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The Role of (^tBuPOCOP)Ir(I) and iridium(III) Pincer Complexes in the Catalytic Hydrogenolysis of Silyl Triflates into Hydrosilanes

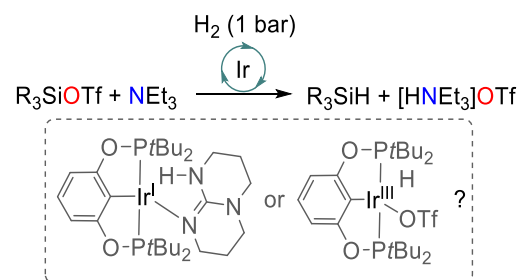
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ABSTRACT: Hydrosilanes are convenient reductants for a large variety of organic substrates, but they are produced via energy-intensive processes. These limitations call for the development of general catalytic processes able to transform Si–O into Si–H bonds. We report here the catalytic hydrogenolysis of R₃SiOTf (R = Me, Et, Ph) species in the presence of a base (e.g. NEt₃), by the hydride complexes [(^tBu-POCOP)IrH(X)] (X = H, OTf; (^tBuPOCOP = [(1,3-C₆H₃)(OPtBu)₂]). Syntheses and crystal structures of new iridium(I) and iridium(III) complexes are presented as well as their role in the R₃SiOTf to R₃SiH transformation. The mechanisms of these reactions have been examined by DFT studies, revealing that the rate-determining step is the base-assisted splitting of H₂



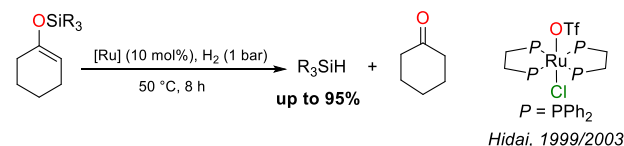
Introduction

The activation of siloxanes and silicon oxide derivatives is a key strategy to enter the value chain of silicon chemistry. While SiH₄ and SiCl₄ are the main starting blocks in the synthesis of silicon compounds, they require the use of silicon(0) obtained from energy intensive processes.¹ 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.^{2,3} In synthetic chemistry, they promote highly efficient and selective reactions such as the functionalization of inactivated C–H bonds in catalytic processes⁴ or the reduction of carbonyl-containing molecules.^{5–8} Recent studies have highlighted new utilizations for hydrosilanes to recover valuable molecules through C–O bond reduction/cleavage of oxygenated feedstock such as CO₂,⁹ wood lignin¹⁰ and plastics¹¹ toward a circular economy with low oil dependency. Currently, hydrosilane synthetic strategies rely on energy-intensive processes which involve strong reducing agents such as LiAlH₄.¹² Hydrogenolysis of Si–X bonds has been introduced by the groups of Hidai,^{13,14} Shimada,^{15,16} Schneider¹⁷ and Cantat¹⁸ as an alternative way to hydrosilanes and would be a convenient approach when using green H₂ 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.

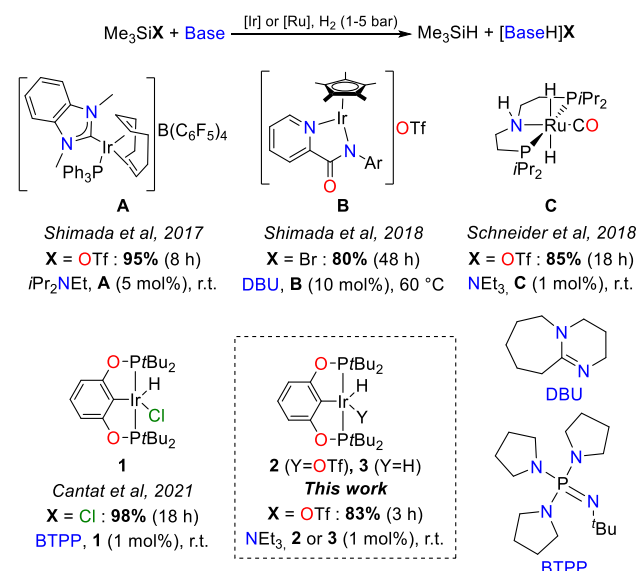
In 1999 and 2003, Hidai *et al.* reported the catalytic hydrogenolysis of silyl enol ether into R₃SiH and ketones using

[(dppe)₂RuCl(η²-H₂)]OTf as catalyst under mild conditions (50 °C, 1 bar H₂). Although not focused towards the formation of hydrosilanes, this report demonstrated that hydrogenolysis can occur on Si–O linkages.^{13,14}

Silyl enol ethers

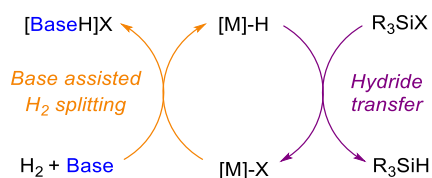


Silyl halides and triflates



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^{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 NⁱPr₂Et 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_{4-n}SiX_n 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 Schneider¹⁷ also reported in 2018 excellent conversion and yields in Me₃SiH, Me₂SiH₂ or Me₂SiH(OTf) 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 [(^tBu^{POCOP})IrHCl] (**1**) as an efficient catalyst in the hydrogenolysis of [Si]–Cl compounds when combined with superbases such as BTTP (BTTP = (*t*Bu-imino)tri(pyrrolidino)phosphorane).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 H₂ (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 R₃Si–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^{21,22} and hydrosilylation reactions²³ 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 ^tBu^{POCOP} pincer complexes of iridium(III) and iridium(I) with the presence of a nitrogen base. The chemical behavior of the potential iridium(III) precatalysts [(^tBu^{POCOP})IrH(X)] (X = H, Cl, OTf) was studied in presence of stoichiometric quantities or excess of the reagents H₂, R₃SiOTf and the base NEt₃ 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 [(^tBu^{POCOP})Ir^{III}H(OTf)] (**2**), [(^tBu^{POCOP})Ir^{III}H(NCMe₂)₂]OTf (**5**), [(^tBu^{POCOP})IrH₂(TBDH)] (**6_{cis}**), [(^tBu^{POCOP})Ir^I(TBDH)] (**7**) and [(^tBu^{POCOP})Ir^{III}H(TBD)] (**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. Me₃SiOTf, Et₃SiOTf 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. C₆D₆, Tol-*d*₈ and THF-*d*₈ were dried over sodium/benzophenone and vacuum-distilled before use. CD₃CN was dried over CaH₂, 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 [(^tBu^{POCOP})IrHCl] (**1**) was synthesized according to literature procedure²² from commercial bis(1,5-cyclooctadiene)diiridium(I) dichloride ([COD]IrCl₂)₂ and ^tBu^{POCOP}H ([1,3-C₆H₄)(OP*t*Bu)₂], prepared from commercial resorcinol [1,3-C₆H₄(OH)₂] and CIP(*t*Bu)₂ (Sigma-Aldrich). Ph₃SiOTf was obtained from commercial Ph₃SiCl and AgOTf (Sigma-Aldrich) according to literature procedure.²³ 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 MBraun 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 ¹H and ¹³C) or external reference (for ¹¹B, ¹⁹F and ³¹P) and reported in parts per million (ppm) relative to tetramethylsilane (¹H, ¹³C), phosphoric acid (³¹P), BF₃·OEt₂ (¹¹B) or trifluoroacetic acid (¹⁹F). 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 SLBTM-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 laboratorien at Lindlar (Germany).

Crystallography. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer²⁵ using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The crystals were introduced into glass capillaries with a protective coating of Paratone-N oil (Hampton Research). The data (combinations of ϕ - and ω -scans with a minimum redundancy of at least 4 for 90% of the reflections) were processed with HKL2000.²⁵ Absorption effects were corrected empirically with SCALEPACK.²⁶ The structures were solved by intrinsic phasing with SHELXT,²⁷ expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on F^2 with SHELXL.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 CH₃, 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-3.²⁹

Computational details. Calculations were performed using the Gaussian16 suite of software.³⁰ The PBE0³¹-D3³² functional was used in conjunction with the Def2TZVP^{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 the solvation by benzene were included in the energy calculations using the SMD model through single point calculations on the gas-phase optimized geometry.⁵⁵

Catalytic Protocols

General procedure for the hydrogenolysis of silyl triflates:

In a J. Young NMR tube, the iridium complex (1 mol%) was dissolved in 0.5 mL C₆D₆. 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_xSi signals versus an internal standard (1,3,5-trimethylbenzene). Et₃SiH and Ph₃SiH were also quantified by GC-MS (see SI 1.4 for details).

Synthetic procedures

[(^tBuPOCOP)IrH(OTf)] (**2**): In a glove box, **1** (200 mg, 0.32 mmol) and AgOTf (91 mg, 0.35 mmol) were dissolved in toluene (20 mL) in a 50 mL round bottom flask. The solution protected from light was stirred 14 h at room temperature (r.t.) and then filtered on a frit of porosity 4 and extracted with toluene (2x10 mL). The solvent was evaporated under vacuum affording **2** as an orange powder in 96 % yield (225 mg, 0.31 mmol). ¹H NMR (400 MHz, 23 °C, C₆D₆): 6.66 (t, 1H, *J* = 8.0 Hz, *p*-H_{Ar}), 6.56 (d, 2H, *J* = 8.0 Hz, *m*-H_{Ar}), 1.19 (vt, *J*_{P-H} = 10.8 Hz, 36H, ^tBu), -42.88 (t, ²*J*_{P-H} = 10.8 Hz, 1H, Ir-H). ¹³C{¹H} NMR (100 MHz, C₆D₆): 162.81 (Cq, vt, *J*_{P-C} = 5.6 Hz, C_{Ar-ortho}), 123.74 (CH, C_{Ar-para}), 99.81 (CH, vt, *J*_{P-C} = 5.3 Hz, C_{Ar-meta}), 37.99 (Cq, vt, *J*_{P-C} = 12.5 Hz, 2 P(*t*Bu)₂), 34.15 (Cq, vt, *J*_{P-C} = 12.5 Hz, P(*t*Bu)₂), 22.18 (CH₃, vt, *J*_{P-C} = 3.1 Hz, P(*t*Bu)₂), 21.71 (CH₃, vt, *J*_{P-C} = 3.1 Hz, P(*t*Bu)₂). ¹⁹F{¹H} (376 MHz, 23 °C, C₆D₆): -81.93. ³¹P{¹H} NMR (162 MHz, 23 °C, C₆D₆): 177.0. Anal. Calcd for C₂₃H₄₀F₃IrO₅P₂S (M = 739.79 g.mol⁻¹): C, 37.34; H, 5.45; F, 7.70. Found: C, 37.35; H, 5.43; F, 7.69.

[(^tBuPOCOP)IrH(NCMe)₂]OTf (**5**): In a 50 mL round bottom flask, **1** (200 mg, 0.32 mmol) was suspended in freshly distilled CH₃CN (10 mL). Me₃SiOTf (64 μL, 0.35 mmol, 1.1 eq) was then added *via* a syringe and the clear yellow solution obtained was stirred for 15 min at r.t. The solvent was removed under vacuum and the solid residue was washed with pentane (2 x 5 mL) to give **4** as a white yellowish powder isolated in 78 % yield (205 mg, 0.25 mmol). ¹H NMR (400 MHz, 23 °C, CD₃CN): 6.81 (t, 1H, *J* = 8.0 Hz, *p*-H_{Ar}), 6.46 (d, 2H, *J* = 8.0 Hz, *m*-H_{Ar}), 2.18 (s, 3H, CH₃CN_{cis}), 1.99 (s, 3H, CH₃CN_{trans}), 1.51 (vt, *J*_{P-H} = 6.4 Hz, 18H, *t*Bu), 1.31 (vt, *J*_{P-H} = 6.4 Hz, 18H, *t*Bu), -20.92 (t, ²*J*_{P-H} = 8.2 Hz, 1H, Ir-H). ¹³C{¹H} NMR (100 MHz, CD₃CN): 164.86 (Cq, vt, *J*_{P-C} = 5.5 Hz, C_{Ar-ortho}), 125.73 (CH, s, C_{Ar-para}), 104.97 (CH, vt, *J*_{P-C} = 5.2 Hz, C_{Ar-meta}), 41.37 (Cq, vt, *J*_{P-C} = 12 Hz, 2 P(*t*Bu)₂), 40.98 (Cq, vt, *J*_{P-C} = 12 Hz, P(*t*Bu)₂), 27.81 (CH₃, vt, *J*_{P-C} = 2.9 Hz, 2 P(*t*Bu)₂), 2 P(*t*Bu)₂), 27.16 (CH₃, vt, *J*_{P-C} = 2.9 Hz, 2 P(*t*Bu)₂). ¹⁹F{¹H} (376 MHz, 23 °C, CD₃CN): -79.35. ³¹P{¹H} NMR (162 MHz, 23 °C, C₆D₆): 162.27. Anal. Calcd for C₂₇H₄₆F₃IrN₂O₅P₂S (M = 821.89 g.mol⁻¹):

¹): C, 39.46; H, 5.64; N, 3.41; F, 6.93. Found: C, 39.59; H, 5.66; N, 3.80; F, 7.36.

[(^tBuPOCOP)IrH₂(TBDH)] (**6_{cis}**): 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 [TBDH₂]Cl, 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 **6_{cis}** isolated as a pale orange powder (85 %, 49 mg, 0.067 mmol). ¹H NMR (400 MHz, C₆D₆): 8.68 (s, 1H, NH), 6.81 (m, 1H, *p*-H_{Ar}), 6.74 (m, 2H, *m*-H_{Ar}), 3.84 (m, 2H, TBDH(CH₂)), 2.74 (td, *J* = 5.9 Hz, 2.5 Hz, 2H, TBDH(CH₂)), 2.51 (t, *J* = 6.4 Hz, 2H, TBDH(CH₂)), 2.30 (t, *J* = 5.9 Hz, 2H, TBDH(CH₂)), 1.56 (vt, *J* = 6.6 Hz, 18H, P(*t*Bu)₂), 1.50 (vt, *J* = 6.6 Hz, 18H, P(*t*Bu)₂), 1.33 (m, 2H, TBDH(CH₂)), 1.17 (p, *J* = 5.9 Hz, 2H, TBDH(CH₂)), -9.16 (tdd, *J*_{P-H} = 14.7 and *J*_{H-H} = 11.4 Hz, 1H, Ir-H), -9.59 (td, *J*_{P-H} = 17.7 and *J*_{H-H} = 11.4 Hz, 1H, Ir-H). ¹³C{¹H} NMR (100 MHz, C₆D₆): 163.48 (Cq, t, *J*_{P-C} = 6.5 Hz, C_{Ar-ortho}), 149.59 (Cq, s, TBDH), 121.16 (CH, s, C_{Ar-para}), 118.29 (Cq, t, *J*_{P-C} = 5.2 Hz, C_{Ar-ipso}), 103.26 (CH, t, *J*_{P-C} = 5.5 Hz, C_{Ar-meta}), 59.88 (CH₂, s, TBDH), 48.79 (CH₂, s, TBDH), 48.20 (CH₂, s, TBDH), 40.55 (CH, t, *J*_{P-C} = 12.5 Hz, P(*t*Bu)₂), 39.03 (CH₂, s, TBDH), 38.16 (CH, t, *J*_{P-C} = 11.5 Hz, P(*t*Bu)₂), 28.58 (CH₃, t, *J*_{P-C} = 3.7 Hz, P(*t*Bu)₂), 28.44 (CH₃, t, *J*_{P-C} = 3.4 Hz, P(*t*Bu)₂), 24.45 (CH₂, s, TBDH), 22.70 (CH₂, s, TBDH). ³¹P{¹H} NMR (162 MHz, C₆D₆): 167.99. Anal. Calcd for C₃₁H₅₅IrN₄O₂P₂ (M = 730.92 g.mol⁻¹): C, 47.65; H, 7.45; N, 5.75. Found: C, 47.84; H, 7.30; N, 5.62.

[(^tBuPOCOP)Ir(TBDH)] (**7**) and [(^tBuPOCOP)IrH(TBDH)] (**8**): The orange complex **1** (50 mg, 0.08 mmol) and white TBDH (22 mg, 0.16 mmol, 2eq) were dissolved in toluene (5 mL) in a 20 mL round bottom flask. The resulting yellow solution containing a white deposit was stirred for 2 h at r.t. Pentane was then added to increase the salt deposit and the solution was filtered through a syringe filter (0.2 μm). The product is further extracted from the salt with a 1:1 mixture of pentane and toluene (2x5 mL) and filtered as above. The yellow solution was evaporated to dryness to yield complexes **7** and **8** as yellow powder in 82 % yield (48 mg, 0.066 mmol). Anal. Calcd for C₂₉H₅₂IrN₃O₂P₂ (M = 728.92 g.mol⁻¹): C, 47.79; H, 7.19; N, 5.76. Found: C, 47.83; H, 7.33; N, 5.85. **7**: ¹H NMR (400 MHz, C₆D₆): 7.82 (s, 1H, NH), 7.03 (t, *J* = 7.7 Hz, 1H, *p*-H_{Ar}), 6.91 (d, *J* = 7.7 Hz, 2H, *m*-H_{Ar}), 3.43 (m, 2H, TBDH(CH₂)), 2.75 (td, *J* = 5.9 Hz, 2.3 Hz, 2H, TBDH(CH₂)), 2.44 (t, *J* = 5.9 Hz, 2H, TBDH(CH₂)), 2.34 (t, *J* = 5.9 Hz, 2H, TBDH(CH₂)), 1.49 (vt, *J* = 6.4 Hz, 18H, P(*t*Bu)₂), 1.45 (m, 2H, TBDH(CH₂)), 1.41 (vt, *J* = 6.4 Hz, 18H, P(*t*Bu)₂), 1.24 (p, *J* = 5.9 Hz, 2H, TBDH(CH₂)). ¹³C{¹H} NMR (100 MHz, C₆D₆): 167.61 (Cq, t, *J*_{P-C} = 8.2 Hz, C_{Ar-ortho}), 149.07 (Cq, s, TBDH), 132.82 (Cq, t, *J*_{P-C} = 5.2 Hz, C_{Ar-ipso}), 120.68 (CH, s, C_{Ar-para}), 102.85 (CH, t, *J*_{P-C} = 5.8 Hz, C_{Ar-meta}), 50.79 (CH₂, s, TBDH), 47.30 (CH₂, s, TBDH), 46.44 (CH₂, s, TBDH), 41.41 (CH, t, *J*_{P-C} = 10.8 Hz, P(*t*Bu)₂), 39.73 (CH, t, *J*_{P-C} = 10.4 Hz, P(*t*Bu)₂), 38.41 (CH₂, s, TBDH), 29.52 (CH₃, t, *J*_{P-C} = 3.9 Hz, P(*t*Bu)₂), 27.76 (CH₃, t, *J*_{P-C} = 4.1 Hz, P(*t*Bu)₂), 23.20 (CH₂, s, TBDH), 22.37 (CH₂, s, TBDH). ³¹P{¹H} NMR (162 MHz, C₆D₆): 164.22. **8**: ¹H NMR (400 MHz, C₆D₆): 6.84 (m, 1H, *p*-H_{Ar}), 6.78 (m, 2H, *m*-H_{Ar}), 3.23 (t, *J* = 5.7 Hz, 2H, TBDH(CH₂)), 3.14 (t, *J* = 5.7 Hz, 2H,

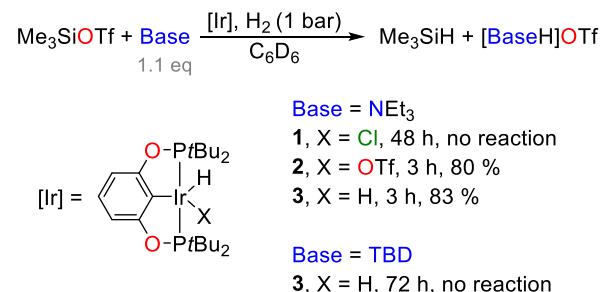
TBDH(CH₂), 2.70 (t, *J* = 5.7 Hz, 2H, TBDH(CH₂)), 2.66 (t, *J* = 5.7 Hz, 2H, TBDH(CH₂)), 1.66 (m, 4H, TBDH(CH₂)), 1.46 (vt, *J* = 6.7 Hz, 18H, P(*t*Bu)₂), 1.33 (t, *J* = 6.7 Hz, 18H, P(*t*Bu)₂), -24.71 (t, *J* = 15.5 Hz, 1H, IrH). ¹³C{¹H} NMR (100 MHz, C₆D₆): 165.67 (Cq, t, *J*_{P-C} = 6.0 Hz, C_{Ar-ortho}), 159.17 (Cq, s, TBDH), 122.94 (CH, s, C_{Ar-para}), 103.66 (CH, t, *J*_{P-C} = 5.3 Hz, C_{Ar-meta}), 46.13 (CH₂, s, TBDH), 46.00 (CH₂, s, TBDH), 45.75 (CH₂, s, TBDH), 41.51 (CH₂, s, TBDH), 40.85 (CH, t, *J*_{P-C} = 11.1 Hz, P(*t*Bu)₂), 39.91 (CH, t, *J*_{P-C} = 11.5 Hz, P(*t*Bu)₂), 28.82 (CH₃, t, *J*_{P-C} = 3.3 Hz, P(*t*Bu)₂), 27.77 (CH₃, t, *J*_{P-C} = 3.5 Hz, P(*t*Bu)₂), 24.65 (CH₂, s, TBDH), 24.11 (CH₂, s, TBDH). C_{Ar-ipso} is not observed. ³¹P{¹H} NMR (162 MHz, C₆D₆): 150.89.

Results and discussion

Synthesis and characterization of the complexes

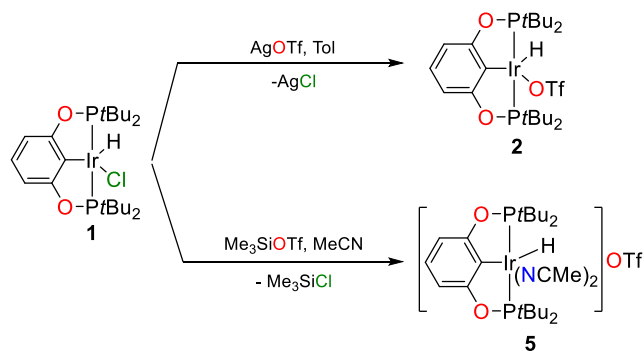
Recently, we have shown that [(^tBu)POCOP]IrHCl (1) is an efficient catalyst for the hydrogenolysis of chlorosilanes in the presence of strong bases.¹⁸ We therefore decided to investigate its behavior and that of related [(^tBu)POCOP]IrHX derivatives in the hydrogenolysis of the more reactive silyl triflates into hydrosilanes, in order to collect information on the species that are active during catalysis and the corresponding mechanism.

In a first experiment, 1 (1 mol%) was added to a mixture of Me₃SiOTf and NEt₃ in the 1:1:1 ratio under 1 bar H₂ in benzene. ¹H NMR monitoring of this mixture did not show any evolution after 48 h at r.t. However, when replacing 1 with the triflate analogue [(^tBu)POCOP]IrH(OTf) (2) or the dihydride derivative [(^tBu)POCOP]IrH₂ (3), catalysis occurred and Me₃SiH was obtained in 83% yield after 3 h (Scheme 3). ¹H NMR monitoring evidenced the growth of a doublet at 0.00 ppm and a multiplet at 4.15 ppm, in the respective 9:1 integration ratio, characteristic of the gaseous Me₃SiH, as well as the presence of [(^tBu)POCOP]Ir(H)₂(H₂) (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.



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 H₂ splitting. We thus synthesized the new complexes 2 and [(^tBu)POCOP]IrH(NCMe)₂][OTf] (5) to gather information on the chemical behavior of the [(^tBu)POCOP]IrH(X) (X = Cl (1), OTf (2), H (3)) precursors when placed in presence of each of the reagents H₂, R₃SiOTf or the nitrogen base (NEt₃ 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 triflate (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 ¹H NMR spectrum of 2 revealed a triplet for the Ir–H signal at δ = -42.9 ppm (²*J*_{P-H} = 10.8 Hz) (vs. δ = -40.9 ppm for 1 in C₆D₆).

The direct reaction of 1 with a slight excess of Me₃SiOTf in MeCN rapidly gave a pale yellow solution of the ion pair [(^tBu)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 diethylether. Compound 5 exhibits in ¹H NMR (CD₃CN) a triplet at δ = -22.31 ppm (²*J*_{P-H} = 8.2 Hz) for the Ir–H signal which is shifted downfield in comparison to the resonance of the neutral counterpart 2. Its related congener [(^tBu)POCOP]IrH(MeCN)₂[B(C₆F₅)₄]⁵⁶ exhibits an Ir–H resonance at δ = -20.9 ppm (²*J*_{P-H} = 14.7 Hz) close to that observed in 5. Views of the crystal structures of [(^tBu)POCOP]IrH(OTf) (2) and its cationic derivative 5 are presented in Figure 1, together with selected bond lengths and angles. The Ir³⁺ 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 apical position and the metal ion displaced by 0.1347(13) Å from the basis. Complex 5 comprises a six-coordinate Ir³⁺ ion in a distorted octahedral geometry 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.⁵⁷ 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 ^RPOCOP iridium(I) and iridium(III) complexes reported in the Cambridge Structural Database (CSD, version 5.40)⁵⁷ and in which the Ir–P distances extend over the range 2.2408(9)–2.412(1) Å. The Ir–η¹-O(OTf) is classical for Ir–OTf complexes⁵⁸ and the Ir–N(acetonitrile) distances in 5 are comparable to those found in the two other reported iridium(III)-acetonitrile pincer complexes.^{59,60} The Ir–H distances in 2 (1.52(4) Å) and 5 (1.46(4) Å) are quite identical to those in the complexes [(^tBu)POCOP]IrHCl (1.49(6) Å),⁶¹ the cation [(^tBu)POCOP]IrH(HSiEt₃)[B(C₆F₅)₄] (1.425(18) Å)⁶² and the analogue of 4, [(C₆H₂(CF₃)₃)POCOP]IrH₂(H₂) (average 1.69 (3) Å).⁶³ Within the (^RPOCOP)Ir(III) series, these Ir–H distances

scatter from 1.29(3) Å and 1.36(3) Å for [(^tBu-POCOP)IrH₂(H₂PMes)] to 1.74(4) Å in [(^tBu-POCOP)IrH₂(BH₃)].^{64,65}

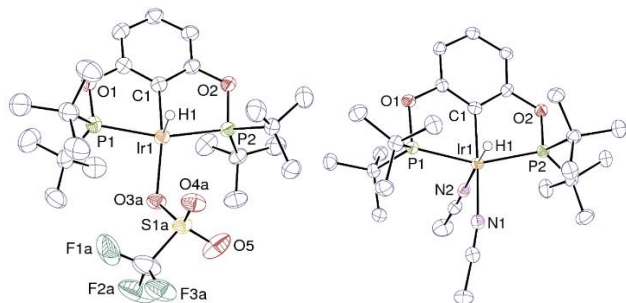
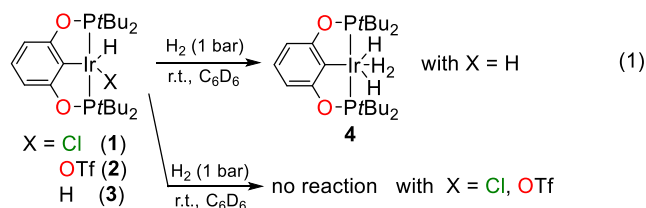
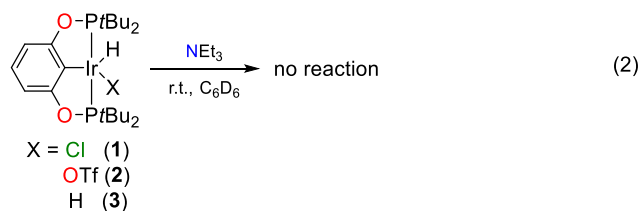


Figure 1. ORTEP views of **2** (left) and the cation [(^tBu-POCOP)IrH(MeCN)₂]⁺ in **5** (right). Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted and only one position of the disordered triflate anion in **2** is shown. Selected bond lengths (Å) and angles (°). **2**: Ir1–C1 1.990(3), Ir1–O3a 2.211(3), Ir1–P1 2.2969(9), Ir1–P2 2.3147(9), Ir1–H1 1.52(4), C1–Ir1–O3a 167.74(14), P1–Ir1–P2 160.54(3), C1–Ir1–H1 88.5(16), C1–Ir1–P1 80.28(10), C1–Ir1–P2 80.33(10), O3a–Ir1–P1 93.56(9), O3a–Ir1–P2 105.17(9). **5**: Ir1–C1 2.024(4), Ir1–N1 2.101(3), Ir1–N2 2.159(3), Ir1–P1 2.3251(8), Ir1–P2 2.3308(9), Ir1–H1 1.46(4), C1–Ir1–N1 175.97(11), C1–Ir1–N2 97.44(13), P1–Ir1–P2 155.69(3), N1–Ir1–N2 85.34(12), C1–Ir1–P1 79.73(9), C1–Ir1–P2 79.11(9), N1–Ir1–P1 97.11(7), N1–Ir1–P2 103.42(8), N2–Ir1–P1 95.94(7), N2–Ir1–P2 98.53(7).

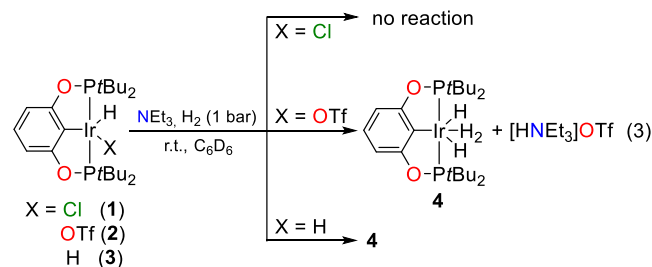
Because all neutral complexes **1–3** display good solubility in benzene, we then studied their reactivity in this solvent. Coordination of H₂ onto the complexes might be required for its further activation and use as a source of hydride. We first considered the behavior of the hydride species **1–3** under hydrogen (1 bar). If the formation of the dihydrogen complex **4** is well known from **3**,⁶⁶ coordination of H₂ was not detected on the more electron-deficient halide and triflate 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 [(^tBu-POCOP)IrH(X)] species in benzene under inert atmosphere (Eqn 2).

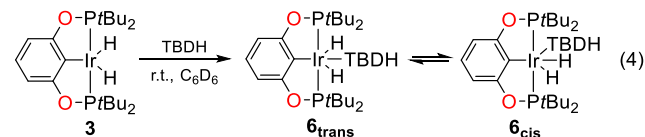


The absence of coordination of the triethylamine may be related to its steric congestion since the ammonia adduct [(^tBuPCP)IrH(Cl)(NH₃)] (^tBuPCP = C₆H₃(CH₂P^tBu₂)₂) is known⁷¹ and the two pincer ligands have similar steric hindrance. Some dihydride iridium pinners are also known to trap a variety of Lewis bases (NH₂NH₂, CO, phosphine).^{64,72} No adduct of [(^tBu-POCOP)IrH(Cl)] has been reported except the carbonyl derivative [(^tBu-POCOP)IrH(Cl)(CO)].⁷³ 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 [(^tBu-POCOP)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).

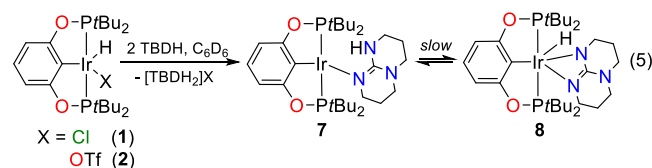


In addition to its steric congestion, the Brønsted basicity^{74,75} of the base plays also an important role in its interaction with the metal center and/or its ability to deprotonate dihydrogen or hydride ligands. Guanidine TBDH is a stronger base (pK_a = 26.0 in MeCN) than NEt₃ (pK_a = 18.8 in MeCN) and is used in a variety of base-mediated organic transformations and catalytic processes.^{76–79}

Treatment of dihydride **3** with 1 equiv. TBDH afforded quantitatively the adduct [(^tBu-POCOP)IrH₂(TBDH)] (**6**) (Eqn 4). The latter is present as two isomers in solution (cis and trans). This results in two ³¹P{¹H} NMR signals superimposed at 168.0 ppm as well as relatively complex hydridic signals : two triplets at δ = –9.05 and 9.41 (J_{P-H} = 14.5 and 15.9 Hz respectively) for the trans isomer and two triplets of doublets at δ = –9.16 and –9.59 (J_{P-H} = 14.7 and 17.7 Hz and J_{H-H} = 11.4 Hz) for the cis isomer. This cis/trans isomerism has been reported for the closely related carbonyl complexes by Goldberg, Heinekey, *et al.*⁷¹

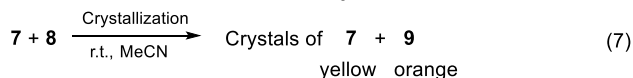
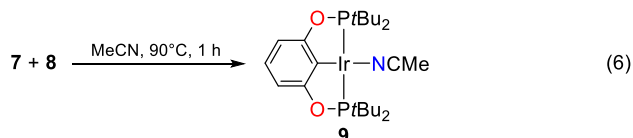


In contrast, the reaction of [(^tBu-POCOP)IrH(X)] (X = Cl, OTf) with 2 equiv. of TBDH in benzene led to the formation of [(^tBu-POCOP)Ir(TBDH)]. NMR spectroscopy evidenced formation of a mixture of **7** and its iridium(III) counterpart [(^tBu-POCOP)IrH(TBD)] (**8**) in the ratio 60:40 from the chloro 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. [TBD]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 $[(^t\text{BuPCP})\text{Ir}]$ which reacted with the amine $\text{NH}_2(m\text{-xylyl})$ to give $[(^t\text{BuPCP})\text{IrH}(\text{NH}(m\text{-xylyl}))]$.⁸⁰ ^1H and $^{31}\text{P}\{^1\text{H}\}$ 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 $[(^t\text{BuPOCOP})\text{Ir}(\text{NCMe})]$ **9** (Eqn 6), which has already been reported⁸¹ when reacting $\text{NaO}t\text{Bu}$ with **1** in acetonitrile.



Crystallization by slow cooling of a saturated acetonitrile solution of **7** and **8** afforded concomitantly large pale-yellow blocks of $[(^t\text{BuPOCOP})\text{Ir}(\text{TBDH})]$ (**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 $[(^{\text{CF}_3}\text{PCP})\text{Ir}(\text{DBU})]$.⁸² 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 strain hindering its coordination. This could explain the displacement of TBDH ligand with acetonitrile.

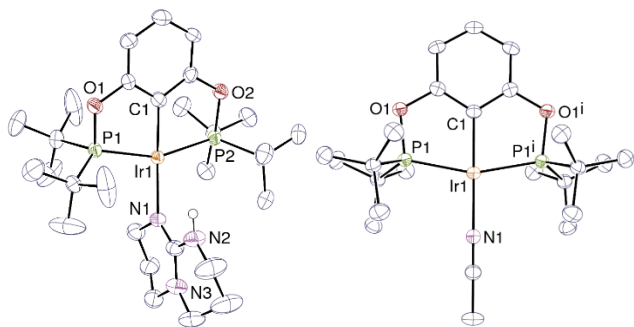
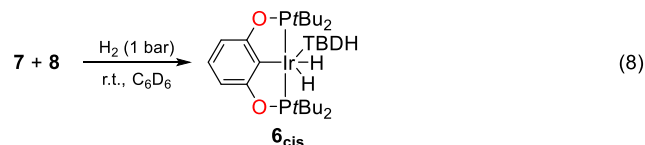


Figure 2. ORTEP views of complexes **7** (left) and **9** (right). Displacement ellipsoids are drawn at the 50% probability level and carbon-bound hydrogen atoms are omitted. Symmetry code: $i = x, y, 1/2 - z$. Selected bond lengths (Å) and angles (°). **7**: Ir1–C1 2.015(4), Ir1–N1 2.192(3), Ir1–P1 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–P1ⁱ 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 ($\text{KO}t\text{Bu}$, LiEt_3BH , and KH) is expected,⁸³ 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.⁸²

Note that under 1 bar of H_2 , the mixture of **7** and **8** is entirely converted into the dihydride iridium(III) complex **6_{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 TBD ligand (Eqn 8).



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

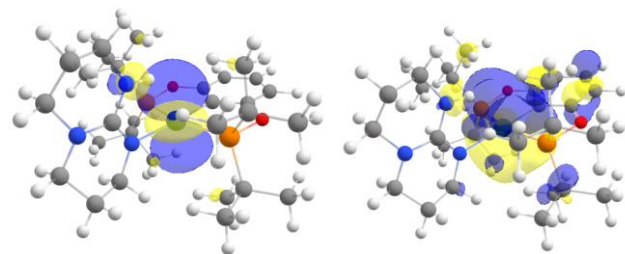
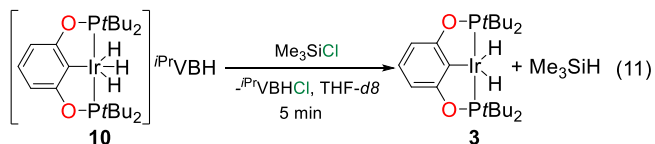
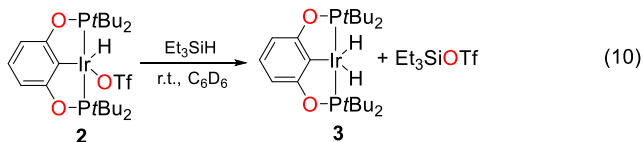


Figure 3. HOMO-1 (left) and LUMO (right) of **7**

The reactivity of metal hydride complexes **1–3** and **4** was then considered with Me_3SiOTf 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_3SiOTf , either at room temperature or at 90°C (Eqn 9). Similarly, the hydrogen 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 $[(\text{HN}\{\text{CH}_2\text{CH}_2\text{P}(\text{Pr})_2\}_2)\text{Ru}(\text{H})_2(\text{CO})]$ which readily transfers a hydride to Me_3SiX ($\text{X} = \text{Cl}, \text{OTf}$) to give Me_3SiH and $[(\text{HN}\{\text{CH}_2\text{CH}_2\text{P}(\text{Pr})_2\}_2)\text{RuH}(\text{X})(\text{CO})]$ 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_3SiH , $[(^t\text{BuPOCOP})\text{IrH}(\text{OTf})]$ 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_3SiH but only when the ion pair $[(^t\text{BuPOCOP})\text{IrH}(\text{acetone})][\text{B}(\text{C}_6\text{F}_5)_4]$ was added as catalyst.⁵⁶ We have also shown in a recent study¹⁸ 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_3SiCl (Eqn 11). However, such active species could only be generated in the presence of very strong bases such as Verkade's base ($i^t\text{VB} = 2,8,9\text{-Triisopropyl-}2,5,8,9\text{-tetraaza-}1\text{-phosphabicyclo}[3.3.3]\text{undecane}$) or phosphazene.

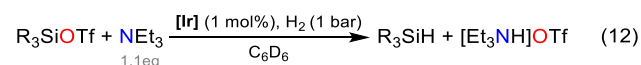


The weak NEt₃ base does not induce formation of an anionic [POCOP]IrH₃⁻ species (Eqn 3) and the above results would suggest that **3** is most likely the active species in hydride transfer. Although the [(^tBu)POCOP]IrH(X)] complexes proved unable to reduce a silyl triflate into an hydrosilane (Eqn 9), 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** were expected to behave similarly, since they can both evolve to **4** in the presence of NEt₃ and H₂. Effectively, both **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 R₃SiX has already been noticed by the groups of Shimada and Schneider.^{16,17}

Table 1. Catalytic hydrogenolysis of silyl triflates^[a]



Entry	[Ir]	Substrate	Base	Conv ^[b] (%)	Product (yield ^[b])	Time (h)
1	1	Me ₃ SiOTf	NEt ₃	0	-	48
2	2	Me ₃ SiOTf	NEt ₃	83	Me ₃ SiH (80%)	3
3	3	Me ₃ SiOTf	NEt ₃	85	Me ₃ SiH (83%)	3
4	7/8	Me ₃ SiOTf	NEt ₃	80	Me ₃ SiH (78%)	3
5 ^[c]	3	Me ₃ SiOTf	TBDH	0	-	72
6	3	Et ₃ SiOTf	NEt ₃	88	Et ₃ SiH (83%) (82%) ^[d]	8
7	3	Ph ₃ SiOTf	NEt ₃	60	Ph ₃ SiH (55%) (59%) ^[d]	300

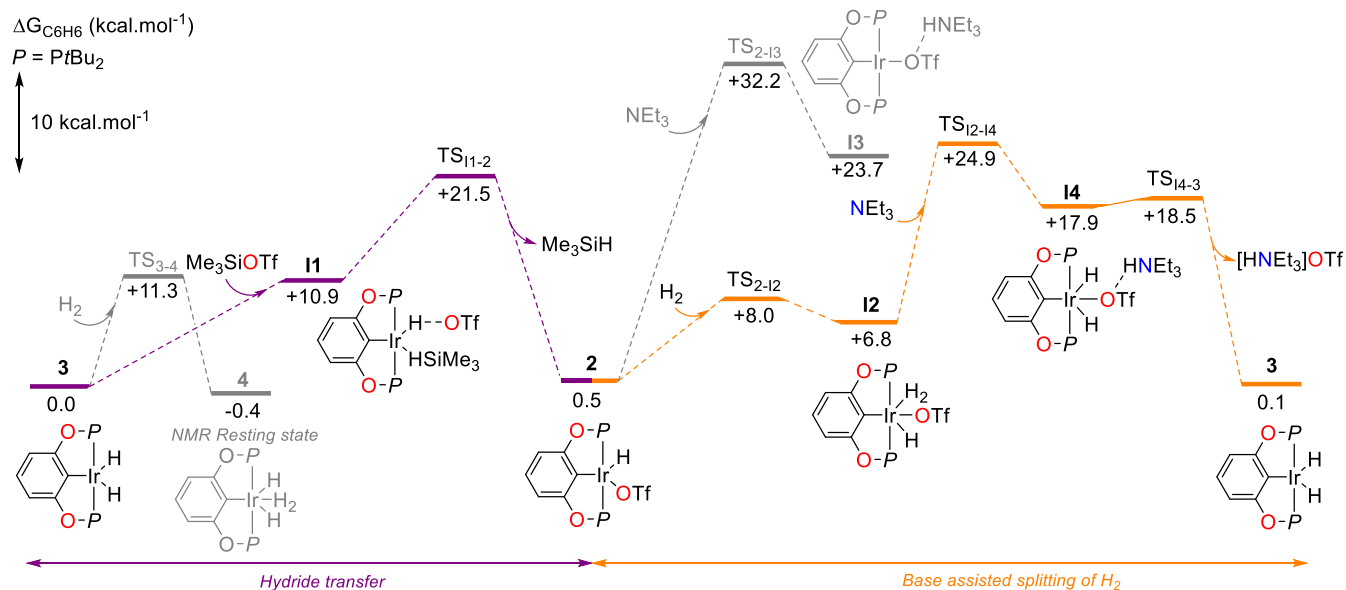
^[a] General conditions: 0.1 mmol of substrate, 1 μmol of catalyst, 1 bar of H₂, 0.5 mL of C₆D₆, room temperature. ^[b] Conversions/yields were determined by ¹H NMR integration of all signals in the R₃Si region around 0 ppm versus an internal standard (1,3,5-trimethylbenzene). ^[c] r.t. to 90°C. ^[d] 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 [(HN{CH₂CH₂P(Pr)₂}₂)Ru(H)₂(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 was computed, and the formation of Me₃SiH + [TBDH₂]OTf appears to be much more exergonic than that with [NEt₃H]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 (ΔG = -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 TS₃₋₄ 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 **II** is exergonic (ΔΔG° = -10.4 kcal.mol⁻¹) with a high energetic barrier involving TS_{II-2} (ΔG° = +21.5 kcal.mol⁻¹).

Coordination of H₂ onto **2** proceeds through TS₂₋₁₂ (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 (TS₁₃₋₁₄) which leads to the ion pair **14** (ΔG° = +17.9 kcal.mol⁻¹). Finally, regeneration of the dihydride **3** is facile and proceed through TS₁₄₋₃ (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 TS₁₂₋₁₄ 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 [(^tBu-

POCOP)Ir(OTf)][HNEt₃] (**13**) (23.7 kcal.mol⁻¹) by deprotonation of **2** with NEt₃ was considered. Its formation reveals a high energetic barrier ($\Delta G^\circ = 32.2$ kcal.mol⁻¹ for TS₂₋₁₃) that makes it unlikely. DFT calculations suggest that the splitting of H₂



Scheme 5. Computed pathway for the mechanism of the catalytic transformation of Me₃SiOTf into Me₃SiH by **3**. Values given are Gibbs free energies in kcal.mol⁻¹ with respect to **3** + Me₃SiOTf (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 R₃SiOTf (R = Me, Et, Ph) in the presence of the NEt₃. The reaction proceeds under mild conditions (r.t., 1 bar H₂) and affords the corresponding hydrosilanes with good yields and selectivity. The reaction works well in benzene in the presence of the base NEt₃ but not with the guanidine TBDH which reacts rapidly with silyl triflates (R₃SiOTf) to give the insoluble and deactivated species [R₃Si-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 H₂ 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).^{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 which revealed that only iridium(III) complexes are efficient *via* σ -bond metathesis steps and hydride transfers.

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would result from iridium(III) rather than iridium(I) species. This is in agreement with the experiment where no iridium(I) intermediate has been evidenced by reacting **1**, **2** or **3** with NEt₃ (Eqn 4).

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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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