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Reduction of Alkyl Halides by Triethylsilane Based on a Cationic Iridium Bis(phosphinite) Pincer Catalyst: Scope, Selectivity and Mechanism

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Abstract: A highly efficient procedure for the reduction of a broad range of alkyl halides by triethylsilane based on a cationic iridium bis(phosphinite) pincer catalyst has been discovered and developed. This reduction chemistry is chemoselective and has unique selectivities compared with conventional radical-based processes and the aluminum trichloride/triethylsilane ($AlCl_3/Et_3SiH$) and triphenylmethyl tetrakis[pentafluorophenyl]borate/triethylsilane {$[Ph_3C]$ $[B(C_6F_5)_4]/Et_3SiH$} systems. Reductions use three equivalents of triethylsilane relative to the halide and can be carried out with very low catalyst loadings and in a solvent-free manner, which may provide an environmentally attractive and safe alternative to many currently practiced methods for reduction of alkyl halides. Mechanistic studies reveal a unique catalytic cycle. The cationic iridium hydride 2,6-bis[di-(*tert*-butyl)phosphinyloxy)phenyl-(hydrido)iridium, $(POCOP)IrH^+$ {POCOP = 2,6-$[OP(t\text{-}Bu)_2]_2C_6H_3$} binds and activates the silane. This complex serves as a potent silylating reagent to generate silyl halonium ions, Et_3SiXR^+, which are reduced by the neutral iridium dihydride to yield alkane product and regenerate the cationic $(POCOP)IrH^+$, thus closing the catalytic cycle. All key intermediates have been identified by *in situ* NMR monitoring and kinetic studies have been completed. An application of this reduction system to the catalytic hydrodehalogenation of a metal chloride complex is also described.

Keywords: alkyl halides; chemoselectivity; mechanistic studies; reduction; silanes; solvent-free process

Introduction

Reduction of alkyl halides to alkanes is a frequently practiced synthetic transformation. The most common method employed is the use of Bu_3SnH in a radical chain process.[1] While this is an efficient process, alternative reduction methods are desired owing to the toxicity of tin reagents and difficulties in work-up and separation of tin halide by-products from the desired organic products.[2] Other organometallic compounds such as Bu_3GeH and RHgH complexes have been explored as alternatives to Bu_3SnH as halide reducing agents, but they are not viable options for many applications due to high cost or high toxicity.[2,3]

Although thermodynamically feasible, the use of readily available and inexpensive trialkylsilanes in place of tin hydrides for reduction is not effective due to the high bond energy of the Si–H bond which will not support a radical chain process.[2] It was demonstrated that silicon-hydrogen bonds can be weakened by substitution of silyl groups on the Si–H group.[2] Tris(trimethylsilyl)silane (TTMSS), therefore, is an efficient hydrogen donor and was developed by Chatgilialoglu et al. as a new free radical reducing reagent.[2] However, this TTMSS reagent is not economically attractive and not easily made. It has also been reported that Et_2SiH_2 and Et_3SiH can reduce certain classes of alkyl halides to the corresponding alkanes in the presence of a suitable initiator and alkanethiols as polarity reversal catalysts.[2,4]

Strong Lewis acids like $AlCl_3$ have been explored to mediate the reduction of alkyl halides by Et_3SiH.[5a] Extensive skeletal rearrangements or Friedel–Crafts alkylation can occur accompanying this reduction chemistry. High loadings of Pd(II) salts have been reported to induce Et_3SiH reduction of certain classes of alkyl halides.[5b] P,N-chelated Pt(II) complexes in combination with $HSiMe_2Ph$ have also been shown to reduce alkyl chlorides and the following order of reactivity was observed: $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$.[5c]

The combination of $[Ph_3C]$ $[B(C_6F_5)_4]$ and Et_3SiH was recently demonstrated by Ozerov and co-workers to be capable of catalytic reduction of C(sp^3)–F

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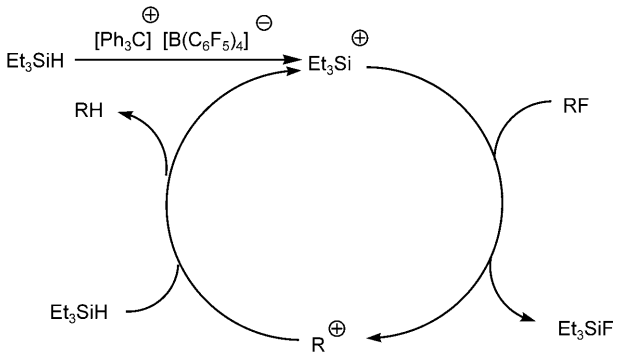
bonds *via* a mechanism involving generation of carbocations through fluoride abstraction by Et_3Si^+ followed by hydride transfer to the carbocation by Et_3SiH (Scheme 1).[6a,b] Müller has described similar chemistry using hydride- and fluoride-bridged disilyl cations.[6c]



Scheme 1. Proposed mechanism for reduction of alkyl fluorides with the $[Ph_3C]$ $[B(C_6F_5)_4]/Et_3SiH$ system.[6a]

As a part of our continuing interest in incorporation of Si–H bond activation chemistry into catalytic cycles we have discovered and recently communicated[7] that the cationic iridium bis(phosphinite) pincer complex **1** (Figure 1) is a highly efficient catalyst for

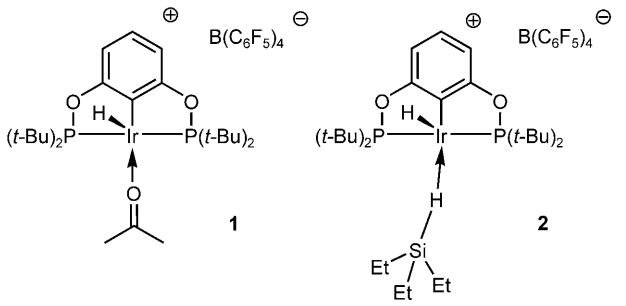


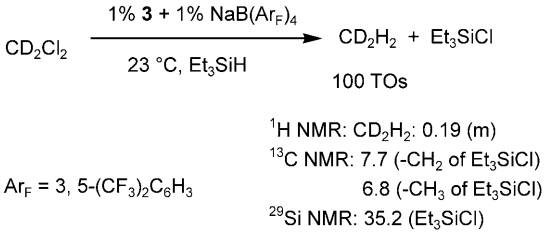
Figure 1. Cationic iridium pincer catalysts **1** and cationic iridium η^1-silane complex **2**.

the reduction of a broad range of alkyl halides by triethylsilane reagents. Our preliminary studies argue against a radical pathway and the catalytic cycle appears to operate by a unique process involving an unprecedented highly electrophilic η^1-silane complex, **2**[8] (Figure 1). In the present paper, we report a full account of this chemistry including catalyst discovery and development, substrate scope and selectivity and mechanistic studies. In addition, this reduction chemistry has also been extended to the catalytic hydrodehalogenation of a metal halide complex.

Results and Discussion

Initial Observations and Synthesis of an Active Well-Defined Iridium Catalyst

Previously we have shown that iridium bis(phosphinite) pincer complexes are precursors to highly active catalysts for the transfer dehydrogenation of alkanes[9] and are capable of N–H bond activation.[10] Abstraction of chloride from (POCOP)Ir(H)(Cl) {**3**, POCOP = 2, 6-$[OP(t\text{-}Bu)_2]_2C_6H_3$} with $NaB(Ar_F)_4$ [Ar_F = 3,5-$(CF_3)_2C_6H_3$], generates a solvated cationic iridium monohydride *in situ*, which was found to catalyze the reduction of dichloromethane to methane by Et_3SiH at room temperature with 100 turnovers (TOs) (Scheme 2).



Scheme 2. Initial discovery of iridium-catalyzed reduction of CD_2Cl_2 to CD_2H_2 by Et_3SiH.

Interestingly, since CD_2HCl should be the initial reduction product of CD_2Cl_2, the observation that only traces of CD_2HCl were identified during the reduction of CD_2Cl_2 indicates that the reduction of CD_2HCl is much more rapid than that of CD_2Cl_2. This observation suggests that this reduction chemistry probably does not go through the conventional radical-based process. The combination of a novel mechanism and practical utility strongly encouraged us to explore the scope, selectivities and mechanism of this reduction chemistry.

The inactivity of Ir(POCOP)HCl (**3**) under identical conditions for reduction of CD_2Cl_2 excludes the possibility of **3** as the catalytically active species for this reduction. Similarly, $NaB(Ar_F)_4$ was excluded as the active species. Thus, the catalytically active species must be the *in situ* generated cationic monohydride complex from the reaction between Ir(POCOP)HCl and $NaB(Ar_F)_4$.

Catalysis with the *in situ* generated complex sometimes produces inconsistent results; therefore, the cationic iridium dichloromethane complex, $(POCOP)Ir(H)(CH_2Cl_2)^+$ $B(Ar_F)_4^-$, **4**, was synthesized and isolated by treatment of **3** with a slight excess of $NaB(Ar_F)_4$ in dichloromethane [Eq. (1)]. Complex **4** was characterized by NMR spectroscopy and elemental analysis (see Experimental Section).

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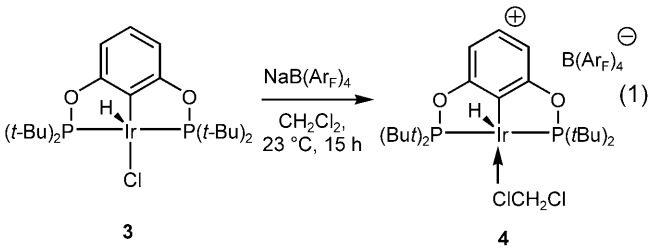
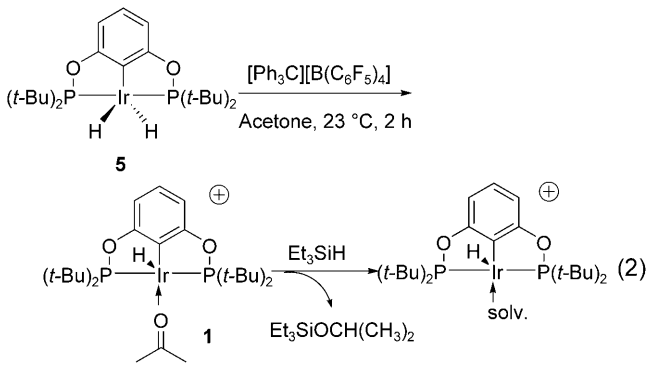


Complex **4** was found to be an efficient catalyst for the reduction of a variety of alkyl chlorides and bromides. However, at higher reaction temperatures (60 °C or 110 °C) and with certain substrates, a small amount of Et_3SiF was identified by ^{13}C and ^{19}F NMR, presumably due to the attack of "Et_3Si^+" on the $B(Ar_F)_4^-$ counteranion.[11] To generate a more stable catalyst, we sought to replace $B(Ar_F)_4^-$ by the $B(C_6F_5)_4^-$ counteranion.

Reduction of Alkyl Halides with Et_3SiH Catalyzed by Iridium Acetone Complex (1)

Synthesis and isolation of **4** possessing a $B(C_6F_5)_4^-$ counteranion is not straightforward. The chloride abstraction route analogous to that described in Eq. (1) is not very efficient under several conditions presumably due to the poor solubility of $KB(C_6F_5)_4$ in CH_2Cl_2 and the strong Ir–Cl bond. An alternate synthetic route (involving hydride transfer) was then employed. Acetone complex **1** is readily prepared by treatment of dihydride **5**[12] with $[Ph_3C]$ $[B(C_6F_5)_4]$ in acetone [Eq. (2)].[7] Complex **1** is significantly more stable than **4** due to the strong coordinating ability of acetone and can be stored in a dry box at room temperature for at least 1 year. Exposure of **1** to Et_3SiH results in rapid hydrosilation of acetone and forms noncoordinating $(CH_3)_2CHOSiEt_3$ and the highly reactive solvated complex which initiates reduction reactions [Eq. (2)]. Thus **1** is an ideal initiator for catalytic reductions.



A broad spectrum of alkyl halides was conveniently reduced by triethylsilane in the presence of 0.5 mol% (or less) of **1** at 23–60 °C in chlorobenzene. Fluorobenzene, dichlorobenzene or even neat alkyl halides (see below) have also proved to be suitable solvents. Results of typical reactions are illustrated in Table 1. Conversions were determined by NMR spectroscopy. Entries 1 and 2 show that highly efficient reduction of benzyl halides can be achieved at 23 °C with 0.5% catalyst loading. With 0.01% **1** 3200 turnovers (TOs) for the reduction of benzyl chloride were obtained after 29 h at 23 °C. At 0.075% catalyst loading rapid and complete reduction of benzyl bromide to toluene is accomplished in 2.5 h.

Results for the reduction of primary alkyl halides are shown in entries 3–7. Rapid reductions of 1-bromopentane and 1-chloropentane occur at 60 °C; note that the bromide (1.5 h) is reduced faster than the chloride (7 h). Surprisingly, reduction of iodide is very slow; 48 h are required for complete conversion of 1-iodopentane to pentane at 60 °C with 0.5% loading of **1**. Entry 6 shows that 1-fluoropentane can also be reduced at 2% catalyst loading at 60 °C although with reduced efficiency (46 TOs based on loss of C–F bonds) and selectivity (unidentified products in addition to pentane are observed). Similarly, efficient reductions of secondary halides can be accomplished at either 23 or 60 °C (entries 8–11) and again bromides are more reactive than chlorides. Bromocycloheptane is efficiently and selectively reduced to cycloheptane without observation of any skeletal rearrangement product, methylcyclohexane (entry 11). The tertiary chlorides, *t*-pentyl chloride and trityl chloride, are rapidly reduced at 23 °C (entries 12 and 13).

Catalytic reductions can also be carried out in a solvent-free manner as illustrated in Table 2. Thus complete reduction of neat benzyl chloride can be achieved with 0.5 mol% catalyst loading in less than 20 min at room temperature (entry 1). Similarly, primary and secondary chlorides and bromides are reduced efficiently at 23 °C without a solvent (entries 2–5).

Competition Experiments to Determine Relative Reactivities: Comparison with Conventional Radical-Based Reduction Chemistry

In radical-based reduction processes the general order of reactivities is RI > RBr > RCl and 2° RX > 1° RX (2° RX = secondary alkyl halides; 1° RX = primary alkyl halides).[1] Quite different selectivities are seen for the **1**/Et_3SiH system. Relative reduction rates of 1° RX *vs.* 2° RX were determined by carrying out head-to-head competition experiments in one flask. These results were previously described in detail[7] and provided the following relative reactivities:

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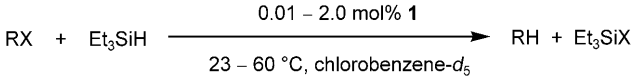
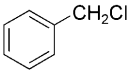
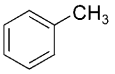
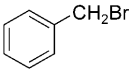
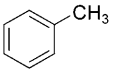
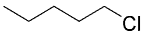
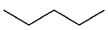
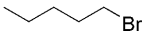
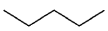
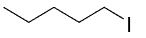
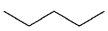
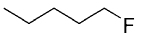
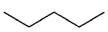
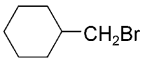
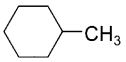
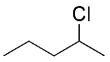
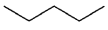
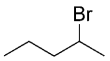
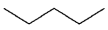
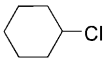
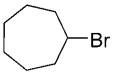
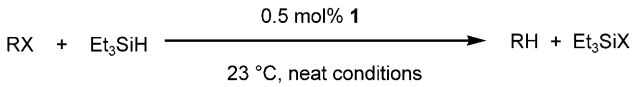
Table 1. Iridium-catalyzed reduction of alkyl halides by Et_3SiH.[a]

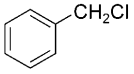
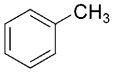
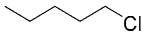
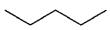
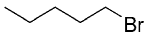
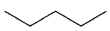
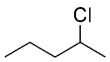
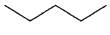
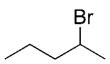
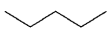


Entry	Catalyst [mol%]	RX	Temperature [°C]	Time [h]	Conversion[c][%]	Product
1	0.5		23	0.3	>99	
	0.01[b]		23	29	32	
2	0.5		23	0.3	>99	
	0.075		23	2.5	>99	
3	0.5		60	7	>99	
4	0.5		60	1.5	>99	
5	0.5		60	48	>99	
6[d]	2.0		60	50	92	
7	1.0		23	51	>99	
8[e]	0.5		60	2.3	>99	
9[e]	0.5		60	0.7	>99	
10[e]	0.5		60	16	>99	
11[e]	0.5		23	0.3	>99	
12[e]	0.5		23	0.3	>99	
13	0.5		23	0.3	>99	

[a] *Reaction conditions:* 3 equiv. of Et_3SiH.
[b] Reduction was carried out in $C_6D_4Cl_2$.
[c] Determined by loss of alkyl halides by NMR.
[d] Products in addition to pentane are observed.
[e] In addition to alkane, traces of olefin and H_2 were observed which convert to alkanes at longer reaction times.

Table 2. Solvent-free reduction of alkyl halides with Et_3SiH catalyzed by **1**.[a]



Entry	RX	Time [h]	Conversion[b] [%]	Product
1		0.3	99	
2		20	86	
3		3.3	98	
4[c]		9	99	
5[c]		3.3	98	

[a] Reaction conditions: 3 equiv. of Et_3SiH.
[b] Determined by loss of alkyl halides by NMR.
[c] In addition to alkane, traces of olefin and H_2 were observed and converted to alkanes at longer reaction times.

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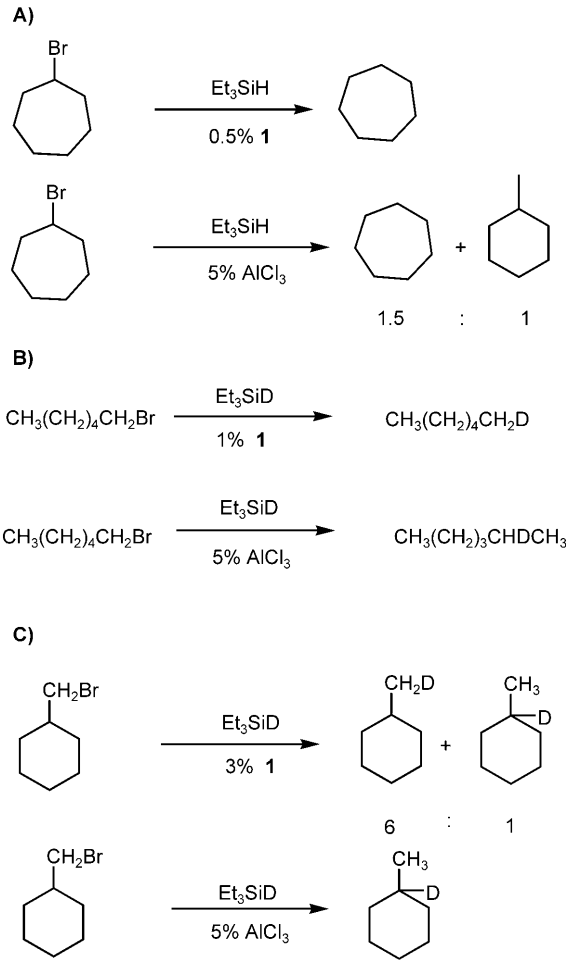
1° RCl:2° RCl = 2.6:1.0, 1° RBr:2° RBr = 2.0:1.0, 1° RI:2° RI = 1.6:1.0.

Entries 3–5 in Table 1 show surprising relative reactivities of primary chloride *vs.* primary bromide *vs.* primary iodide with RBr > RCl > RI when reductions are carried out in separate flasks. Entries 8 and 9 show a similar order for secondary bromide *vs.* secondary chloride. Quite different results were obtained when head-to-head competition experiments were carried out in the same flask. Using primary halides, relative reactivities were found to be RI:RCl = 1200:1, RBr:RCl = 260:1, RI:RBr = 80:1.[7] Only traces of CD_2HCl were observed during the reduction of CD_2Cl_2 by **1**/Et_3SiH which shows that CD_2HCl is reduced much faster than CD_2Cl_2, a result which is also inconsistent with a radical mechanism. Qualitative comparisons of selectivities of radical-based reduction of alkyl halides and reductions employing **1**/Et_3SiH are shown in Scheme 3.

Conventional Bu_3SnH-based method:	1/ Et_3SiH process:
RI > RBr > RCl	RI > RBr > RCl (head-to-head competition)
RF no reaction	RBr > RCl > RI (separate flasks)
3° RX > 2° RX > 1° RX	1° RX > 2° RX (head-to-head competition)
$CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$	$CH_3Cl > CH_2Cl_2$

Scheme 3. Selectivities for alkyl halide reductions observed in the **1**/Et_3SiH system compared with conventional radical-based reductions.



Scheme 4. Comparison of reductions using **1**/Et_3SiH *versus* $AlCl_3/Et_3SiH$.[5a]

Comparison of 1/Et_3SiH with $AlCl_3/Et_3SiH$

Use of the strong Lewis acid $AlCl_3$ in combination with Et_3SiH was explored by Doyle et al.[5a] to mediate the reduction of alkyl halides. No major difference in reactivities was found between comparable alkyl bromides and chlorides.[5a] Reduction by triethylsilane was often accompanied by Friedel–Crafts alkylation reactions or extensive skeletal rearrangements (Scheme 4).[5a] Rearrangement to methylcyclohexane was observed in the reduction of bromocycloheptane.[5a] Formation of 2-deuteriohexane or 1-deuterio-1-methylcyclohexane from reductions of 1-bromohexane and (bromomethyl)cyclohexane,[5a] respectively, using $AlCl_3/Et_3SiD$ suggested a mechanism involving carbocation-like intermediates in which the carbocation rearrangement precedes the reduction event.

In contrast to the $AlCl_3$-catalyzed process, we observed quite different chemistry for the **1**/Et_3SiH system (Scheme 4). Cycloheptane was the only observable reduction product (>98%) of bromocycloheptane. When treated with Et_3SiD, 1-bromohexane yielded solely 1-deuteriohexane while (bromomethyl)-cyclohexane gave (deuteriomethyl)cyclohexane as the major reduction product and 1-deuterio-1-methylcyclohexane as the minor product (*ca.* 6:1 ratio as determined by $^{13}C\{^1H\}$ NMR spectroscopy). These results show that extensive carbocation isomerizations involving both hydride and alkide shifts are observed in the $AlCl_3$ system in contrast to the $(POCOP)IrH^+$ system where only minor rearrangement occurs in the most favorable circumstances, i.e., 1° to 3° conversions *via* a 1,2 hydride shift. (Additional comments concerning these isomerizations appear below in discussing the overall mechanism.)

Comparison of 1/Et_3SiH with $[Ph_3C]$ $[B(C_6F_5)_4]$/Et_3SiH

The combination of $[Ph_3C]$ $[B(C_6F_5)_4]/Et_3SiH$ was recently reported to catalytically reduce alkyl fluorides *via* a mechanism involving generation of carbocations through fluoride abstraction by Et_3Si^+ followed by hy-

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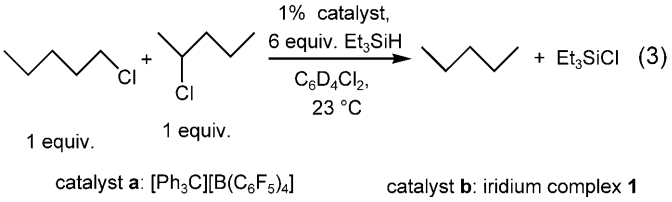
dride transfer to the carbocation by Et_3SiH.[6a] To gain more insight into the (POCOP)IrH$^+$ system studied here, we compared the catalytic reactivities of **1** with $[Ph_3C]$ $[B(C_6F_5)_4]$ for alkyl chloride reductions. Thus a mixture of a 1:1 molar ratio of 1-chloropentane and 2-chloropentane was treated with 6 equiv. of Et_3SiH and 1% catalyst (**a**: $[Ph_3C]$ $[B(C_6F_5)_4]$; **b**: complex **1**) and the reaction was monitored by ^1H NMR spectroscopy [Eq. (3)].



As shown in Figure 2 (*left*), in the $[Ph_3C]$ $[B(C_6F_5)_4]$/Et_3SiH system, the secondary chloride was reduced more rapidly but only up to 80% conversion presumably due to the decomposition of the catalyst. If formation of a carbocation is rate-determining, then this is the expected order. In contrast, in the reduction system based on **1** (Figure 2, *right*), head-to-head competition establishes that the primary chloride is more reactive than the secondary chloride, which is inconsistent with rate-determining formation of a carbocation intermediate.

Mechanistic Studies

In situ ^{31}P and ^1H NMR Monitoring of the Working Catalyst System: Identification of Catalytic Resting State(s) and Key Intermediates

Potential catalytic intermediates were generated independently using methods described in Scheme 5 and their ^{31}P NMR spectra were recorded.[7] To identify

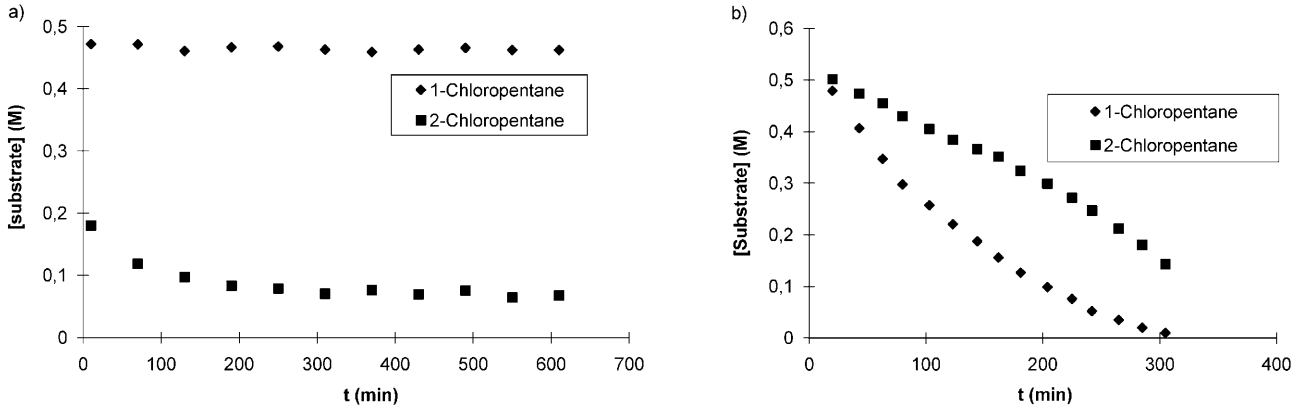
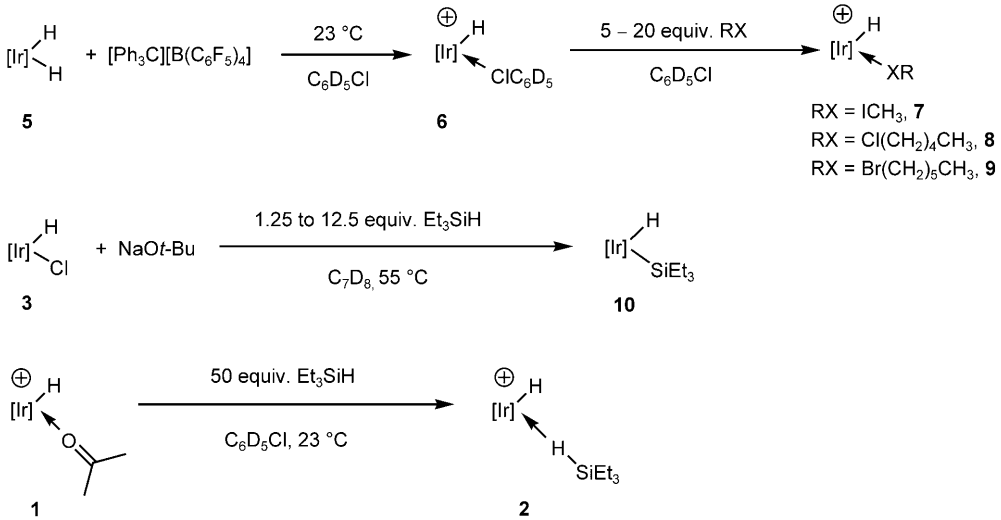


Figure 2. Plot of substrate concentration *vs.* time for reduction of alkyl halides catalyzed by catalyst **a**: $[Ph_3C]$ $[B(C_6F_5)_4]$ (*left*), and by catalyst **b**: iridium complex **1** (*right*).



Scheme 5. Methods for generating potential intermediates.

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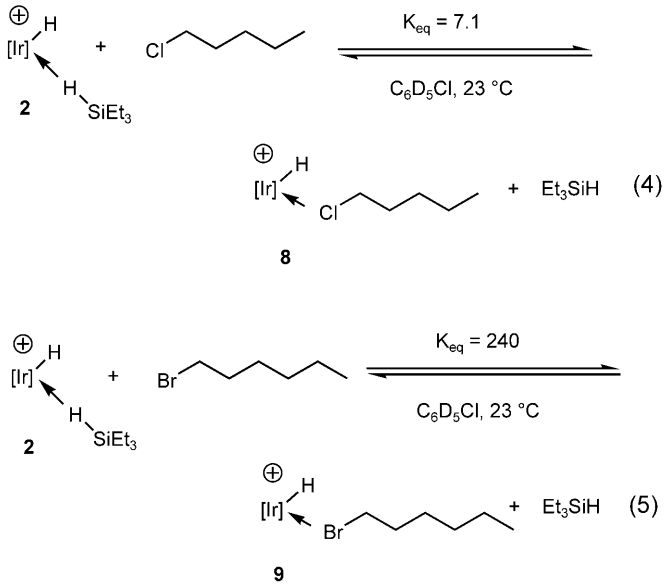
potential catalyst resting states and key intermediates for this process, the reduction of alkyl halides was performed under catalytic conditions and monitored by ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectroscopy.

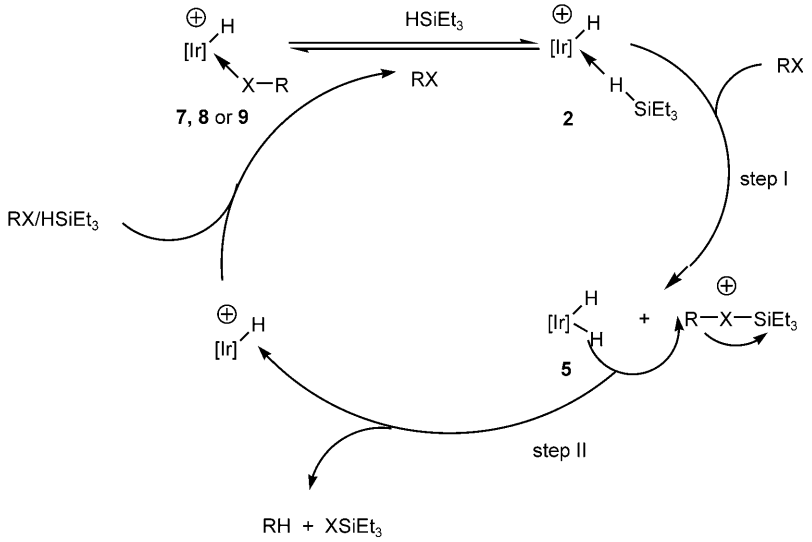
The catalyst resting state(s) were found to depend on the relative binding affinities of the silane and the alkyl halide.[13] Following the *in situ* reduction of CH_3I at 23 °C shows that the dominant iridium species is the CH_3I complex, **7**. However, following the reduction of either 1-chloropentane or 1-bromohexane shows that the Ir species exist as an equilibrium mixture of the halide complex (**8** or **9**) and the silane complex (**2**) with the ratio depending on the ratio of silane:halide and the nature of the halide [Eq. (4) and Eq. (5)]. At several stages of conversion when both the concentrations of silane complex (**2**) and alkyl halide complex (**8** or **9**) could be measured the equilibrium constants were determined to be 7.1 and 240 for reductions of 1-chloropentane and 1-bromohexane, respectively, consistent with the proposition that equilibrium is maintained between the silane complex **2** and the halide complex (**8** or **9**) throughout the catalytic reduction.



The Catalytic Cycle

A plausible catalytic cycle accounting for all observations is shown in Scheme 6. The cationic iridium hydride $(POCOP)IrH^+$ binds and activates the silane. The η^1-silane complex, **2**, serves as a potent silylating reagent to generate silyl halonium ions, Et_3SiXR^+, which are reduced by the neutral iridium dihydride, **5**, to yield alkane product and regenerate the cationic $(POCOP)IrH^+$, thus closing the catalytic cycle. This mechanism has parallels to that proposed by Piers et al.[14] for hydrosilylation of ketones using $(C_6F_5)_3B$/Et_3SiH wherein the silane is activated by $(C_6F_5)_3B$ and transfers Et_3Si^+ to ketone to produce $R_2C{=}OSiR_3^+$ and $H(C_6F_5)_3B^-$. The catalytic cycle is closed by hydride reduction of $R_2C{=}OSiR_3^+$.

The cationic silane complex is in rapid equilibrium with the halide complexes and the position of equilibrium depends on the relative binding affinities and concentrations of the silane and the alkyl halide. The observation that equilibrium is maintained between the silane complex (**2**) and the chloride or bromide complex (**8** or **9**) throughout the catalytic reduction indicates that this equilibrium is established rapidly relative to the reduction. The equilibrium between alkyl iodide complexes and the σ-silane complex was



Scheme 6. Proposed catalytic cycle for iridium-catalyzed reduction of RX by Et_3SiH.

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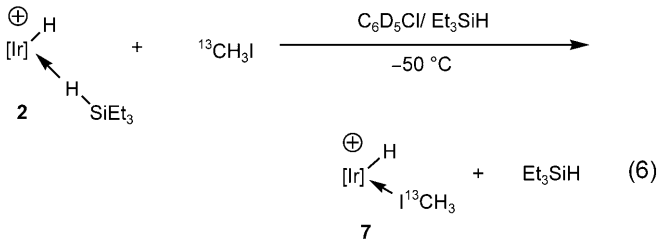
not observable by NMR spectroscopy due to the very low equilibrium concentration of the iridium σ-silane complex due to the much tighter binding of alkyl iodide versus silane to Ir(III). However, a low temperature NMR experiment using ^{13}C-labeled iodomethane shows that the reaction between silane complex (**2**) and $^{13}CH_3I$ *initially* yields the iridium $^{13}CH_3I$ complex (**7**) with no appreciable formation of reduction product $^{13}CH_4$ [Eq. (6)]. Thus the equilibrium between the iodomethane complex (**7**) and silane complex (**2**) is established prior to the reduction event.



(6)

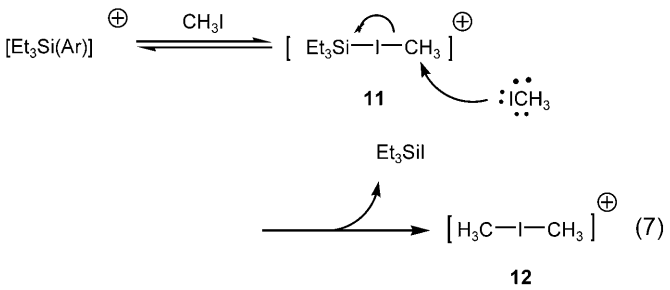
Kinetic studies[7] of the reduction of CH_3I show that the turnover frequency is zero-order in $[CH_3I]$ and first-order in $[Et_3SiH]$, consistent with the proposed catalytic cycle where **7**, $[Ir]H(ICH_3)^+$, is the catalyst resting state. The proposed mechanism explains the differing relative reactivities of halides in separate flasks versus the same flask. Alkyl iodides bind tightly to Ir and result in very low concentrations of complex **2** thus retarding the overall rate. However, the silane complex reacts preferentially with alkyl iodides when offered a choice among alkyl iodides, bromides and chlorides in the "same flask" experiments. Similarly, alkyl bromides are favored over alkyl chlorides in head-to-head competition. This reactivity order is consistent with observations of Reed who has shown that the binding affinities of hexahalo-carborane anions to *i*-Pr_3Si^+ are in the order I > Br > Cl.[15]

Kinetic studies cannot distinguish step I (silylation) or step II (hydride transfer) as the turnover-limiting step, and this may well depend on the nature of the substrate (RCl *vs.* RBr *vs.* RI and 1° RX *vs.* 2° RX *vs.* 3° RX). It is tempting to suggest that the relatively small difference in competitive rates of reduction of 1° and 2° halides indicates that step I, Et_3Si^+ transfer, is turnover-limiting. The basicity of the halide in 1° *vs.* 2° systems should differ little and the steric differences between 1° and 2° substrates should not significantly influence rates of Et_3Si^+ transfer. However, it is known that when Y is an exceptionally good leaving group, relative rates of nucleophilic attack on 1° *vs.* 2° RY systems are compressed due to the high carbocationic character in the transition state.[16] Certainly $XSiEt_3$ species will be excellent leaving groups thus step II cannot be completely discounted as the turnover-limiting step.

The presumed intermediates in the $AlCl_3/Et_3SiH$ and **1**/Et_3SiH systems are Cl_3AlXR and Et_3SiXR^+. The Lewis acidity of Et_3Si^+ is greater than that of $AlCl_3$ so it would seem that Et_3SiXR^+ would be more prone to carbocation rearrangements than Cl_3AlXR. In the case of $AlCl_3/Et_3SiH$ system, Et_3SiH is the hydride donor while in the **1**/Et_3SiH system $(POCOP)Ir(H)_2$ (**5**) is the hydride donor. We have established that **5** is 10^4 times more reactive for reduction of $Et_2OSiEt_3^+$ than Et_3SiH.[17] Thus, more rapid reduction of Et_3SiXR^+ by **5** relative to Et_3SiH reduction of Cl_3AlXR likely explains the observation of a lower fraction of reduction products resulting from carbocation rearrangements in the **1**/Et_3SiH system.

Generation and Reactivity of the Triethylsilyl-(methyl)iodonium Ion,[18–20] $Et_3SiICH_3^+$

To gain deeper insight into the catalytic mechanism we sought to generate the proposed intermediate $Et_3SiICH_3^+$, **11**, and explore its reactivity toward $(POCOP)Ir(H)_2$, **5**. Observation of the kinetic products of reduction of **11** could reveal whether step I or step II was turnover-limiting. If step II were turnover-limiting, Et_3SiH and CH_3I would be initially observed while if step I were turnover-limiting CH_4 and Et_3SiI would be initially observed. Unfortunately, all attempts to cleanly generate **11** at low temperatures always resulted in a mixture of two species. Thus, when *in situ* generated arene-stabilized triethylsilyl cation $[Et_3Si(arene)]^+$ $[B(C_6F_5)]^-$ (arene = C_6D_6 or C_6D_5Cl)[21,19] is treated with a solution of $^{13}CH_3I$ in C_6D_5Cl at −40 °C both the ^{1}H and ^{13}C NMR spectra exhibit two sets of $^{13}CH_3$ resonances. One species exhibits a sharp ^{13}C resonance at $\delta = 10.3$ and a sharp doublet at $\delta = 2.18$ ($^1J_{C,H} = 158$ Hz) in the ^{1}H NMR spectrum. This species can be assigned to dimethyliodonium ion $^{13}CH_3I^{13}CH_3^+$, **12**, previously prepared by Olah.[22] This species presumably forms from attack of $^{13}CH_3I$ on the initially formed $Et_3SiI^{13}CH_3^+$, **11**, as shown in [Eq. (7)].[22] A second set of methyl resonances is observed which consists of a broadened ^{13}C resonance at $\delta = -8$ together with a methyl doublet in the ^{1}H NMR spectrum at $\delta = 1.95$ ($^1J_{C,H} = 157$ Hz). We assign these signals to rapidly averaging signals of



(7)

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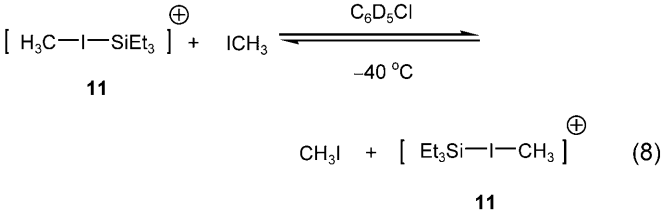
$Et_3SiI^{13}CH_3^+$, **11**, and free $^{13}CH_3I$ in the degenerate exchange equilibrium shown in Eq. (8). In support of this assignment we note that increasing the concentration of free $^{13}CH_3I$ results in moving the averaged ^{13}C shift upfield toward that of $^{13}CH_3I$ ($\delta = -23.4$). As the ^{13}C NMR shift moves upfield, the $^1J_{C,H}$, as measured by the ^1H doublet, decreases consistent with the lower value of $^1J_{C,H}$ in free $^{13}CH_3I$ (151 Hz). It is interesting to note that $CH_3ICH_3^+$ does not engage in CH_3I exchange which implies that CH_3I attacks **11** at Si [Eq. (8)] much more rapidly than it attacks $CH_3ICH_3^+$.

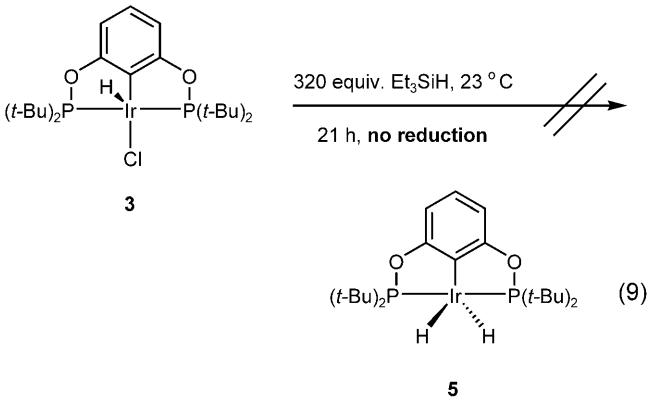


(8)

Upon treating the $-35\,^\circ C$ C_6D_5Cl solution containing **11**, **12** and free $^{13}CH_3I$ with iridium dihydride **5** rapid formation of $^{13}CH_4$ (^{13}C NMR: $\delta = -3.7$, $^1J_{C,H} = 126$ Hz), iridium iodomethane complex, **7** (^{13}C NMR: $\delta = -4.0$, $^1J_{C,H} = 155$ Hz) and free $^{13}CH_3I$ (^{13}C NMR: $\delta = -23.4$, $^1J_{C,H} = 151$ Hz) occurs accompanying disappearance of **11** and **12**. Reduction of **12** will result in production of CH_4 and CH_3I, and any of the (POCOP)IrH$^+$ generated will rapidly bind CH_3I to produce **7**. We cannot quantitate the species sufficiently accurately to determine if **12** is the sole source of methane. In addition, there is sufficient Et_3SiH present from generation of $Et_3Si(arene)^+$ that the change in concentration of Et_3SiH cannot be accurately determined. Thus, these experiments do not provide an answer to which step, I or II, is turnover-limiting. They do however establish that both **11** and **12** rapidly react with dihydride **5** at low temperatures. In addition, the observation of the facile formation of **12** suggests a further potential addition to the catalytic scheme: the initially produced Et_3SiXR^+ species (see Scheme 6) may react with RX to produce RXR^+ which could then be reduced by **5** to give RH and RX.

Catalytic Hydrodechlorination of 3 with Et_3SiH

To further broaden the scope of this reduction chemistry, we have extended it to the catalytic hydrodehalogenation of a metal halide, **3**. While a control experiment shows that there is no reaction of iridium hydrochloride **3** with excess (320 equiv.) Et_3SiH for 21 h [Eq. (9)], it could be readily converted to iridium dihydride **5** in the presence of catalytic amounts of **1** at room temperature in 40 min [Eq. (10)].



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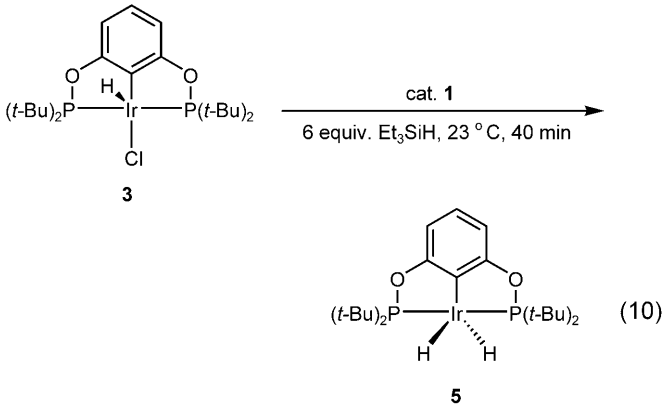

(10)

Conclusions

In summary, we have discovered and developed a highly efficient procedure for the reduction of a broad range of alkyl halides using three equivalents of triethylsilane and a cationic iridium bis(phosphinite) pincer catalyst. This reduction chemistry is chemoselective and has unique selectivities compared with conventional radical-based processes, and the $AlCl_3/Et_3SiH$ and $[Ph_3C]$ $[B(C_6F_5)_4]/Et_3SiH$ systems. In addition, catalyst loadings as low as 0.01% have proved successful and the process can be carried out in a solvent-free manner, which in many cases may provide an environmentally attractive and safe alternative to currently practiced reductions of alkyl halides.

In-depth mechanistic studies have been carried out which have revealed a unique catalytic cycle. The electrophilic iridium hydride complex binds and activates the silane. This complex transfers "Et_3Si^+" to the halide forming a highly active bridged halonium ion which is rapidly reduced by the iridium dihydride remaining following silyl transfer and the cationic iridium hydride complex is thus regenerated. In certain case the intermediate alkyl silyl halonium ions can exhibit β-elimination and carbocationic rearrangements, but generally these are not competitive with reduction

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by the iridium dihydride, **5**. This reduction chemistry has also been extended to catalytic hydrodehalogenation of a metal chloride complex.

Experimental Section

General Considerations

All manipulations were carried out using standard Schlenk, high-vacuum and glove-box techniques. Argon and nitrogen were purified by passage through columns of BASF R3–11 catalyst (Chemalog)[23] and 4 Å molecular sieves. THF was distilled under a nitrogen atmosphere from sodium benzophenone ketyl prior to use. Pentane, dichloromethane and toluene were passed through columns of activated alumina and degassed by either freeze-pump-thaw methods or by purging with argon. Acetone was dried with 3 Å molecular sieves and degassed by freeze-pump-thaw methods. Et_3SiH was dried with $LiAlH_4$ and vacuum transferred into a sealed flask. Et_3SiD was dried with $LiAlD_4$ and vacuum transferred into a sealed flask. All the substrates, 1,3,5-tris(trifluoromethyl)benzene, and all the haloarene solvents were dried with either CaH_2 or activated 4 Å molecular sieves and vacuum transferred to a sealed flask. NMR spectra were recorded on Bruker spectrometers (DRX-400, AVANCE-400, AMX-300 and DRX-500). ^1H and ^{13}C NMR spectra were referenced to residual protio solvent peaks. ^{31}P NMR chemical shifts were referenced to an external H_3PO_4 standard. ^{19}F NMR shifts were referenced to external C_6F_6 [δ $^{19}F(C_6F_6) = -162.9$ *vs.* $CFCl_3$]. ^{29}Si NMR chemical shifts were referenced to external $(CH_3)_4Si$. $K[B(C_6F_5)_4]$ and $NaB(Ar_F)_4$ [$Ar_F = 3,5\text{-}(CF_3)_2C_6H_3$] were purchased from Boulder Scientific and dried under vacuum at 120 °C for 24 h. All other reagents were purchased from Sigma–Aldrich or Strem. (POCOP)Ir(H)$_2$ (**5**)[12], (POCOP)Ir(H)(Cl) (**3**)[9b] and $[Ph_3C]$ $[B(C_6F_5)_4]$[6a] were prepared according to published procedures.

Synthesis of $[(POCOP)Ir(H)(acetone)]^+$ $[B(C_6F_5)_4]^-$, **1**, *in situ* generation of **6–10**, competition experiments to determine relative reactivities of RX (X = Br, Cl, I) and 1° RX *vs.* 2° RX, and kinetic studies of reduction of iodomethane have been previously described in a preliminary communication.[7]

Synthesis of $[(POCOP)Ir(H)(CH_2Cl_2)]^+[B(Ar_F)_4]^-$ $[Ar_F = 3, 5\text{-}(CF_3)_2C_6H_3]$ (4)

A flame-dried Schlenk flask was charged with (POCOP)Ir(H)(Cl) (**3**) (200 mg, 0.319 mmol), and $NaB(Ar_F)_4$ (311 mg, 0.351 mmol) under argon. Dichloromethane (20 mL) was added and the mixture was stirred at room temperature for 15 h. The solution was cooled in an ice bath, and NaCl and excess $NaB(Ar_F)_4$ were removed *via* cannula filtration. The filtrate was concentrated before pentane (40 mL) was added to precipitate an orange solid. The solid was filtered, washed with pentane (5 mL, three times), and dried under vacuum for 2 h to give **4** as an orange powder; yield: 300 mg (61%). ^1H NMR (300 MHz, 23 °C, CD_2Cl_2): $\delta = 7.72$ [s, 8H, $B(Ar_F)_4$], 7.56 [s, 4H, $B(Ar_F)_4$], 7.02 (t, 1H), 6.69 (d, 2H), 5.33 (s), 1.36 (m, 36H), −42.34 (t, 1H, IrH); $^{31}P\{^1H\}$ NMR (162 MHz, 23 °C, CD_2Cl_2): $\delta =$ 177.9; anal. calcd. for $C_{55}H_{54}BF_{24}O_2P_2IrCl_2$ (1538.96): C 42.92, H 3.54; found: C 42.74, H 3.45.

General Procedure for the Reduction of Alkyl Halides Using an *in situ* Generated Catalyst

Chlorobenzene-d_5 (0.5 mL) was added to a J-Young NMR tube charged with **3** (6.3 mg, 0.01 mmol, 1 mol%) and $NaB(Ar_F)_4$ (8.9 mg, 0.01 mmol, 1 mol%). The NMR tube was agitated at room temperature for 1 hour. Triethylsilane (240 μL, 1.50 mmol, 1.5 equiv.) and substrate (1.00 mmol, 1.0 equiv.) were then added by syringe under argon. The reactions were allowed to stand at room temperature or heated in an oil bath and the progress was followed by NMR spectroscopy. Conversions were determined by loss of alkyl halides by ^1H NMR spectroscopy. Reduction products were identified using ^1H and $^{13}C\{^1H\}$ NMR in comparison to literature data or authentic samples.

General Procedure for the Reduction of Alkyl Halides Catalyzed by 4

Triethylsilane (240 μL, 1.50 mmol, 1.5 equiv.) was added to a solution of **4** (14.5 mg, 0.0094 mmol, 1 mol%) in C_6D_5Cl (0.5 mL) in a J. Young NMR tube and the contents were well shaken. The substrate (1.00 mmol, 1.0 equiv.) was then added. The reactions were allowed to stand at room temperature or heated in an oil bath and the progress was followed by NMR spectroscopy. Conversions were determined by loss of alkyl halides by ^1H NMR spectroscopy. Reduction products were identified using ^1H and $^{13}C\{^1H\}$ NMR in comparison to literature data or authentic samples.

General Procedure for the Reduction of Alkyl Halides Catalyzed by 1

Triethylsilane (480 μL, 3.00 mmol, 3 equiv.) was added to a solution of **1** (6.7 mg, 0.005 mmol, 0.5 mol%) in C_6D_5Cl (0.3 mL) in a J. Young NMR tube and the contents were well shaken. The substrate (1.00 mmol, 1 equiv.) was then added. The reactions were allowed to stand at room temperature or heated in an oil bath and the progress was followed by NMR spectroscopy. Conversions were determined by loss of alkyl halides by ^1H NMR spectroscopy (conversions for alkyl fluoride reductions were determined by ^{19}F NMR spectroscopy). Reduction products were identified using ^1H and $^{13}C\{^1H\}$ NMR in comparison to literature data or authentic samples.

General Procedure for the Reduction of Alkyl Halides Catalyzed by 1 without Solvent

Triethylsilane (480 μL, 3.00 mmol, 3 equiv.) was added to a J. Young NMR tube with **1** (6.7 mg, 0.005 mmol, 0.5 mol%) and a sealed capillary tube with C_6D_6 as internal standard. To this suspension was then added the substrate (1.00 mmol, 1 equiv.), and the tube was quickly inverted to ensure complete mixing. The reactions were allowed to stand at room temperature and the progress was monitored by NMR spectroscopy. Conversions were determined by loss of alkyl halides by ^1H NMR spectroscopy. Reduction products were identified using ^1H and $^{13}C\{^1H\}$ NMR in comparison to literature data or authentic samples.

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Reduction of 1-Bromohexane with Et_3SiD Catalyzed by 3

Et_3SiD (160 μL, 1.00 mmol, 2 equiv.) was added to a solution of **1** (6.7 mg, 0.005 mmol, 1 mol%) in $C_6D_4Cl_2$ (0.3 mL) in a J. Young NMR tube. The contents were well shaken and 1-bromohexane (70.2 μL, 0.50 mmol, 1 equiv.) was added. The reaction was allowed to stand at room temperature and the progress was followed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. $CH_3(CH_2)_4CH_2D$ was the only observable alkane product as determined by $^{13}C\{^1H\}$ NMR. *$CH_3(CH_2)_4CH_2D$:* $^{13}C\{^1H\}$ NMR ($C_6D_4Cl_2$, 100.6 MHz): $\delta = 31.71$ (s), 31.68 (s), 22.75 (s), 22.66 (s), 14.0 (s), 13.7 (t, $J_{D,C} = 19.1$ Hz).

Reduction of (Bromomethyl)cyclohexane with Et_3SiD Catalyzed by 1

Et_3SiD (240 μL, 1.50 mmol, 3 equiv.) was added to a solution of **1** (20 mg, 0.015 mmol, 3 mol%) in $C_6D_4Cl_2$ (0.5 mL) in a J. Young NMR tube and the contents were well shaken. (Bromomethyl)cyclohexane (70 μL, 0.50 mmol, 1 equiv.) was then added. The reaction was allowed to stand at room temperature the progress was followed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The NMR spectra of the reaction products were analyzed by comparison with $^{13}C\{^1H\}$ NMR data of undeuterated methylcyclohexane. (Deuteriomethyl)cyclohexane was identified as the major reduction product and 1-deuterio-1-methylcyclohexane was the minor one (*ca.* 6:1 ratio as determined by $^{13}C\{^1H\}$ NMR spectroscopy). *(Deuteriomethyl)cyclohexane:* $^{13}C\{^1H\}$ NMR ($C_6D_4Cl_2$, 100.6 MHz): $\delta = 35.4$ (s), 32.7 (s), 26.5 (s), 26.4 (s), 22.5 (t, $J_{D,C} = 19.1$ Hz).

The minor product *1-deuterio-1-methylcyclohexane* was identified and quantified by a triplet for $^{13}C_1$-D ($\delta = 32.2$, $J_{D,C} = 19.0$ Hz) and a $^{13}CH_3$ signal at δ 22.6 overlapping the triplet of -CH_2D ($\delta = 22.5$, $J_{D,C} = 19.1$ Hz).

Competition Experiments to Determine Relative Reactivities of Primary and Secondary Chlorides with 1/Et_3SiH System

A stock solution of **1** (16.7 mM) was prepared in $C_6D_4Cl_2$ in a glove-box. Triethylsilane (480 μL, 3.00 mmol, 6 equiv.) was then added to an aliquot (300 μL, 1 mol% Ir) of this stock solution in a J. Young NMR tube and the contents were well shaken. 1-Chloropentane (0.50 mmol, 60.5 μL, 1 equiv.), 2-chloropentane (0.50 mmol, 61.3 μL, 1 equiv.) and 1,3,5-tris(trifluoromethyl)benzene (0.16 mmol, 30.0 μL, 0.32 equiv.; used as an internal standard) were then added. The reaction was allowed to stand at room temperature, and the progress was followed by NMR spectroscopy.

Competition Experiments to Determine Relative Reactivities of Primary and Secondary Chlorides in [Ph_3C] [$B(C_6F_5)_4$]/Et_3SiH System

Triethylsilane (480 μL, 3 mmol, 6 equiv.) was added to a solution of [Ph_3C] [$B(C_6F_5)_4$] (4.6 mg, 0.005 mmol, 1 mol%) in $C_6D_4Cl_2$ (0.3 mL) in a J. Young NMR tube and the contents were well shaken. 1-Chloropentane (60.5 μL, 0.50 mmol, 1 equiv.) and 2-chloropentane (61.3 μL, 0.50 mmol, 1 equiv.) were then added. The reaction was allowed to stand at room temperature, and the progress was followed by NMR spectroscopy.

Reaction between Cationic Silane Complex (2) and $^{13}CH_3I$ at Low Temperature

Triethylsilane (320 μL, 2 mmol, 200 equiv.) was added to a solution of **1** (13.3 mg, 0.01 mmol, 1 equiv.) in C_6D_5Cl (0.5 mL) in a screw-cap NMR tube in a dry-box and the contents were well shaken. A solution of $^{13}CH_3I$ in C_6D_5Cl (0.2 M, 0.1 mL, 2 equiv.) was added by syringe at −78 °C and the NMR tube was placed in the pre-cooled NMR probe at −50 °C. The progress of the reaction was followed by ^1H, ^{31}P and ^{13}C NMR spectroscopy. Characteristic shifts (in C_6D_5Cl/Et_3SiH at −50 °C) used to determine **7**, $^{13}CH_3I$ and $^{13}CH_4$: **7** [^1H NMR (coordinated $^{13}CH_3I$): $\delta = 2.17$ (d, $^1J_{C,H} = 155$ Hz), ^{13}C NMR (coordinated $^{13}CH_3I$): $\delta = -4.0$, ^{31}P NMR: $\delta = 178.6$.]; $^{13}CH_3I$ [^1H NMR: $\delta = 1.70$ (d, $^1J_{C,H} = 151$ Hz), ^{13}C NMR: $\delta = -23.4$]; $^{13}CH_4$ [^1H NMR: $\delta = 0.21$ (d, $^1J_{C,H} = 126$ Hz), ^{13}C NMR: $\delta = -3.7$]

Attempted *in situ* Generation of Triethylsilyl Iodonium Ion, [Et_3SiICH_3] [$B(C_6F_5)_4$] (11)

Triethylsilane (3.5 μL, 0.022 mmol, 1.1 equiv.) was added to a solution of [Ph_3C] [$B(C_6F_5)_4$] (18.4 mg, 0.02 mmol, 1.0 equiv.) in C_6D_5Cl (0.5 mL) in a screw-cap NMR tube. The tube was quickly inverted to ensure complete mixing and put into a −78 °C bath. Iodomethane-^{13}C (0.1 mL of 0.2 M stock solution in C_6D_5Cl, 1.0 equiv.) was added by syringe and the NMR tube was placed in the pre-cooled NMR probe at −40 °C. Both the ^1H and the ^{13}C NMR spectra exhibited formation of Ph_3CH and two sets of CH_3 resonances. The sharp resonance at $\delta = 10.3$ ($^1J_{C,H} = 158$ Hz) in ^{13}C NMR was assigned to $^{13}CH_3I^{13}CH_3^+$, **12**. A broadened ^{13}C resonance at $\delta = -8$ ($^1J_{C,H} = 157$ Hz) was attributed to rapidly averaging signals of $Et_3SiI^{13}CH_3^+$, **11**, and free $^{13}CH_3I$ in the degenerate exchange equilibrium. Similar results have also been obtained by treating *in situ* formed [$Et_3Si(C_6D_6)$]$^+$ [$B(C_6F_5)_4$]$^-$[21a] with $^{13}CH_3I$ in C_6D_5Cl at −40 °C.

Reactions of 11 and 12 with 5

A stock solution of **5** (0.067 M) was prepared in C_6D_5Cl in a glove-box. An aliquot of the stock solution of **5** (300 μL, 0.02 mmol, 1.0 equiv.) was added by syringe to the mixture of **11** and **12** in a −78 °C bath. The NMR tube was then placed in the pre-cooled NMR probe at −35 °C. The progress was monitored by NMR spectroscopy. Observations are summarized in the text.

Hydrodechlorination of (POCOP)Ir(H)(Cl) (3) with Et_3SiH Catalyzed by 1

Catalysis with 25% 1: (POCOP)Ir(H)(Cl) (**3**) (12.52 mg, 0.02 mmol, 1 equiv.) and **1** (6.7 mg, 0.005 mmol, 25 mol%) were dissolved in 0.5 mL of C_6D_5Cl in a J. Young NMR tube. Triethylsilane (16 μL, 0.1 mmol, 5 equiv.) was added and the contents were well shaken. In less than 40 min **3** was quantitatively converted to **5**.

Catalysis with 10% 1: A stock solution of **1** (10 mM) was prepared in $C_6D_4Cl_2$ in a glove-box. An aliquot (150 μL, 0.0015 mmol, 10 mol% Ir) of this stock solution was added to a solution of (POCOP)Ir(H)(Cl) (**3**) (9.8 mg, 0.016 mmol, 1 equiv.) and Et_3SiH (15 μL, 0.094 mmol, 6 equiv.) in 650 μL of $C_6D_4Cl_2$ in a J. Young NMR tube. The reaction was al-

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lowed to stand at room temperature and monitored by the ^1H and $^{31}P\{^1H\}$ NMR. In less than 40 min **3** was quantitatively converted to **5**.

(POCOP)IrH$_2$ (5): ^1H NMR (C_6D_5Cl, 400 MHz, 23 °C): $\delta = 7.08$ (t, $^3J_{H,H} = 7.6$ Hz, 1H, 4-H), 6.87 (d, $^3J_{H,H} = 7.6$ Hz, 2H, 3- and 5-H), 1.30 (m, 36H, 4×*t*-Bu), −17.0 (t, $^2J_{P,H} = 5.8$ Hz, 1H, IrH); $^{31}P\{^1H\}$ NMR (C_6D_5Cl, 162 MHz, 23 °C): $\delta = 204.8$.

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