A recyclable catalyst that precipitates at the end of the reaction

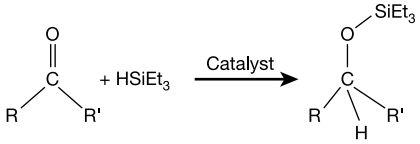
Vladimir K. Dioumaev & R. Morris Bullock

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000, USA

Homogeneous catalysts—which exist in the same (usually liquid) phase as reactants and products—are usually more selective than heterogeneous catalysts and far less affected by limitations due to slow transport of reactants and products, but their separation from reaction products can be costly and inefficient. This has stimulated the development of strategies that facilitate the recycling of homogeneous catalysts[1–4]. Some of these methods exploit the preference of a catalyst for one of two solvents with thermoregulated miscibility[5,6]; others exploit a dramatic decrease in catalyst solubility as one reagent is consumed[7,8] or temperature changed after completion of the reaction[9–14]. Here we describe a tungsten catalyst for the solvent-free hydrosilylation of ketones that retains its activity until essentially all of the liquid substrate is converted to liquid products, which we can then simply decant to separate the catalyst that precipitates from the products of the reaction. We attribute the ability of the catalyst to retain its solubility and hence activity until completion of the reaction to the transient formation of liquid clathrate[15,16] that contains a few molecules of the substrate per molecule of the otherwise solid catalyst. Insights into the fundamental processes controlling the formation of this liquid clathrate might help to tailor other catalysts and substrates, so as to develop efficient and solvent-free schemes for reactions of practical interest.

The principles of 'green' chemistry[17] and 'green' engineering[18] dictate that avoiding the use of solvents[19] is an important way to prevent generation of waste. Furthermore, a solvent-free transformation from pure reagents to pure products potentially yields a dramatic change in the properties of the medium and offers a tantalizing opportunity for attaining catalyst self-precipitation. Precipitation, in turn, helps to avoid using solvents in the subsequent separation stages, further preventing waste generation. Whereas the concept is trivial, striking the right balance between maintaining catalyst solubility throughout the reaction and precipitation at the end is a very difficult problem. An ideal catalyst should stay at least somewhat soluble until the last molecule of the substrate is consumed. Rare instances of such retention of solubility are known among compounds with a low aptitude for crystal lattice formation. Such compounds can furnish a liquid phase—a liquid clathrate[15,16]—with just a few equivalents of the solvent per equivalent of the otherwise solid component[20]. This behaviour is observed among ionic complexes with weakly coordinating counter ions, where the charges are delocalized over large molecular fragments, and the crystal packing forces are weakened[21–23].

To explore the concept of self-separation, two cationic complexes with weakly coordinating $B(C_6F_5)_4^-$ anions have been probed as catalysts for hydrosilylation of carbonyl compounds: $[CpM(CO)_2(IMes)]^+[B(C_6F_5)_4]^-$ (where Cp = cyclopentadienyl, IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene; in **1Mo** M = Mo, in **1W** M = W). Hydrosilylation is a suitable model reaction as it starts with a polar liquid substrate (ketone or ester) and ends with a non-polar liquid product (alkoxysilane, equation (1) below).



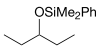
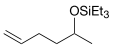
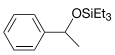
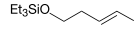
(1)

Hydrosilylation is also a reaction of considerable practical interest as it is widely used for both large- and small-scale syntheses[24,25]. Not only are alkoxysilanes precursors to silicon-containing polymers and ceramic materials, but they are also valuable in organic synthesis. Thus, for the conversion of carbonyl compounds to alcohols, hydrosilylation is often used as a convenient alternative to hydrogenation, particularly in asymmetric synthesis.

The choice of catalysts is based on our prior experience with **1Mo** and **1W** in the hydrogenation of ketones[26], a reaction which is mechanistically related to hydrosilylation and is often catalysed by similar complexes. We have previously found **1Mo** and **1W** to be soluble in ketones, insoluble in non-polar hydrocarbon solvents, and prone to the formation of oily precipitates—liquid clathrates—instead of crystalline products. We have also found that the *N*-heterocyclic carbene ligand, IMes, stabilizes the electronically unsaturated $16e^-$ **1Mo** and **1W** complexes by formation of a weak bond between the metal centre and one of the C=C double bonds of a mesityl group[26]. Although stabilization of catalytic intermediates inhibits catalysis, moderate stabilization is required for recycling, as the catalyst and its resting states should be able to withstand recycling conditions and should show reasonable tolerance to common impurities in the system.

Complexes **1W** and **1Mo** indeed catalyse hydrosilylation of carbonyl compounds under mild conditions, and the tungsten

Table 1 **Hydrosilylation of carbonyl compounds by W catalysts**

Substrate	Products	Initial TOF (h^{-1})	Total TON	yield (%)	Time (h)
		370	446	89	1
		20	36	7	
		~5	15	3	
		>2,000	447	93	0.25*
		>100	24	5	
		150	489	98	19
		110	446	89	23
		<5	11	2	
	$EtOSiEt_3$	170	468	94	26†
	Et_2O	<1	30	6	
		30	386	77	168
		<1	70	14	

Reactions were conducted at 23 °C in pure liquid substrates without solvent: ketone / $HSiEt_3$ / **1W** = 100 / 120 / 0.2. Turnover number (TON) is the number of moles of a carbonyl substrate consumed to yield a given product per the number of moles of catalyst. TOF is the average initial turnover frequency measured within the first 15–20 min of the reaction (TOF = TON/ time).
*$HSiMe_2Ph$ was used instead of $HSiEt_3$
†The ratios were: ester / $HSiEt_3$ / **1W** = 100 / 220 / 0.2.

complex **1W** proves to be much more active than the molybdenum complex **1Mo**. The reactions exhibit good rates, high conversions, and an excellent selectivity for hydrosilylation of C=O versus C=C double bonds (Table 1 and Supplementary Information). Hydrosilylation of aromatic substrates yields a brown oily precipitate towards the end of the reaction, but some of the catalyst remains soluble. Similarly, hydrosilylation with an aromatic silane, Me_2PhSiH, also results in a partially soluble catalyst and a small amount of a brown oily precipitate. Aliphatic substrates, on the other hand, yield colourless solutions at the end of the reaction with no detectable soluble metal-containing species in the proton nuclear magnetic resonance (^{1}H NMR) spectra. Conversion of the last traces of the carbonyl substrate can be monitored visually as the precipitate transforms from a purple oil into a pale yellow solid (Fig. 1). Fortunately, the precipitate is somewhat sticky, and can be readily recovered by decanting the liquid products without any special precautions to retain the catalyst, and no solvent is needed for the reaction work-up.

The actual resting state of the tungsten catalyst that is recycled has been found to be a mixture of $[CpW(CO)_2(IMes)(SiEt_3)H]^+[B(C_6F_5)_4]^-$ (**2W**) and $[CpW(CO)_2(IMes)(H)_2]^+[B(C_6F_5)_4]^-$ (**3W**). The assignment is confirmed by the independent syntheses of both compounds from **1W** and $HSiEt_3$ or dihydrogen (see Supplementary Information for complete characterization). The solubility of **2W** and **3W** in the products of hydrosilylation of $Et_2C{=}O$ is below the detection limits of ^{1}H NMR spectroscopy. The residual solubility of all species with a $B(C_6F_5)_4^-$ counter-ion has been measured by fluorine nuclear magnetic resonance (^{19}F NMR) spectroscopy to be $\sim 4 \times 10^{-4}$ mol l^{-1}, which corresponds to ~5% of the loaded 0.2 mol% catalyst. In other words, more than 95% of the loaded catalyst has precipitated as the resting state, and is amenable for recycling. The recovered catalyst exhibits up to twice the activity after the first recycle, and retains good activity for all five cycles performed (Table 2). Thus, either **2W**, or **3W**, or both, are better catalyst precursors than **1W**.

The ketone complex $[CpW(CO)_2(IMes)(Et_2C=O)]^+[B(C_6F_5)_4]^-$ (**4W**) is also a resting state present during hydrosilylation of $Et_2C=O$, giving a purple colour to the reaction mixture (λ_{max}(toluene) = 498 nm, $\epsilon = 1 \times 10^3$ l mol^{-1} cm^{-1}). Identified by multinuclear NMR and infrared (IR) spectroscopy, the assignment of **4W** has been confirmed by an independent synthesis from **1W** and $Et_2C=O$. Complex **4W** is most abundant at the beginning of the hydrosilylation and is gradually replaced by **2W** and **3W**. The formation of the dihydride complex **3W** is due to traces of H_2 produced from $HSiEt_3$ and residual water. The equilibrium for the formation of **3W** is very favourable; $K_{eq} = [\mathbf{3W}][Et_2C=O]/[\mathbf{4W}] \times [H_2] \approx 1 \times 10^3$ at 298 K (determined by ^{1}H NMR; $[H_2]$ was corrected for the presence of 25% of *para*-H_2, which is NMR-silent). As is often the case with excessively stable compounds, **3W** inhibits hydrosilylation. The origin of inhibition is readily traced to the presence of dihydrogen. Thus, reaction in a vial open to an inert atmosphere shows an almost threefold acceleration in initial turnover frequency compared to the same reaction in a closed tube. Note that both samples have been maintained homogeneous to eliminate uncertainties of precipitation and have been taken from the same stock solution of acetophenone, $HSiEt_3$ and **1W**.

Table 2 **Recycling of catalyst for the hydrosilylation of $Et_2C{=}O$**

Cycle no.	1	2	3	4	5
Time of measurement (min)	15	10	10	10	10
TOF (h^{-1})	370	780	870	760	620

Reaction conditions and TOF are the same as those in Table 1.

The key element of the catalyst activity and solubility at the final stages of the reaction of aliphatic substrates—the liquid clathrate—is metastable. It eludes characterization by rapidly changing its composition and converting into solid **2W** and **3W**. The liquid clathrates formed with aromatic substrates, on the other hand, are more stable and are amenable for analysis. Thus a liquid clathrate formed in the course of hydrosilylation of acetophenone has been characterized by ^{1}H NMR to have a composition of ~3.4 equivalents of the alkoxysilane Ph(Me)CH–OSiEt$_3$ per equivalent of tungsten. Note that this particular liquid clathrate is not critical to the catalyst activity, as the catalyst is somewhat soluble in the aromatic substrates anyway. In a broader sense, however, the characterization of this clathrate illustrates how only a few equivalents of the right component can retain the catalyst in a liquid phase, even if it is not soluble in the bulk of the reaction mixture[20].

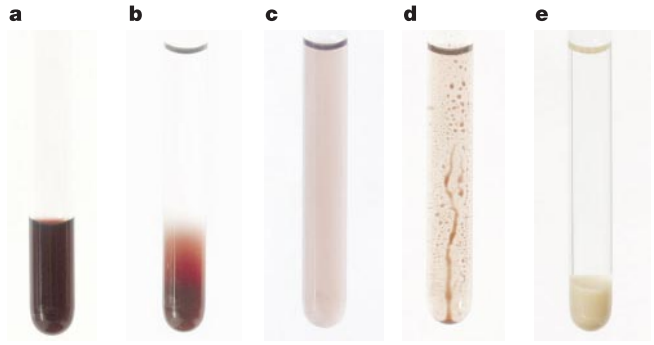


Figure 1 Photographs of the catalytic hydrosilylation of $Et_2C{=}O$ by $[CpW(CO)_2(IMes)]^+[B(C_6F_5)_4]^-$. **a**, Ketone complex **4W** before adding $HSiEt_3$. **b**, $HSiEt_3$ added, liquid not yet mixed. **c**, Mixed and homogeneous. **d**, Liquid clathrate formed. Reaction nearing completion. **e**, End of reaction. Catalyst has precipitated.

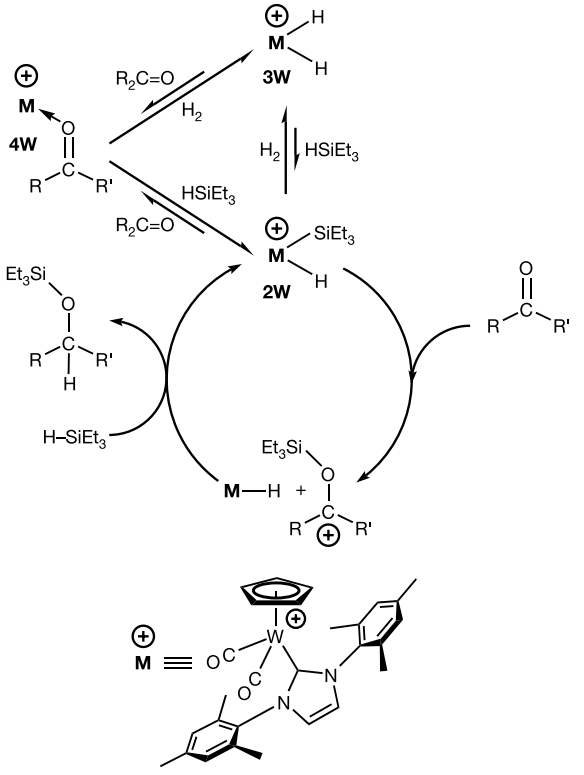


Figure 2 Proposed mechanism for catalytic ionic hydrosilylation.

The mechanism of hydrosilylation (Fig. 2) can be tentatively visualized as a modified ionic hydrogenation mechanism, which has been previously formulated for similar catalysts[27,28]. Trialkylsilyl cation (silylium ion) is transferred from the metal to the ketone, yielding a carbocation intermediate. The carbocation abstracts a hydride (H^-) from $HSiEt_3$ or from the metal, furnishing alkoxysilane and closing the catalytic cycle. The transfer of silylium and hydride ions could be concerted to some degree, but the observed cationic rearrangement in the reaction of cyclopropyl methyl ketone indicates an appreciable contribution of a cationic intermediate. A more detailed mechanistic investigation is needed to expand upon these preliminary findings.

The method for catalyst recycling and recovery presented here offers significant advantages, since it is solvent-free and requires no temperature changes, but this strategy is also prone to limitations. Examples of catalyst self-separation demonstrated thus far are restricted to aliphatic substrates, and the solvent-free approach is limited to both substrates being liquids. A challenge for future development is to tailor catalysts and hydrosilanes with the aim of engaging a broader scope of substrates into such solvent-free reactions with catalyst self-separation. A more general goal is to understand the fundamental aspects of liquid clathrate formation and to convert other catalysts into 'clathrate-enabled' catalysts, broadening the potential applicability of this recovery method to other classes of substrates and reactions. □

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Correspondence and requests for materials should be addressed to M.B. (bullock@bnl.gov).

Southern Ocean origin for the resumption of Atlantic thermohaline circulation during deglaciation

Gregor Knorr[1,2] **& Gerrit Lohmann**[1,2]

[1]*Institut für Meteorologie, Universität Hamburg, Bundesstrasse 55, 20146 Hamburg, Germany*
[2]*Fachbereich für Geowissenschaften und Forschungszentrum Ozeanränder, Universität Bremen, PO 330 440, 28334 Bremen, Germany*

During the two most recent deglaciations, the Southern Hemisphere warmed before Greenland[1,2]. At the same time, the northern Atlantic Ocean was exposed to meltwater discharge[3], which is generally assumed to reduce the formation of North Atlantic Deep Water[4,5]. Yet during deglaciation, the Atlantic thermohaline circulation became more vigorous, in the transition from a weak glacial to a strong interglacial mode[6]. Here we use a three-dimensional ocean circulation model[7] to investigate the impact of Southern Ocean warming and the associated sea-ice retreat[8] on the Atlantic thermohaline circulation. We find that a gradual warming in the Southern Ocean during deglaciation induces an abrupt resumption of the interglacial mode of the thermohaline circulation, triggered by increased mass transport into the Atlantic Ocean via the warm (Indian Ocean) and cold (Pacific Ocean) water route[9,10]. This effect prevails over the influence of meltwater discharge, which would oppose a strengthening of the thermohaline circulation. A Southern Ocean trigger for the transition into an interglacial mode of circulation provides a consistent picture of Southern and Northern hemispheric climate change at times of deglaciation, in agreement with the available proxy records.

Ice-core and ocean-sediment records reveal that during the last deglaciation, warming in the Southern Hemisphere preceded Greenland warming by more than 1,000 years (ref. 1), a time lag that was even longer for the penultimate deglaciation[2]. One candidate for an interhemispheric teleconnection is provided by the oceanic thermohaline circulation (THC). Proxy data[6] and modelling studies[7,11,12] indicate that the last deglaciation was characterized by a transition from a weak glacial to a strong interglacial Atlantic THC. During the Bølling–Allerød (B/A) warm period, the sea surface temperatures (SSTs) in the North Atlantic almost reached interglacial values, consistent with active deep water formation, corroborated by benthic $\delta^{13}C$ data[6]. While most studies investigate processes responsible for a shut-down of the THC, we consider the question of how the conveyor gets restarted after a glacial mode with

