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Selective partial reduction of quinolines: Hydrosilylation vs. transfer hydrogenation

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Abstract

Two mild and versatile catalytic routes give regioselective hydrogenation of the heterocyclic ring of quinoline derivatives avoiding the high pressures of hydrogen required in the conventional hydrogenation route. Hydrosilylation using H_3SiPh and catalyzed by $[Rh(nbd)(PPh_3)_2]PF_6$ at room temperature gives dihydroquinoline, a product not obtainable via direct hydrogenation. Hydrosilylation of the C=N bond of PhCH=NPh is also observed under these conditions while PhCH=CHPh is unreactive. Initial *in situ* disproportionation of phenylsilane to H_2SiPh_2 and SiH_4, catalyzed by the same catalyst, was required for substrate reduction, as SiH_4 proved to be the active reductant. No *N*-silyl intermediates were ever observed, hydrolysis presumably occurring *in situ.* This disproportionation reaction is of potential use in gaining access to silane (SiH_4), a material otherwise not readily available. In a separate approach, transfer hydrogenation from isopropanol using $[Ir(cod)(NHC)PPh_3]BF_4$ (NHC = 1-neopentyl-4-*n*-butyl triazole-5-ylidene) as catalyst exclusively produces the tetrahydro product.

Keywords: Silane disproportionation; Rhodium; Iridium; Phosphine; 1,2-Dihydroquinoline

1. Introduction

Regioselective partial reduction of quinoline derivatives is a convenient route to dihydro and tetrahydroquinolines. Tetrahydroquinolines are important organic synthetic intermediates for alkaloids, agrochemicals, dyes, and pharmaceuticals, while dihydroquinolines can be useful antimicrobials [1] and precursors to biologically active compounds. The catalytic reduction of quinolines is a challenging task in organic synthesis and normally requires high pressures of hydrogen when carried out by homogeneous or heterogeneous hydrogenation with Pt [2], Rh [3–5], Ru [6,7], or Ir [8]. Enantioselective variants are known with chiral bidentate phosphine complexes of rhodium [9] and iridium [10–14]. In addition, direct hydrogenation always yields the tetrahydro product [15]. The dihydro product, to the best of our knowledge, has been obtained from quinoline only by reduction using stoichiometric amounts of $LiAlH_4$ [16,17]. We now describe the catalytic reduction strategies that can be selective either for the dihydro or the tetrahydro product.

Catalytic hydrosilylation of alkenes, alkynes, and carbonyl compounds is well known [18], but hydrosilylation of nitrogen-containing compounds has not yet received as much attention. Hydrosilylation of imines, although still challenging, has been reported with rhodium [19], zinc [20], titanium [21], iridium [22], and palladium [23] catalysts. Reduction of pyridines via hydrosilylation has also been reported using palladium [24] and titanium [25] catalysts. We have now screened catalysts for imine hydrosilylation and then applied the best ones to aromatic heterocycles such as quinolines. It has been generally assumed that

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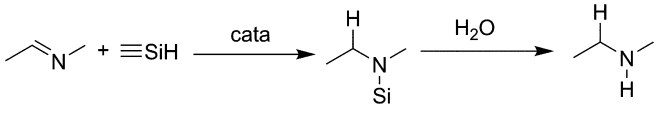
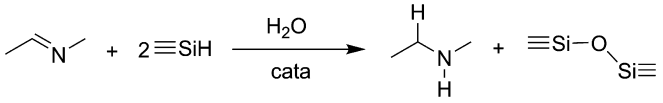
hydrosilylation of imines (Eq. (1)[1]) involves formation of a N–Si bond subsequently cleaved during work-up. This is not the only possibility, however. We also consider two other mechanisms outlined in Eqs. (2) and (3). In Eq. (2), protons from water and hydrides from the silane reduce the substrate with formation of siloxane as side product. In Eq. (3), one hydrogen from each of 2 equiv. silane reduces the substrate with formation of disilane as side product [23].



(1)



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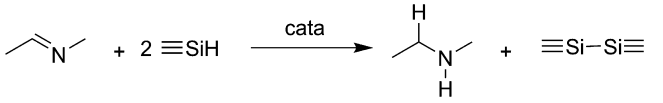
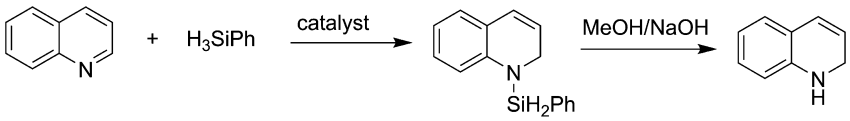


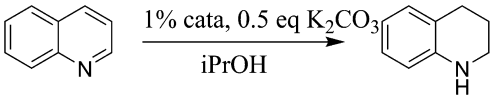
(3)

Applying the most widely accepted mechanism of Eq. (1) to quinoline gives the pathway of Eq. (4) but, as shown below, the reaction proves to be more complex than this.



(4)

The second route we investigated, transfer hydrogenation, is of interest due to its use of isopropanol, a greener reductant, thus avoiding costly reducing agents such as $LiAlH_4$ that also generate undesirable stoichiometric waste byproducts. A recent review summarizes the mechanistic studies on transition metal catalyzed hydrogen transfer reactions [26]. The reaction has been extensively studied for C=O reduction and has led to important applications such as the racemization of chiral alcohols [27] and asymmetric reduction of ketones [28]. Extension to C=N reduction has proved valuable in the pharmaceuticals industry [29]. Noyori et al. have used formic acid/triethylamine azeotrope to reduce imines under mild conditions with high enantiomeric excesses [30]. Transfer hydrogenation of quinoline and its derivatives, however, has not been extensively studied [31]. We recently reported a catalytic system that was active for imine reduction and reductive amination via hydrogen transfer [32] and we now report the extension of this system to transfer hydrogenation of heteroaromatics (Eq. (5)).



(5)

Here we use both hydrosilylation and transfer hydrogenation as mild and efficient methods for selectively reducing quinoline derivatives either to 1,2-dihydroquinoline or to 1,2,3,4-tetrahydroquinoline.

2. Results and discussion

2.1. Hydrosilylation

An initial catalytic screen of selected Rh, Ir, Ru, Pt, and Pd compounds at 3% loading with diphenylsilane in reagent-grade toluene with 4 equiv. silane in a closed 10 mL vial revealed very low activity for the reaction. We did, however, identify the most promising catalyst candidate, $[Rh(cod)(PPh_3)_2]PF_6$ (**1**). Moving to tricyclohexylphosphine did not have a significant effect on activity. Analogous compounds with diphenylphosphinoethane (DPPE) gave significantly lower catalytic activity. Similarly, substituting one or both phosphines with *N*-heterocyclic carbenes (IMe) also proved to be deleterious to catalytic activity. The analogous iridium phosphine and IMe catalysts were also tested, but their activities were also significantly lower. To optimize the silane, we screened several silanes, as shown in Table 1. Phenylsilane gave the best activity, with 80% total yield after 8 h to give two products after base work-up, dihydroquinoline and tetrahydroquinoline.

The initial activation of the catalyst normally involves loss of the diene ligand by hydrosilylation and this step is typically enhanced if cyclooctadiene (cod) is replaced with norbornadiene (nbd) [35]. The complex $[Rh(nbd)(PPh_3)_2]PF_6$ (**2**) indeed proved more active and gave 95% yield under the same conditions.

Table 1
Hydosilylation of quinoline using 3 mol% $[Rh(cod)(PPh_3)_2]PF_6$ and 4 equiv. silane, in toluene at 90 °C for the time specified

Entry	Silane	Product ratio (dihydro:tetrahydro)[a]	Time (h)	Yield (%)
1	H_2SiPh_2	0:100	24	12
2	H_3SiPh	10:90	8	80
3	$HSiCl_3$	0:100	24	46
4	$HSi[(CH_3)_3SiO]_3$	n/a	48	0

[a] Dihydro = 1,2-dihydroquinoline and tetrahydro = 1,2,3,4-tetrahydroquinoline.

[1] ≡SiH=organosilane.

Table 2
Influence of solvent in the reaction of quinoline with H_3SiPh

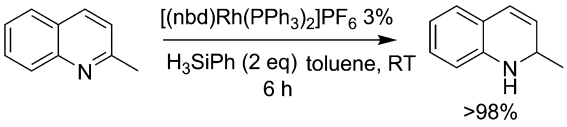
Entry	Solvent	Time (h)	Yield (%)	Product (dihydro:tetrahydro)[a]
1	Toluene	24	98	57:43
2	THF	24	94	45:55
3	DCM	24	72	42:58
4	MeCN	48	0	n/a

Conditions: 3 mol % $[Rh(nbd)(PPh_3)_2]$ PF_6 and room temperature, 24 h.
[a] Products as in Table 1; DCM = dichloromethane.

In an effort to make the reaction selective for either one of the two products, we examined variations in solvent, temperature of the reaction and the amount of silane. Table 2 shows that the reaction is strongly favored by non-polar solvents, and that increasing solvent polarity or coordinating power can be deleterious. For example, toluene and THF were highly satisfactory, but MeCN failed.

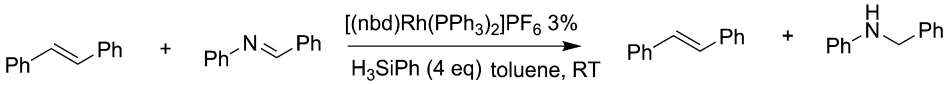
Table 3 shows that low temperature favored the dihydro product but conversion was low, perhaps because of reduced catalyst solubility at −20 °C. A temperature of −10 °C provides a convenient selectivity-activity compromise.

In reactions catalyzed by $[Rh(cod)(PPh_3)_2]PF_6$ the fraction of dihydro product was somewhat smaller than with $[Rh(nbd)(PPh_3)_2]PF_6$. This would imply that changing the olefin ligands affects not only the activation, but presumably somewhat different active catalysts may be formed in the two cases. This could be due to the fact that unlike the more reactive norbornadiene, cyclooctadiene is not completely removed from the metal by reaction with the silane. These reactions must be performed under anhydrous conditions to give optimal yields presumably due to sensitivity of the silane to catalyzed hydrolysis. The dihydro/tetrahydro ratio is somewhat variable depending on the purity of the silane and solvent used, but the yield always remains above 95%. The formation of dihydro product is enhanced in NMR scale reactions with fresh silane and anhydrous deuterated toluene (>98%, 97:3 dihydro/tetrahydro, Eq. (6)), while in larger scale reactions using dried reagent-grade toluene, the dihydro product is slightly less favored (>95%, 87:13 dihydro:tetrahydro). Excess silane was found to be necessary for optimal yields but no direct correlation was found between amount of silane used and dihydro/tetrahydro ratio.



(6)

In no case was a product containing a C–Si bond obtained in any of the reactions studied. In a competition experiment between *trans*-stilbene and *N*-benzylideneaniline under the catalytic conditions of Eq. (7), the only product observed was the hydrogenated imine; the stilbene was not consumed under the reaction conditions. Thus our reaction conditions are not effective for standard hydrosilylation of olefins, accounting for the fact that we do not observe silicon–carbon bonds in the products from quinoline.



(7)

Table 3
Variation of temperature in the reaction of 2-methyl quinoline with phenylsilane

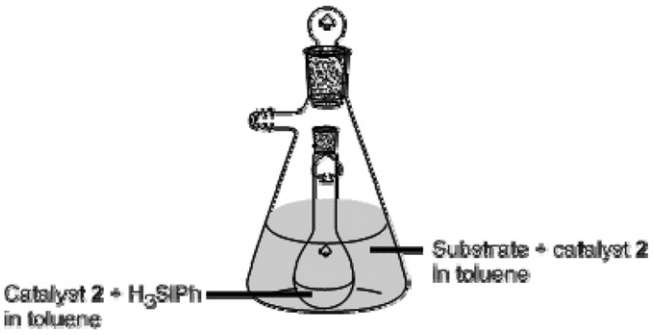
Temperature (°C)	% Conversion	Product (dihydro:tetrahydro)[a]
−20	14	93:8
−10	70	84:16
0	78	75:25
25	98	57:43
90	70	28:72

Conditions: 3 mol% $[Rh(nbd)(PPh_3)_2]$ PF_6, 24 h.
[a] Products as in Table 1.

If the $PhSiH_3$ and catalyst are combined in the absence of substrate, a gas is evolved over a few minutes. If the gaseous products of this reaction are released into the open air, they spontaneously inflame. This, taken with the formation of 1 equiv. Ph_2SiH_2 strongly implies that the disproportionation of $PhSiH_3$, as shown in Eq. (8), is catalyzed under these conditions. Indeed, the disproportionation proceeds essentially to completion over 20–30 min as judged by the formation of Ph_2SiH_2. Rh-catalyzed disproportionations of silanes have been reported previously [33]. Confirmation of the identity of the gaseous product as SiH_4 was obtained from GC–MS data acquired for the reaction of phenylsilane in toluene solution catalyzed by **2**. This gave a set of intense peaks from 28 to 32 *m*/*z*. No prior report of the mass spectral characteristics of SiH_4 seems to exist, but we propose that this pattern (see Section 4) constitutes the signature of SiH_4. In a control experiment involving phenylsilane in the absence of catalyst but under otherwise identical conditions, no peaks were observed at 28–32 *m*/*z*, but a similar pattern of multiple peaks was seen at 105–108 *m*/*z* that we assign to phenylsilane.

$$H_3SiPh \xrightarrow{catalyst} H_2SiPh_2 + H_4Si \quad (8)$$

A possible mechanism may involve initial hydrosilylation of the C=N bond, followed by isomerization of the C=C bond to the imine position. The presence of excess silane is thus necessary for the second hydrosilylation. The stoichiometry of the reaction involves two moles of $PhSiH_3$ for the dihydro product, suggesting one mole of SiH_4 is

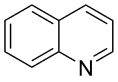
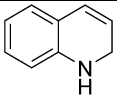
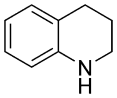
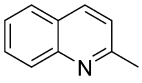
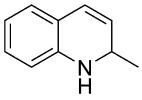
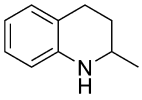
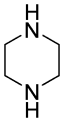
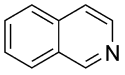
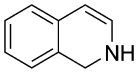
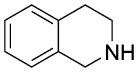
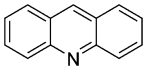
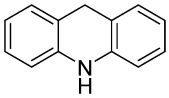
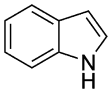
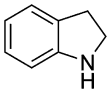


Scheme 1.

sufficient for this step, so each SiH_4 provides two hydrogens in the final product. The stoichiometry of the hydrosilylation of the imine is therefore most consistent with the mechanism of Eq. (1) where 1 mole of SiH_4 is required.

The disproportionation raises uncertainty about the active reductant in these reactions. $PhSiH_3$ is an unlikely candidate because it is depleted by disproportionation at a much faster rate than the rate of hydrogenation. In an attempt to identify the reductant, we conducted a reaction in which a solution of $PhSiH_3$ and rhodium catalyst was placed in a small vessel enclosed within a larger container holding the substrate and catalyst in toluene solution (Scheme 1). This ensured that essentially only the volatile SiH_4 was able to diffuse into the larger closed vessel and react with the catalyst and substrate. Within 12 h the hydrogenated product was indeed formed in the outer vessel, albeit in a slightly reduced yield (68%). We also tested whether the rhodium catalyst is involved in the reaction with substrate, or if its role is limited to producing reactive silane gas which attacks the quinoline directly. We thus repeated the reaction described above using the same two vessels, but omitting the catalyst from the outer vessel so that the gas produced was allowed to react with the substrate alone. These reactions did not show any product formation, indicating that the rhodium catalyst acts first to disproportionate phenylsilane, and then also to catalyze the reaction between the substrate and the gas produced from this reaction. Diphenylsilane, as noted earlier, was

Table 4
Regioselective reduction of *N*-heteroaromatic compounds by (a) hydrosilylation using 3 mol% **1** and 4 equiv. silane, in toluene at room temperature and (b) transfer hydrogenation using 1 mol% **3** in isopropanol 0.5 equiv. K_2CO_3 at 82 °C for the time specified

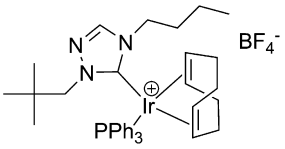
Entry	Substrate	Product	Hydrosilylation		Transfer hydrogenation	
			Yield (%)	Time (h)	Yield (%)	Time (h)
1			>95	6	–	–
			–	–	67	24
2			>95	6	–	–
			–	–	50	24
3			10	12	100	24
4			5	12	0	0
			87	12	0	24
5			93	12	<5	24
6			82	12	<5	24

found to be inactive for this reaction. In a further control, catalyst was omitted from the inner vessel to check that $PhSiH_3$ alone is not equally capable of carrying out the reaction by diffusion into the outer vessel; a much lower yield of hydrogenation product was obtained (14%), resulting from the insufficient volatility of this silane.

No extensive mechanistic information is yet available but some further observations were made. No *N*-silyl intermediates were ever observed, so if the direct hydrosilylation mechanism of Eq. (1) applies, spontaneous hydrolysis of the N–Si bond must occur under the reaction conditions. The pathway of Eq. (2) involving silane hydrolysis could not be definitively eliminated, however careful drying of the solvents did not lower the efficiency of the reaction and addition of water was deleterious.

2.2. Transfer hydrogenation

Prior work in our group has shown that catalyst **3** is particularly active for the reduction of imines under transfer hydrogenation conditions [32]. To test this catalyst for transfer hydrogenation of nitrogen heterocycles, we initially took quinoline as substrate. Treatment of quinoline (1 mmol) with 0.5 equiv. K_2CO_3 and 10 mL of *i*-PrOH under refluxing conditions for 24 h with 1 mol% of iridium catalyst **3** yielded 67% of 1,2,3,4-tetrahydroquinoline. The rhodium analogue also gave similar results, but the use of the iridium catalyst is preferable due to its lower cost. We achieved a TON of 67 which is comparable to a rhodium bis-bipyridine complex (TON = 54, $T = 82$ °C) [36]. Catalyst **1**, $[Rh(cod)(PPh_3)_2]PF_6$, was not active under these conditions (<5% conversion to 1,2,3,4-tetrahydroquinoline).



Attempts to extend this methodology to other heteroaromatic compounds showed that the method is not yet general (Table 4). Only one other substrate, pyrazine, showed complete conversion. On the hypothesis that the nitrogen lone pairs of the substrate were blocking the catalytic sites, two of the heterocyclic substrates pyridine and 2,2′-bipyridine were *N*-methylated to give 1-methylpyridinium iodide and 1-methyl-2,2′-bipyridinium iodide respectively. These modified substrates, however, did not react. Future work may identify the right conditions to extend the generality of this procedure.

Similar results were obtained using a different hydrogen source (HCOOH) and no base. Treating 1 mmol of quinoline with 1 equiv. HCOOH and 1 mol% catalyst **3** yielded

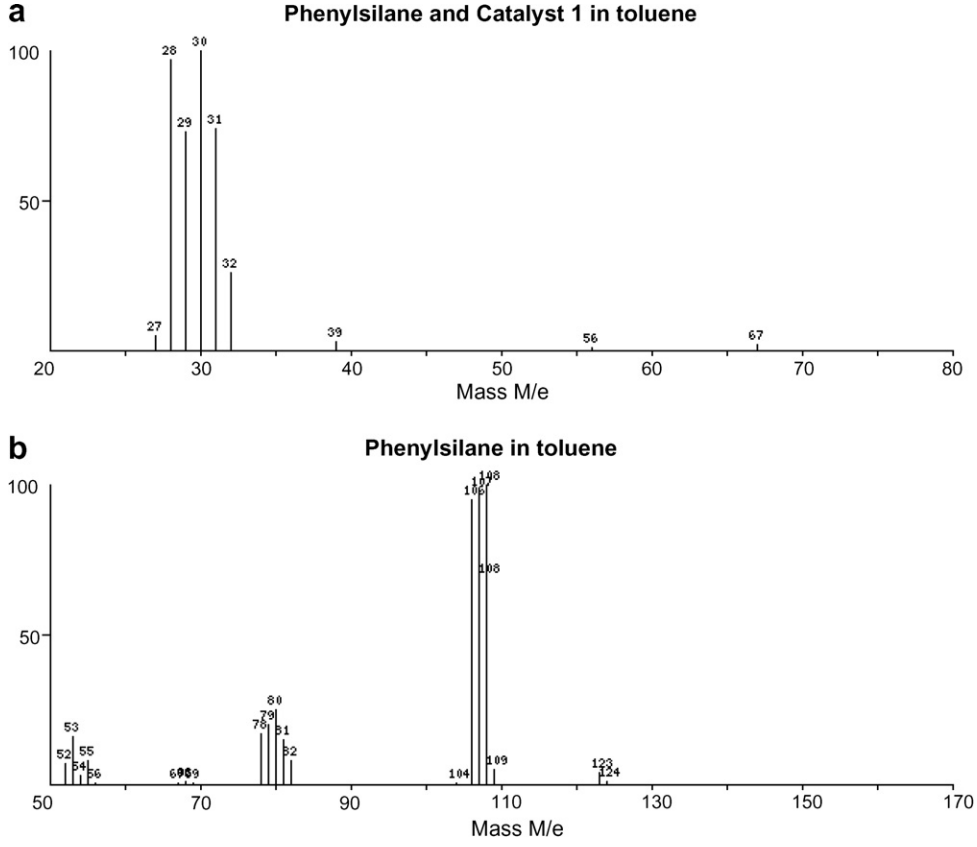
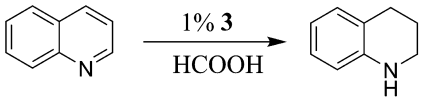


Fig. 1. Mass spectra of the vapor phase from (a) the reaction of phenylsilane in toluene solution catalyzed by **2** and (b) of phenylsilane in toluene in the absence of catalyst **2**.

40% of 1,2,3,4-tetrahydroquinoline at 80 °C. Increasing the quantity of HCOOH to 5 equiv. increased the yield to 60%. No further improvement was seen with higher amounts and this method was equally limited in its scope (Eq. (9)). In no case was the dihydroquinoline ever seen.



1 eq HCOOH, 40% yield
5 eq HCOOH, 60% yield (9)

2.3. Generality/selectivity of methods

A variety of heterocycles were surveyed as substrates for reduction using both methods. For hydrosilylation, the quinolines, acridine and indole all gave the dihydro products in satisfactory yield. Isoquinoline gave a mostly the tetrahydro product. Pyrazine was inefficiently reduced to the tetrahydro compound, however. Transfer hydrogenation showed less generality, only the quinolines and pyrazine being efficiently reduced to the tetrahydro products. 7,8-benzoquinoline gave no products under either conditions, perhaps because this substrate cyclometallates very easily. For a fuller list of substrates, see Supplementary Material.

3. Conclusions

We have shown two mild and versatile routes the regioselective hydrogenation of quinoline derivatives without the use of high pressures of hydrogen gas. Hydrosilylation offers a selective reduction of the quinoline to dihydroquinoline, which is not possible with direct hydrogenation, while transfer hydrogenation uses only isopropanol as a hydrogen source. The reaction is very selective for particular substrates. The disproportionation of phenylsilane by $[Rh(cod)(PPh_3)_2]PF_6$ observed is of potential use in gaining access to silane (SiH_4), otherwise not readily available.

4. Experimental

4.1. General considerations

All the operations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene was distilled from sodium-benzophenone. All starting materials and reagents were obtained from commercial sources and used as received unless otherwise noted. All glassware was dried overnight prior to use. ^1H, ^{13}C and ^{31}P NMR spectra were obtained using a Bruker spectrometer operating at 400 MHz or 500 MHz. Chemical shifts are reported in ppm with the residual solvent peak as an internal reference. $[Rh(nbd)Cl]_2$ was prepared by the method of Abel [34], while $[Rh(cod)(PPh_3)_2]PF_6$ and $[Rh(nbd)(PPh_3)_2]PF_6$ were prepared by the method of Schrock [35]. Preparation of compound **3** has also been previously described [32]. Silane (SiH_4) is a potentially hazardous, pyrophoric material implying that particular care is needed in carrying out these reactions.

4.2. Hydrosilylation reactions

4.2.1. Example of general procedure: preparation of 1,2-dihydroquinaldine

A flame-dried Schlenk tube was charged with $[Rh(cod)(PPh_3)_2]PF_6$(10.0 mg, 10.2 μmol), 1,3,5-tri-*tert*-butylbenzene as internal standard, a stir bar and placed under a nitrogen atmosphere. Toluene (1.00 mL) was added via syringe, followed by quinaldine (50.0 μL) and then phenylsilane (200 μL) in quick succession. After stirring at room temperature for 6 h, the flask was flushed with nitrogen gas, then carefully opened. 1 mL of a 1:15 solution of 50% aqueous NaOH/methanol was added dropwise over 5 min. After 10 min of additional stirring, the solvent was removed and the residue was dissolved in 2 mL dichloromethane and extracted with water. The organic fractions was dried over $MgSO_4$ and purified by flash chromatography on silica gel. ^1H and ^{13}C NMR spectra were compared with literature data for all products.

4.2.2. Mass spectral identification of SiH_4

A 1-mL vial fitted with a screw cap with a septum was charged with a stir bar and $[Rh(nbd)(PPh_3)_2]PF_6$ (**2**) (10.0 mg, 10.2 μmol) under an inert atmosphere. Toluene (0.10 mL) was added, and the catalyst was allowed to dissolve with stirring. Phenylsilane (300 μL) was added and reaction was stirred for additional 10 min. The evolution of a gas was observed. The gas from the headspace of the vial was injected into a GC–MS, and two peaks were observed – one, with retention time 1.62 min, with a mass spectrum of 28–32 *m*/*z* (Fig. 1a) and another at 2.71 min, which gave a major set of peaks at 105–108 *m*/*z* (Fig. 1b).

In a control experiment, identical to the one above but without catalyst **2**, only one peak was observed in the GC trace at 2.71 min retention time, with a mass spectrum identical to that of Fig. 1b.

4.3. Transfer hydrogenation of quinoline

4.3.1. General procedure for reduction of heterocycles with isopropanol

An oven-dried flask was charged with quinoline (118 μL, 1.00 mmol), K_2CO_3 (69 mg, 0.50 mmol), 1,3,5-tri-*tert*-butylbenzene as internal standard and the catalyst $[Ir(cod)(NHC)PPh_3]BF_4$(**3**) (8.4 mg, 9.95 μmol) at 1.0% loading. The flask was evacuated and filled with N_2, 10.0 mL of dry degassed *i*-PrOH was added, and the mixture refluxed for 24 h. An aliquot (0.50 mL) of the mixture was quenched with 2 mL of pentane and the resulting solution was filtered through Celite to remove insoluble inorganic material. The volatiles were then removed under vacuum and the conversion was checked with ^1H NMR. The conversion is based on moles of substrate and compar-

ison to internal standard. The data reported are based on an average of two catalytic runs.

4.3.2. General procedure for reduction of quinoline with HCOOH

An oven-dried flask was charged with quinoline (118 μL, 1.00 mmol), 1,3,5-tri-*tert*-butylbenzene as internal standard, HCOOH acid (185 μL) (5 equiv.) and the catalyst $[Ir(cod)(NHC)PPh_3]BF_4$ (**3**) (8.4 mg, 9.95 μmol) at 1.0% loading. The flask was then evacuated and filled with N_2. The mixture was then placed in an oil bath at 82 °C to reflux for 24 h. The mixture was then quenched with pentane (2 mL) and the resulting solution filtered through Celite to remove insoluble inorganic material. The volatiles were then removed under vacuum and the conversion checked with ^1H NMR. The conversion is based on moles of substrate and comparison to internal standard. The data reported are based on an average of two catalytic runs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.02.004.

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