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The Role of \((^3\text{BuPOCOP})\text{Ir(I)}\) and iridium(III) Pincer Complexes in the Catalytic Hydrogenolysis of Silyl Triflates into Hydrosilanes

Gabriel Durin, Jean-Claude Berthet, Emmanuel Nicolas, Pierre Thuéry, and Thibault Cantat*

Université Paris-Saclay, CEA, CNRS, NIMBE, 91919 Gif-sur-Yvette Cedex, France

*Email: thibault.cantat@cea.fr

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ABSTRACT: Hydrosilanes are convenient reductants for a large variety of organic substrates, but they are produced via energy-intensive processes. These limitations call for the development of general catalytic processes able to transform Si–O into Si–H bonds. We report here the catalytic hydrogenolysis of \(R_3\text{SiOTf}\) (\(R = \text{Me, Et, Ph}\)) species in the presence of a base (e.g. \(\text{NEt}_3\)), by the hydride complexes \([(^3\text{BuPOCOP})\text{IrH}_2\text{X}]\) (\(X = \text{H, OTf}; (^3\text{BuPOCOP} = [(1,3-\text{C_6H_3})\text{OP}2\text{Bu}_2])\)). Syntheses and crystal structures of new iridium(I) and iridium(III) complexes are presented as well as their role in the \(R_3\text{SiOTf}\) to \(R_3\text{SiH}\) transformation. The mechanisms of these reactions have been examined by DFT studies, revealing that the rate-determining step is the base-assisted splitting of \(H_2\).

Introduction

The activation of siloxanes and silicon oxide derivatives is a key strategy to enter the value chain of silicon chemistry. While \(\text{SiH}_4\) and \(\text{SiCl}_4\) are the main starting blocks in the synthesis of silicon compounds, they require the use of silicon(0) obtained from energy intensive processes. In contrast, the use and re-use of oxidized derivatives such as siloxanes, silanols and silicon (pseudo)halides is appealing to produce basic organosilicon synthons. Among them, hydrosilanes are mild and versatile reducing agents which are common industrial compounds for the synthesis or the functionalization of organosilicon polymers by dehydrocoupling reactions or hydrosilylation of alkenes. In synthetic chemistry, they promote highly efficient and selective reactions such as the functionalization of inactivated C–H bonds in catalytic processes or the reduction of carbonyl-containing molecules. Recent studies have highlighted new utilizations for hydrosilanes to recover valuable molecules through C–O bond reduction/cleavage of oxygenated feedstock such as \(\text{CO}_2\),\(^9\) wood lignin\(^{10}\) and plastics\(^{11}\) toward a circular economy with low oil dependency. Currently, hydrosilane synthetic strategies rely on energy-intensive processes which involve strong reducing agents such as \(\text{LiAlH}_4\).\(^{12}\) Hydrogenolysis of Si–X bonds has been introduced by the groups of Hidai,\(^{13,14}\) Shimada,\(^{15,16}\) Schneider\(^{17}\) and Cantat\(^{18}\) as an alternative way to hydrosilanes and would be a convenient approach when using green \(\text{H}_2\) generated via both electrochemical and photochemical splitting of water (Scheme 1).\(^{19,20}\) Due to the paucity of work in this area, the development of novel systems favoring Si–X to Si–H conversion is crucial and their studies should give a better understanding of the intrinsic mechanism of such transformation.

In 1999 and 2003, Hidai \textit{et al.} reported the catalytic hydrogenolysis of silyl enol ether into \(R_3\text{SiH}\) and ketones using \([\text{dppe}\text{RuCl}(\eta^3-\text{H}_2)]\text{OTf}\) as catalyst under mild conditions (50 °C, 1 bar \(\text{H}_2\)). Although not focused towards the formation of hydrosilanes, this report demonstrated that hydrogenolysis can occur on Si–O linkages.\(^{13,14}\)

Silyl enol ethers

\[
\text{OSiR}_3 + \text{[Ir]} \rightarrow \text{R}_3\text{SiH} + \text{[HNEt}_3\text{]OTf}
\]

Hidai, 1999/2003

Silyl halides and triflates

\[
\text{Me}_3\text{SiX} + \text{Base} \rightarrow \text{Me}_3\text{SiH} + \text{[Base]H}_X
\]

Selected examples for the synthesis of hydrosilanes through catalytic hydrogenolysis of silyl enol ethers or halides.

\[
\begin{align*}
\text{Shimada et al, 2017} & \quad X = \text{OTf} : 95\% (8 \text{ h}) \\
\text{Shimada et al, 2018} & \quad X = \text{Br} : 80\% (48 \text{ h}) \\
\text{Schneider et al, 2018} & \quad X = \text{OTf} : 85\% (18 \text{ h})
\end{align*}
\]

Scheme 1. Selected examples for the synthesis of hydrosilanes through catalytic hydrogenolysis of silyl enol ethers or halides.
In 2017 and 2018, the group of Shimada\textsuperscript{15,16} described successful catalytic Si–X to Si–H transformations (X = OTf, I, Br) with iridium(III) complexes A and B (Scheme 1). The reactions require high catalytic charges (5–10 mol\%) and the presence of an amine or amidine base such as NPy\textsubscript{2}Et or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). The reaction is sensitive to the steric hindrance of the R groups in R\textsubscript{2}SiX\textsubscript{2} substrates and the reactivity of these silanes is following the leaving group ability of the X moiety in the order OTf > I > Br > Cl. The group of Schneider\textsuperscript{17} also reported in 2018 extensive conversion and yields in Me\textsubscript{2}SiH, Me\textsubscript{2}SiH\textsubscript{2} or Me\textsubscript{2}SiH(OTT) from the corresponding triflates when catalyzed with ruthenium(II) pincer complex C (Scheme 1). Finally, our group recently reported the use of the iridium(III) pincer [\textsuperscript{18}BuPOCOP]Ir[HCl] (1) as an efficient catalyst in the hydrogenolysis of [Si–Cl] compounds when combined with superfuses such as BTPP (BTPP = (\textsuperscript{18}Bu-imino)tri(pyrrolidino)phosphorane).\textsuperscript{18}

Scheme 2. Proposed mechanism for the catalytic hydrogenolysis of silyl halides and triflates.

The proposed mechanism for such a transformation can be split in two distinct parts (Scheme 2). First, the splitting of H\textsubscript{2} (left, in orange) at the metal center with a base that is strong enough to ensure the transformation of [M]–X into [M]–H bonds with the release of a salt. This reaction is particularly difficult when X = Br, Cl because of the inherent strengths of the [M]–X bonds. Second (right, in purple), the [M]–H complex transfers its hydride to the R\textsubscript{2}Si–X species to yield the hydrosilane. The careful choice of the base and of the metal complex is crucial to induce a catalytic turnover. Because iridium pincer complexes such as 1 display good performances in both hydrogenation\textsuperscript{21,22} and hydroxylation reactions\textsuperscript{23} by activating H–H and Si–H bonds, they should also be effective for the reverse reaction i.e. hydrogenolysis of silyl halides and triflates following the micro-reversibility principle in catalysis. Since various formal oxidation states of iridium (I to V) can be reached, a focus on the intermediates that may form during the reaction is of great interest. In this context, silyl triflates represent a good platform to study the hydrogenolysis mechanism.

We present here the catalytic hydrogenolysis of silyl triflates into the corresponding hydrosilanes using \textsuperscript{18}BuPOCOP pincer complexes of iridium(III) and iridium(I) with the presence of a nitrogen base. The chemical behavior of the potential iridium(III) precatalysts [\textsuperscript{18}BuPOCOP]Ir[H(X)] (X = H, Cl, OTf) was studied in presence of stoichiometric quantities or excess of the reagents H\textsubscript{2}, R\textsubscript{2}SiOTf and the base NE\textsubscript{3} or TBDH (= 1,5,7-triazabicyclo[4.4.0]dec-5-ene) to explore the mechanism of the catalytic hydrogenolysis of silyl triflates. Synthesis and characterization of the complexes [\textsuperscript{18}BuPOCOP]Ir[H(OTf)] (2), [\textsuperscript{18}BuPOCOP]Ir[H(NCMe)\textsubscript{2}]OTf (5), [\textsuperscript{18}BuPOCOP]IrH(TBDH) (6a), [\textsuperscript{18}BuPOCOP]Ir(TBDH) (7) and [\textsuperscript{18}BuPOCOP]Ir(\textsuperscript{18}BuH)(TBDH) (8) are presented, as well as several crystal structures. The experimental work has been coupled with DFT calculations to bring mechanistic insights for this reaction.

Experimental Section

General considerations. Me\textsubscript{2}SiOTf, Et\textsubscript{3}SiOTf and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBDH), were purchased from Sigma-Aldrich, degassed and used as received. Commercial triethylamine was obtained from Carlo Erba. It was degassed, dried and then distilled prior to use. C\textsubscript{6}H\textsubscript{6}, Tol-\textsubscript{d} and THF-\textsubscript{d} were dried over sodium/benzophenone and vacuum-distilled before use. CD\textsubscript{3}CN was dried over CaH\textsubscript{2}, distilled before use, and stored over activated molecular sieves (4 Å). Molecular sieves (4 Å; Aldrich) was activated by prolonged drying (48 h) at 250 °C under primary dynamic vacuum. The iridium(III) complex ([\textsuperscript{18}BuPOCOP]Ir[HCl]) (1) was synthesized according to literature procedure\textsuperscript{24} from commercial bis(1,5-cyclooctadienedi)iridium(III) dichloride ([\textsuperscript{18}COD]IrCl\textsubscript{2}) and \textsuperscript{18}BuPOCOP ([1,3-C\textsubscript{6}H\textsubscript{4}H](OPrBu\textsubscript{2})). Prepared from commercial resorcinol ([1,3-C\textsubscript{6}H\textsubscript{4}H](OH)\textsubscript{2}) and ClP(Bu\textsubscript{2}) (Sigma-Aldrich), Ph\textsubscript{3}SiOTf was obtained from commercial Ph\textsubscript{3}SiCl and AgOTf (Sigma-Aldrich) according to literature procedure.\textsuperscript{25} All the syntheses were conducted under ultra-high purity argon with the rigorous exclusion of air and water (< 5 ppm oxygen or water), using standard Schlenk-vessel and vacuum-line techniques and an MBrann LabMaster DP inert atmosphere (Ar) glovebox. Glassware was dried overnight at 75 °C or flame dried before use. Sterile syringe filter (0.2 μm Cellulose Acetate) were purchased from VWR. NMR spectra were recorded on a Bruker AVANCE Neo 400 MHz spectrometer at 25 °C unless otherwise stated. Chemical shifts (δ) values are referenced to solvent residual peaks (for H and T\textsubscript{C}) or external reference (for B\textsubscript{11}B, \textsuperscript{19}F and T\textsubscript{19}P) and reported in parts per million (ppm) relative to tetramethylsilane (T\textsubscript{1}H, T\textsubscript{13}C), phosphoric acid (T\textsuperscript{3}P), BF\textsubscript{3}-OTi\textsubscript{11}B or trifluoroacetic acid (T\textsuperscript{19}F). Coupling constants (J) are given in Hz, multiplicities are named as singlet (s), doublet (d), triplet (t), quartet (q), multiplet or overlapping signals (m) and broad signal (br), solvent is given in parenthesis. GC-MS spectra were collected on a Shimadzu GCMS-QP2010 Ultra gas chromatograph mass spectrometer equipped with a Supelco SLB\textsuperscript{TM}-MS fused silica capillary (30 m x 0.25 mm x 0.25 μm). Elemental analyses of samples sealed under vacuum were performed under inert atmosphere by Medac Ltd at Chobham (Surrey, UK) or Analytische laboratorium at Lindlar (Germany).

Crystallography. The data were collected at 100(2) K on a No-Niessius Kappa-CCD area detector diffractometer\textsuperscript{25} using graphite-monochromated Mo Ku radiation (λ = 0.71073 Å). The crystals were introduced into glass capillaries with a protective coating of Paratone-N oil (Hampton Research). The data (combinations of ϕ- and θ-scans with a minimum redundancy of at least 4 for 90% of the reflections) were processed with HKL2000.\textsuperscript{26} Absorption effects were corrected empirically with SCALEPACK.\textsuperscript{26} The structures were solved by intrinsic phasing with SHELXT,\textsuperscript{27} expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on F\textsuperscript{2} with SHELXL.\textsuperscript{28} All non-hydrogen atoms were refined with anisotropic displacement parameters. When present, the hydrogen atoms bound to iridium and nitrogen atoms were retrieved from residual electron density maps and were fully refined. The carbon-bound hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH\textsubscript{3}, with optimized geometry). The triflate anions in 2 and 4 are disordered, the two components having been refined with occupancy parameters constrained to sum to unity. Crystal data and structure refinement parameters are given in Table S2 (ESI, Section 2). The molecular plots were drawn with ORTEP-3.\textsuperscript{29}

Computational details. Calculations were performed using the Gaussian16 suite of software.\textsuperscript{30} The PBE0\textsuperscript{13}–D3\textsuperscript{32} functional was used in conjunction with the Def2TZVP\textsuperscript{33–36} basis set for
Ir, the 6-311+G(d,p)37–44 basis set for Si and mobile H atoms, and the 6-31G(d)45–54 basis set for all other atoms. All geometries were fully optimized without any symmetry or geometry constraints. Harmonic vibrational analyses were performed to confirm and characterize the structures as minima or transition states. Free energies were calculated within the harmonic approximation for vibrational frequencies. The effects of solvation by benzene were included in the energy calculations using the SMD model through single point calculations on the gas-phase optimized geometry.53

Catalytic Protocols

General procedure for the hydrogencylation of silyl triflates:

In a J. Young NMR tube, the iridium complex (1 mol%) was dissolved in 0.5 mL CH2Cl2. The base (0.11 mmol) and the silyl triflate (0.10 mmol) were then successively added via syringe. The solution was degassed twice by freeze-pump-thaw cycles before being refrozen with liquid nitrogen and filled with H2 (1 bar). The sample was thawed and immediately shaken. After 3–300 h at room temperature, the products were identified by 1H NMR spectroscopy and quantified by relative integration of the R,S,Si signals versus an internal standard (1,3,5-trimethylbenzene). Et, SiH and Ph,SiH were also quantified by GC-MS (see SI 1.4 for details).

Synthetic procedures

[19FPOCOP]IrH2(TBDH)] (19FPOCOP)IrH2(TBDH)] (6ak): A round bottom flask (20 mL) was charged with 1 (50 mg, 0.08 mmol) and TBDH (22 mg, 0.16 mmol, 2 eq), on which toluene (5 mL) was condensed. The initially red solution turned yellow with formation of a white deposit after a few minutes. The flask was filled with dihydrogen (1 bar) and the mixture stirred for 18 h at r.t. during which the solution turned orange. After addition of pentane (5 mL), to increase the precipitation of the salt [TBDH]2Cl, the later deposit was discarded from the orange solution by filtration with a syringe filter (0.2 µm) and the product further extracted from the salt with a 1:1 mixture of pentane and toluene (2x5 mL). The orange solution was then evaporated to dryness and complex 6ak isolated as a pale orange powder (85.%, 49 mg, 0.067 mmol).

1H NMR (400 MHz, CD2Cl2): 8.68 (s, 1H, NH), 6.81 (m, 1H, p-H), 6.74 (m, 2H, m-H), 3.84 (m, 2H, TBDH(Ch2)), 2.74 (td, J = 5.9 Hz, 2.5 Hz, 2H, TBDH(Ch3)), 1.51 (t, J = 6.4 Hz, 3.5 Hz, TBDH(Ch3)), 5.94 (s, 1H, NH), 3.84 (m, 2H, TBDH(Ch2)), 2.71 (td, J = 6.4 Hz, 3.5 Hz, TBDH(Ch3)). The solvent was removed under vacuum.

The mixture was then treated with 14 ml of CH2Cl2, eq), on which toluene (5 mL) was condensed. The initially red solution turned yellow with formation of a white deposit after a few minutes. The flask was filled with dihydrogen (1 bar) and the mixture stirred for 18 h at r.t. during which the solution turned orange. After addition of pentane (5 mL), to increase the precipitation of the salt [TBDH]2Cl, the later deposit was discarded from the orange solution by filtration with a syringe filter (0.2 µm) and the product further extracted from the salt with a 1:1 mixture of pentane and toluene (2x5 mL). The orange solution was then evaporated to dryness and complex 6ak isolated as a pale orange powder (85.%, 49 mg, 0.067 mmol).

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Results and discussion

Synthesis and characterization of the complexes

Recently, we have shown that [[(POCOP)IrHCl]] is an efficient catalyst for the hydrogenolysis of chlorosilanes in the presence of strong bases. We therefore decided to investigate its behavior and that of related [[(POCOP)IrHX]] derivatives in the hydrogenolysis of the more reactive silyl triflates into silanes, in order to collect information on the species that are active during catalysis and the corresponding mechanism.

In a first experiment, I (1 mol%) was added to a mixture of Me_3SiOTf and NEt_3 in the 1:1.1 ratio under 1 bar H_2 in benzene. 1^H NMR monitoring of this mixture did not show any evolution after 48 h at r.t. However, when replacing I with the trflate analogue [[(POCOP)IrH(OTf)]] (2) or the dihydride derivative [[(POCOP)IrH_2]] (3), catalysis occurred and Me_3SiH was obtained in 83% yield after 3 h (Scheme 3). 1^H NMR monitoring evidenced the growth of a doublet at 0.00 ppm and a multiplet at 4.15 ppm, in the respective 1:9 integration ratio, characteristic of the gaseous Me_3SiH, as well as the presence of [[(POCOP)IrH_2(OTf)]] (4) as the sole observable iridium complex (vide infra-Eqn 3). Surprisingly, using a stronger base, TBD, in the presence of 1 mol% of 3 did not lead to any turnover.

\[
\text{Me}_3\text{SiOTf} + \text{Base} \rightarrow [\text{Ir}, \text{H}_2(1 \text{ bar})]_{\text{C}_{4}\text{D}_{6}}^{1.1 \text{ eq}} \rightarrow \text{Me}_3\text{SiH} + [\text{BaseH}]\text{OTf}
\]

Scheme 3. First Catalytic experiments for the hydrogenolysis of silyl triflates

We tried to characterize and isolate the iridium complexes that might form during catalysis in order to highlight the role of the active species for both the hydride transfer and H_2 splitting. We thus synthesized the new complexes 2 and [[[(POCOP)IrH(NCMe)_2)][OTf]] (5) to gather information on the chemical behavior of the [[(POCOP)IrH(X)]] (X = Cl (1), OTf (2), H (3)) precursors when placed in presence of each of the reagents H_2, R_2SiOTf or the nitrogen base (NEt_3 or TBDH). The syntheses of the complexes are described in Scheme 4.

Scheme 4. Synthetic routes to the iridium pincer complexes 2 and 5.

Treatment of the chloro hydride precursor 1 with 1 equiv. of silver trflate (AgOTf) in toluene at r.t. overnight gave 2, isolated after extraction from the silver salt as an orange powder in 96% yield. Red-orange crystals of 2 were obtained by slow cooling of a saturated benzene solution heated under reflux. The 1^H NMR spectrum of 2 revealed a triplet for the Ir–H signal at \( \delta = -42.9 \text{ ppm} \) (\( \gamma_{J_{F-\text{H}}}=10.8 \text{ Hz} \)) (vs. \( \delta = -40.9 \text{ ppm} \) for 1 in CD_3Cl).

The direct reaction of 1 with a slight excess of Me_3SiOTf in MeCN rapidly gave a pale yellow solution of the ion pair [[[(POCOP)IrH(MeCN)_2)][OTf]] (5), which was isolated in 78% yield after washing with pentane. Colorless crystalline blocks were grown from saturated solutions of 5 in MeCN or THF by slow diffusion of diethyl ether. Compound 5 exhibits an Ir–H resonance at \( \delta = -23.1 \text{ ppm} \) (\( \gamma_{J_{F-\text{H}}}=8.2 \text{ Hz} \)) for the Ir–H signal which is shifted downfield in comparison to the resonance of the neutral counterpart 2. Its related congener [[[(POCOP)IrH(MeCN)_2]][B(C_6F_5)_3]] exhibits an Ir–H resonance at \( \delta = -20.9 \text{ ppm} \) (\( \gamma_{J_{F-\text{H}}}=14.7 \text{ Hz} \)) close to that observed in 5. Views of the crystal structures of [[[(POCOP)IrH(OTf)]] (2) and its catonergic derivative 5 are presented in Figure 1, together with selected bond lengths and angles. The Ir^{III} ion in 2 is in a distorted square pyramidal environment, where the atoms P1, P2, C1 and O3A define the square basis (rms deviation 0.062 Å) with the hydrogen atom in apisal position and the metal ion displaced by 0.1347(13) Å from the basis. Complex 5 comprises a six-coordinate Ir^{III} ion in a distorted octahedral ligands with the two acetonitrile ligands in nearly perpendicular positions. One acetonitrile molecule faces the aromatic cycle while the other is trans to the hydride. In both complexes, the hydride is in the cis position compared to the C1 atom of the pincer ligand, a feature always observed in mono and dihydride iridium pincer complexes. The slightly longer bond lengths in 5 certainly reflect the higher coordination number. These Ir–C1 distances of 1.990(3) Å and 2.024(4) Å in 2 and 5, respectively, vary from 1.961(6) Å to 2.10(1) Å in a series of seventy-seven 4POCOP iridium(IV) and iridium(III) complexes reported in the Cambridge Structural Database (CSD, version 5.40) and in which the Ir–P distances extend over the range 2.2408(9)–2.412(1) Å. The Ir–η^{1}O(OTf) is classical for Ir–OTf complexes and the Ir–N(acetonitrile) distances in 5 are comparable to those found in the two other reported iridium(III)-acetonitrile pincer complexes. The Ir–H distances in 2 (1.524(4) Å) and 5 (1.464(4) Å) are quite identical to those in the complexes [[[(POCOP)IrHCl]] (1.496(6) Å)]. the cation [[[(POCOP)IrH(HSiEt_3)][B(C_6F_5)_3]] (1.425(18) Å) and the analogue of 4, [[(CH_2(CH_2)_2)POCH][IrH(C_2H_4)]] (average 1.69 (3) Å). Within the 4POCOP)Ir(III) series, these Ir–H distances...
scatter from 1.29(3) Å and 1.36(3) Å for [(BuPOCOP)IrH(P2-PMes)] to 1.74(4) Å in [(BuPOCOP)IrH2(BH3)]. The absence of coordination of the triethylamine may be related to its steric congestion since the ammonia adduct [(h6PCP)IrH(Cl)(NH3)] (h6PCP = C6H2(CH2Bu)2) is known and the two pincer ligands have similar steric hindrance. Some dihydride iridium pincers are also known to trap a variety of Lewis bases (NH3, NH2, CO, phosphine). No adduct of [(h6PCP)IrH2(Cl)] has been reported except the carbonyl derivative [(h6PCP)IrH2(Cl)(CO)]. Importance of the steric effects in the coordination number of iridium complexes and on the stability of iridium(I) versus iridium(III) compounds has already been clearly underlined.73 Replacing argon with 1 bar H2 on the [(BuPOCOP)IrH(X)]; NEt3 (1:1:1 ratio) mixture gave no reaction with 1 while 4 is quantitatively obtained from 2 and 3 (with the concomitant release of [HNEt3]OTf in the case of 2) (Eqn 3).

Because all neutral complexes 1–3 display good solubility in benzene, we then studied their reactivity in this solvent. Coordination of H2 on the complexes might be required for its further activation and use as a source of hydride. We first considered the behavior of the hydride species 1–3 under hydrogen (1 bar). If the formation of the dihydride complex 4 is well known from 3,66 coordination of H2 was not detected on the more electron-deficient halide and trflate species for which the 1H and 31P NMR signals were left unchanged. (Eqn 1).

Hydrogenation processes catalyzed by metal complexes usually require the use of an anionic or neutral base in order to deprotonate the coordinated H2.67–70 Behavior of the hydride complexes 1–3 in presence of neutral nitrogen bases (NEt3, TBDH) (= 1,5,7-Triazabicyclo[4.4.0]dec-5-ene) was thus investigated both under argon or dihydrogen. No change was observed by 1H NMR spectroscopy when NEt3 (1.1 equiv.) was added to each of the [(BuPOCOP)IrH(X)] species in benzene under inert atmosphere (Eqn 2).

In contrast, the reaction of [(BuPOCOP)IrH(X)] (X = Cl, OTf) with 2 equiv. of TBDH in benzene led to the formation of [(BuPOCOP)IrH(TBDH)], NMR spectroscopy evidenced formation of a mixture of 7 and its iridium(III) counterpart [(BuPOCOP)IrH(TBDH)] (8) in the ratio 60:40 from the chloro hydride 1 or from the triflate hydride 2, respectively, at room temperature (Eqn 5).

Reaction of 2 equiv. TBDH with 1 or 2 or 1 equiv. [TBDH]K and 1 in benzene led to the same distribution of complexes 7 and 8 (60:40 respectively). Complexes 7 and 8 are likely the different...
redox forms of the same product that are in slow equilibrium at the NMR timescale. Such an equilibrium was already observed on iridium pincer complexes, such as $\text{[(}^{(3)}\text{P} \text{POCOP})\text{Ir}(\text{DBU})]\) which reacted with the amine NH$_3$(m-xylyl) to give $\text{[(}^{(3)}\text{P} \text{POCOP})\text{Ir}(\text{NH}(m$-xylyl)).$^{50}$ H and $^{31}$P$^1$H NMR investigations at various temperatures showed slight variations in the 7:8 ratio, which does not give clear evidence for such an equilibrium. We expected that formation of this mixture would be influenced in the presence of a coordinating solvent. Indeed, when heated in acetonitrile, this mixture gave back the sole iridium(I) species $\text{[(}^{(3)}\text{P} \text{POCOP})\text{Ir}(\text{NCMe})]$ in a square-planar environment and complex 9 has mirror symmetry, atoms Ir1, C1, and N1 being located on the mirror plane. In order to minimize steric interactions, the TBDH ligand in 7 adopts a position perpendicular to the plane containing the Ir1, P1, P2, C1 and N1 atoms as it was found in the closely similar complex $\text{[(}^{(3)}\text{P} \text{PCP})\text{Ir}(\text{DBU})].$ The Ir$–$N distance in 7 (2.192(3) Å) is higher than in 9 (2.043(3) Å). Since TBDH is a stronger Lewis base than acetonitrile, the longer Ir$–$N bond length in 7 may indicate a higher steric hindrance its coordination. This could explain the displacement of TBDH ligand with acetonitrile.

\[7 + 8 \xrightarrow{\text{Crystallization}} \begin{array}{c}
\text{Ir} \quad \text{NCMe} \\
\text{P} \quad \text{P} \\
\text{Bu} \quad \text{Bu} \\
\text{O} \\
\end{array} \quad \text{yellow orange} \quad \text{(7)}
\]

Crystallization by slow cooling of a saturated acetonitrile solution of 7 and 8 afforded concomitantly large pale-yellow blocks of $\text{[(}^{(3)}\text{P} \text{POCOP})\text{Ir}(\text{TBDH})]$ (7) and orange crystals of 9 (Eqn 7). ORTEP views of their crystal structures are presented in Figure 2 with selected bond lengths and angles. The iridium(I) metal centers in 7 and 9 are in a square-planar environment and complex 9 has mirror symmetry, atoms Ir1, C1, and N1 being located on the mirror plane. In order to minimize steric interactions, the TBDH ligand in 7 adopts a position perpendicular to the plane containing the Ir1, P1, P2, C1 and N1 atoms as it was found in the closely similar complex $\text{[(}^{(3)}\text{P} \text{PCP})\text{Ir}(\text{DBU})].$ The Ir$–$N distance in 7 (2.192(3) Å) is higher than in 9 (2.043(3) Å). Since TBDH is a stronger Lewis base than acetonitrile, the longer Ir$–$N bond length in 7 may indicate a higher steric hindrance its coordination. This could explain the displacement of TBDH ligand with acetonitrile.

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\text{Ir} \quad \text{NCMe} \\
\text{P} \quad \text{P} \\
\text{Bu} \quad \text{Bu} \\
\text{O} \\
\end{array} \quad \text{yellow orange} \quad \text{(7)}
\]

Figure 2. ORTEP views of complexes 7 (left) and 9 (right). Displacement ellipsoids are drawn at the 50% probability level and carbon-bound hydrogen atoms are omitted. Symmetry code: i = x, y, 1/2$–$z. Selected bond lengths (Å) and angles (°). 7: Ir1$–$C1 2.015(4), Ir1$–$N1 2.192(3), Ir1$–$P1 2.2698(10), Ir1$–$P2 2.2866(11), C1$–$Ir1$–$N1 175.45(15), P1$–$Ir1$–$P2 156.59(4), C1$–$Ir1$–$P1 79.03(12), C1$–$Ir1$–$P2 79.08(13), N1$–$Ir1$–$P1 100.83(10), N1$–$Ir1$–$P2 101.66(10), 9: Ir1$–$C1 2.008(4), Ir1$–$N1 2.043(3), Ir1$–$P1 2.2479(7), C1$–$Ir1$–$N1 178.77(13), P1$–$Ir1$–$P1 159.11(4), C1$–$Ir1$–$P1 79.556(19), N1$–$Ir1$–$P1 100.436(19).

If such a reductive dehydrochlorination of iridium(III) to iridium(I) compounds in the presence of strong anionic bases (KO$\text{Bu}$, LiEt$_3$BH, and KH) is expected, a reduction with neutral bases is rather uncommon. In addition to our work, a single example could be found with neutral organic bases that could generate an iridium(I) complex from iridium(III) chloro hydride precursor.$^{52}$

Note that under 1 bar of H$_2$, the mixture of 7 and 8 is entirely converted into the dihydride iridium(III) complex 6$_{\text{cis}}$. Formation of this latter may result either from H$_2$ oxidative addition on the iridium(I) complex 7 or the deprotonation of coordinated H$_2$ on 8 by its anionic TBDH ligand (Eqn 8).

\[7 + 8 \xrightarrow{\text{H}_2 (1 \text{ bar})} \begin{array}{c}
\text{Ir} \quad \text{H} \\
\text{P} \quad \text{P} \\
\text{Bu} \quad \text{Bu} \\
\text{O} \\
\end{array} \quad \text{cis} \quad \text{6}_{\text{cis}} \quad \text{(8)}
\]

It is interesting to note that the HOMO-1 and LUMO of 7 show a strong overlap between the $dz^2$ orbital centered on the iridium(I) ion and the $\sigma^*$ orbital of the TBDH ligand (Figure 3). This destabilizing interaction favors intramolecular oxidative addition of 7 into 8.

Figure 3. HOMO-1 (left) and LUMO (right) of 7.

The reactivity of metal hydride complexes 1–3 and 4 was then considered with Me$_3$SiOTf in benzene in order to probe their capacity at hydride transfer to form hydrosilanes. No reaction was observed with any of the complexes in presence of 1 equiv. or excess Me$_3$SiOTf, either at room temperature or at 90°C (Eqn 9). Similarly, the hydride adduct 4 was found to be inert under an H$_2$ atmosphere. Hydride transfer is therefore not favored with these iridium(III) complexes. It is in contrast to the ruthenium(II) complex $\text{[(}^{(3)}\text{P} \text{POCOP})\text{Ru}(\text{H})(\text{CO})]$ which readily transfers a hydride to Me$_3$SiX (X = Cl, OTf) to give Me$_3$SiH and $\text{[(}^{(3)}\text{P} \text{POCOP})\text{Ru}(\text{H})(\text{X})]$ almost quantitatively in benzene.$^{66}$ The Si–OTf to Si–H reaction that we wished to perform is actually thermodynamically unfavorable, since the reverse reaction easily took place in benzene (Eqn 10). Indeed, in presence of 5 equiv. Et$_3$SiH, $\text{[(}^{(3)}\text{P} \text{POCOP})\text{Ir}(\text{H})(\text{OTf})]$ was quantitatively transformed into dihydride complex 3 within 18 h at room temperature. Previously, Brookhart et al. reported the conversion of chloro hydride 1 into dihydride 3 with an excess of Et$_3$SiH but only when the ion pair $\text{[(}^{(3)}\text{P} \text{POCOP})\text{Ir}(\text{H})(\text{acetone})]\text{[B(C$_6$F$_5$)$_3$]}}$ was added as catalyst.$^{56}$ We have also shown in a recent study$^{58}$ that the hydride transfer on silyl chloride required a more reactive hydride species such as anionic complex 10 which readily transfers one of its hydride to Me$_3$SiCl (Eqn 11). However, such active species could only be generated in the presence of very strong bases such as Verkade’s base ($^{(9)}$VB $\approx 2.8,9$-Trisopropyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane) or phosaphazene.
The weak NEt₃ base does not induce formation of an anionic [POCOP]IrH₃⁺ species (Eqn 3) and the above results would suggest that 3 is most likely the active species in hydride transfer. Although the [[(POCOP)IrHX]] complexes proved unable to reduce a silyl triflate into an hydrosilane (Eqn 9), it does not necessarily prevent a catalytic turnover as the unfavorable thermodynamics of the hydride transfer might be counterbalanced by the overall favorable hydrogenolysis reaction.

Catalytic hydrogenolysis of silyl triflates

Complexes 1, 2, 3, 7 and 8 have been tested in benzene for the hydrogenolysis of silyl triflates into silanes under 1 bar of H₂ at room temperature and in the presence of triethylamine. The chloro hydride complex 1 did not show any activity, even after 48 h (Table 1, Entry 1). Complexes 2 and 3 displayed a catalytic activity and Me₃SiH was obtained in 80% and 83% yield respectively, after 3 h (Table 1, Entries 2-3). Complexes 7 and 8 are also able to catalyze the reaction, yielding 78% of Me₃SiH after 3 h (Table 1, Entry 4). Replacing the base NEt₃ with TBDH was deleterious to the catalysis, and Me₃SiH was not detected when using 3, even after 72 h (Table 1, Entry 5). Complex 3 is also efficient in the catalytic hydrogenolysis of Et₃SiOTf and Ph₃SiOTf but these reactions required longer reaction times: the corresponding hydrosilanes were formed in 86% and 55% yields after 8 h and 300 h, respectively (Table 1, Entries 6 and 7). The detrimental steric influence of large R groups on RSiX has already been noticed by the groups of Shimada and Schneider.¹⁶,¹⁷

Table 1. Catalytic hydrogenolysis of silyl triflates[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>(μmol)</th>
<th>Base</th>
<th>Conv[Ⅱ] (%)</th>
<th>Product (yield)[Ⅲ]</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me₃SiOTf</td>
<td>NEt₃</td>
<td>0</td>
<td>-</td>
<td>48</td>
</tr>
<tr>
<td>2</td>
<td>Me₃SiOTf</td>
<td>NEt₃</td>
<td>83</td>
<td>Me₃SiH (80%)</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>Me₃SiOTf</td>
<td>NEt₃</td>
<td>85</td>
<td>Me₃SiH (83%)</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>Me₃SiOTf</td>
<td>NEt₃</td>
<td>80</td>
<td>Me₃SiH (78%)</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>TBDH</td>
<td>NEt₃</td>
<td>0</td>
<td>-</td>
<td>72</td>
</tr>
<tr>
<td>6</td>
<td>Et₃SiOTf</td>
<td>NEt₃</td>
<td>88</td>
<td>Et₃SiH (83%)</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>Ph₃SiOTf</td>
<td>NEt₃</td>
<td>60</td>
<td>Ph₃SiH (55%)</td>
<td>300</td>
</tr>
</tbody>
</table>

[a] General conditions: 0.1 mmol of substrate, 1 μmol of catalyst, 1 bar of H₂, 0.5 mL of C₆D₆, room temperature. [b] Conversions/yields were determined by ¹H NMR integration of all signals in the R₃Si region around 0 ppm versus an internal standard (1,3,5-trimethylbenzene). [c] r.t. to 90°C. [d] GC-MS yield (see SI, 2.4).

Complex 3 is active for the conversion of Me₃SiOTf to Me₃SiH that is obtained in 80% yield after 3 h. This result can be compared with that of the group of Schneider, who reported similar yields for the same reaction catalyzed by the bifunctional Ru(II)-MACHO complex [[H(N{CH₂CH₂P(PBu₃)₂})₂]₂Ru(H₂)(CO)] (1 mol%) but after 18 h reaction and under 4 bar of H₂.¹⁷ A surprising result is the total shutdown of the catalysis when a stronger base, TBDH, is used instead of NEt₃. The Gibbs free energies of both reactions were computed, and the formation of Me₃SiH + [TBDH]OTf appears to be more exergonic than that with [NEt₃]OTf (ΔG = -14.1 vs. -0.4 kcal mol⁻¹). While the catalysis should thermodynamically be more favorable with TBDH, the rapid reaction of TBDH with Me₃SiOTf to produce [Me₃Si-TBDH]OTf (AG = -12.1 kcal mol⁻¹) is detrimental. Indeed, the latter species precipitates and is inert even at higher temperatures (up to 90 °C). This side reaction explains the absence of catalytic activity with TBDH. In addition, a similar adduct [Me₃Si-NEt₃]OTf was formed when the reaction with NEt₃ was performed in acetonitrile and the expected hydrosilane was not obtained (See ESI, Section 1.2.3). This is in line with our recent results in the hydrogenolysis of chlorosilanes.¹⁸ The low exergonicity of the reaction with NEt₃ (ΔG = -0.4 kcal mol⁻¹) should lead to an equilibrium, but the poor miscibility of the ionic liquid [HNEt₃]OTf leads to a phase separation that drives the reaction to the formation of Me₃SiH (See ESI, Section 1.2.4).

Density functional theory calculations were performed to obtain further insight on the hydrogenolysis mechanism by these iridium pincer complexes (Scheme 5). The mechanistic route highlights the facile interconversion between complexes 3 and 4 (0 and -0.4 kcal mol⁻¹ respectively) which can proceed in ambient conditions through TS₃₄ at +11.3 kcal mol⁻¹. Both complexes might be the active species. Complex 4 is immediately obtained by hydrogenation of 3 and is observed during the catalysis and at its end (Eqn 2). The hydride transfer from 3 or 4 to Me₃SiOTf is barrierless and leads to the formation of an intermediate at 10.9 kcal mol⁻¹ (II) or at 18.0 kcal mol⁻¹ respectively (see SI Fig. S28). It seems however unlikely that 4 is the active species with such an energetic gap (7.1 kcal mol⁻¹) between these two intermediates and therefore 4 would be an off-cycle species. Formation of the triflate hydride complex 2 with release of Me₃SiH from 11 is exergonic (ΔG° = -10.4 kcal mol⁻¹) with a high energetic barrier involving TS₁₁₂ (ΔG° = +21.5 kcal mol⁻¹).

Coordination of H₂ onto 2 proceeds through TS₂₁₂ (ΔG° = +8.0 kcal mol⁻¹) giving 12 (ΔG° = +6.8 kcal mol⁻¹). Base-assisted splitting of H₂ relies on a high energetic barrier of +24.9 kcal mol⁻¹ (TS₁₂₄) which leads to the ion pair 14 (ΔG° = +17.9 kcal mol⁻¹). Finally, regeneration of the dihydride 3 is facile and proceeds through TS₃₄ (ΔG° = +18.5 kcal mol⁻¹) with the release of [HNEt₃]OTf. For this mechanistic route (purple + orange lines), the energetic span of 25.3 kcal mol⁻¹ is defined by TS₂₄ and 4, and is slightly higher (by 3-4 kcal mol⁻¹) than expected from the experimental conditions at room temperature (Eqn 12). This relatively high value may be related to the difficult approach of the base toward the complex due to steric hindrance. Formation of the iridium(I) adduct [(Ph₃Si)a]}
POCOP)Ir(OTf)[HNEt$_3$] (13) (23.7 kcal.mol$^{-1}$) by deprotonation of 2 with NEt$_3$ was considered. Its formation reveals a high energetic barrier ($\Delta G^0 = 32.2$ kcal.mol$^{-1}$ for TS$_{2\rightarrow3}$) that makes it unlikely. DFT calculations suggest that the splitting of H$_2$

$\Delta G_{\text{CBS}}$ (kcal.mol$^{-1}$)

\[ \Delta G_{\text{CBS}} (P = \text{PBu}_2) = 10 \text{ kcal.mol}^{-1} \]

Scheme 5. Computed pathway for the mechanism of the catalytic transformation of Me$_3$SiOTf into Me$_3$SiH by 3. Values given are Gibbs free energies in kcal.mol$^{-1}$ with respect to 3 + Me$_3$SiOTf (0.0). Computations parameters: Gaussian 16 Rev. C01, PBE0-D3/Def2-TZVP (Ir), 6-311+G(d,p) (Si, mobile H), 6-31G(d) (other atoms), SMD (Solvent: benzene).

Conclusion

We showed that iridium(III) complexes 2 and 3, as well as iridium(I) TBDH adduct 7, are able to catalyze the hydrogenolysis of silyl triflates R$_2$SiOTf (R = Me, Et, Ph) in the presence of the NEt$_3$. The reaction proceeds under mild conditions (r.t., 1 bar H$_2$) and affords the corresponding hydrosilanes with good yields and selectivity. The reaction works well in benzene in the presence of the base NEt$_3$ but not with the guanidine TBDH which reacts rapidly with silyl triflates (R$_2$SiOTf) to give the insoluble and deactivated species [R$_2$Si-TBDH]OTf. The yield and selectivity in hydrosilanes are similar to those afforded by other iridium(III) catalysts, but the reaction conditions are milder (1 bar H$_2$ vs 4 bar). The reaction is however much faster (TOF of 28 h$^{-1}$) than with any other reported catalysts (TOF of 0.2 and 18 h$^{-1}$)\textsuperscript{16,17}. To gain insight into the mechanism, the chemical reactivity of complexes 1-3 with the reagents involved in the catalysis has been scrutinized. Some iridium complexes have been isolated or experimentally characterized and these studies revealed that iridium(I) complexes may form, depending on the nature of the base. However, the involvement of catalytically active iridium(I) species in hydrogenolysis is dismissed by DFT calculations that revealed only iridium(III) complexes are efficient via $\sigma$-bond metathesis steps and hydride transfers.

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ASSOCIATED CONTENT

The following files are available free of charge. Supplementary equations, detailed descriptions of experimental methods, kinetic and mechanism studies are provided in the Supporting Information.

Accession Codes

CCDC 2077245–2077248 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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AUTHOR INFORMATION

Corresponding Author

* E-mail: thibault.cantat@cea.fr; Fax: +33 1 6908 6640; Tel: +33 1 6908 4338
† Université Paris-Saclay, CEA, CNRS, NIMBE, 91191, Gif-sur-Yvette, France.

Author Contributions

The manuscript was written with contributions of all authors. All authors have given approval to the final version of the manuscript.


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