions, we envisioned the possible recycling HMDSO into 2b, as both compounds feature a strong Si–O bond. Although HMDSO has been used for the silylation of carboxylic acids, in the presence of H$_2$SO$_4$ as a catalyst,[20] this procedure could not be transposed to convert FA to 2b presumably because (i) sulphuric acid readily decarboxylates FA[21] and (ii) FA and water form an azetropoic mixture, that prevents shifting the equilibrium towards the consumption of FA by water distillation. This difficulty was overcome through a first activation of HMDSO with sulfuric acid (Scheme 6a), which affords after 5.5 h at reflux of toluene the solid bis(trimethylsilyl)sulfate 8 in 89 % isolated yield. The formulation of 8 as SO$_4$(SiMe$_3$)$_2$ was confirmed by X-Ray diffraction (see SI), formation of which was postulated by Dunogues et al. nearly 55 years ago.[22] Interestingly, 8 features highly electrophilic silicon atoms that readily react with a variety of nucleophiles.[23] Accordingly, 8 reacted with sodium formate to give silyl formate 2b in 70 % isolated yield (92 % purity), after separation from the solid-by-product Na$_2$SO$_4$ and the dibutyl ether solvent by distillation.

The two-step protocol depicted in Scheme 6a affords an efficient recycling procedure for the conversion of the siloxane by-product to the starting trimethylsilyl formate 2b. The net reaction balance involves the utilization of sodium formate and sulphuric acid to obtain methanol and sodium sulfate in 77 % yield in nonane (44 % isolated yield), while 77 % of the silicon compounds can be recycled (45 % isolated yield) (Scheme 6b). This methanol yield outperforms most of the state-of-the-art FA disproportionation protocols and compares well to the recent report of Himeda, Laurency et al., who obtained 75 % MeOH yield in D$_2$O using stoichiometric quantities of H$_2$SO$_4$.[10] The overall process also affords CO$_2$ as a byproduct (2 equiv. relative to methanol), which is inevitably produced during the disproportionation step and can be recycled to formates by a 2-electron reduction.

These results show how shutting down the dehydrogenation of formic acid by replacing a proton with a silyl group can provide a high yielding, globally redox-neutral and operationally simple disproportionation route to methanol. While hydrosilylation chemistry with genuine hydroisilanes is hampered by the generation of siloxane wastes,[8] this work also demonstrates for the first time that reductive chemistry with silicon-based reductants can be amenable to renewability via the recycling of silyl formates from spent siloxanes.

**Keywords:** disproportionation • formic acid • silyl formate • methanol • ruthenium

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[11] H$_2$SO$_4$ improves the kinetics of the reaction by protonation of FA and drives the equilibrium to the right via. its dissecant properties.


