Organic & Biomolecular Chemistry

COMMUNICATION

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Cite this: DOI: 10.1039/c8ob02298d

Received 17th September 2018, Accepted 31st October 2018 DOI: 10.1039/c8ob02298d

rsc.li/obc

Selective alkyl ether cleavage by cationic bis(phosphine)iridium complexes†

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Catalysts capable of heterolytic silane activation have been successfully applied to the conversion of alkyl ethers to silyl ethers *via* C–O bond cleavage. The previously-reported cationic pincer-supported iridium complex for this transformation suffers from poor selectivity with regard to monodealkylation of substrate ethers. We demonstrate that a simple non-pincer iridium complex offers improved selectivity and is capable of benzylic ether cleavage in the presence of reductively-labile alkyl and aryl halide functionality. Preliminary mechanistic experiments suggest a neutral tetrahydridosilyliridium resting state which is consistent with previous mechanistic hypotheses. These experiments suggest that a pincer ligand framework is not required for activity in ether cleavage reactions and that simple cationic bis(phosphine)iridium complexes may offer improved selectivity profiles for applications to morecomplex substrate molecules.

Introduction

Primary and secondary alkyl ethers are robust organic functional groups for which forcing conditions are typically required to effect C–O cleavage. Traditional methods for ether cleavage rely on their conversion to alkyl halides under the influence of strong mineral acids¹ or exhaustive hydrogenolysis to alkanes over heterogeneous catalysts.² Although well-developed and inexpensive, these methods lack the intrinsic selectivity that would be required for their application to complex polyethercontaining molecules including carbohydrate derivatives.³

In recent years a strategy for reductive ether cleavage through catalytic silylation has emerged. These approaches make use of catalyst-promoted silane Si–H heterolysis to generate electrophilic silyloxonium ions which are subject to subsequent attack by hydride. The use of a catalyst opens up

 $\dagger\, Electronic$ supplementary information (ESI) available. See DOI: 10.1039/ c8ob02298d

avenues for the development of systems with catalyst-controlled selectivity that would be applicable to complex molecules. Promising classes of catalysts for this transformation include electrophilic triaryl- and diarylboranes^{4–9} as well as a single example of a cationic iridium complex of a weakly-coordinating anion.^{10,11} In both cases the initial Si–O bondforming step is thought to proceed *via* Lewis acid-promoted silane activation to give a silyloxonium ion and an equivalent of the catalyst hydride.¹²

To our knowledge the only iridium catalyst reported to cleave ethers *via* C–O single bond reduction with silanes is Brookhart's cationic bis(phosphine)pincer iridium complex **1** (Fig. 1, left).¹³ Related non-pincer complexes have been previously reported by Crabtree to effect dehydrosilylation of alcohols.¹⁴ Although the two transformations are distinct, both implicate nucleophilic attack on an iridium σ -silane complex in their respective Si–O bond-forming steps.

Our research group's interest in reactions of alkyl ethers at cationic bis(phosphine)iridium complexes has now led us to explore catalytic ether cleavage *via* C–O silylation. In recent work we demonstrated the stoichiometric C–O cleavage of methyl *tert*-butyl ether by $[(PPh_3)_2IrH_2(THF)_2]PF_6$.¹⁵ We now show that the corresponding BAr^F₄ (Ar^F = 3,5-bis(trifluoromethyl)phenyl) salt (2) is an active catalyst for the cleavage of alkyl ethers with trialkyl silanes. In a key advance, we demonstrate substantially improved selectivity over previous iridium catalysts for this transformation and have applied this system to a promising protecting group-interconversion process that allows for debenzylation in the presence of reductively-labile alkyl and aryl halides.



Fig. 1 Cationic iridium complexes of weakly coordinating anions.



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Results and discussion

At the outset of this study we identified a need for iridium catalysts with improved selectivity profiles. Primary, secondary and tertiary ethers are rapidly cleaved by Brookhart's POCOP iridium catalyst (1) to give silyl ethers; however the resulting silyl ether products are subject to subsequent reduction to the alkanes (Scheme 1, top). This reactivity was employed to great effect by Gagné in a recent report detailing the exhaustive deoxygenation of glucose to hexanes,¹¹ but is also a sign of a lack of intrinsic selectivity that limits applications in the synthesis of functionalized molecules.

The mechanistic similarity between ether silylation and alcohol dehydrosilylation encouraged us to explore non-pincer bis(phosphine)iridium complexes for reductive ether cleavage catalysis. Our hypothesis was that these complexes would also serve as catalysts for ether cleavage, and would provide a tunable platform for 2^{nd} generation catalyst development through the preparation of variants of commercially available monophosphines. Although the hexafluorophosphate complex¹⁵ [(PPh₃)₂IrH₂(THF)₂]PF₆ is inactive under the con-



 Table 1
 Cleavage of unsymmetrical ethers by 2

ditions tested, the BAr_{4}^{F} salt¹⁶ (2) rapidly cleaves a variety of alkyl ethers with triethylsilane.

Initial studies on a collection of unsymmetric ethers suggest that the reactivity of complex 2 depends strongly on the ether (Table 1). Benzyl ethers are highly reactive, undergoing cleavage at the benzylic position in benzyl heptyl ether. Benzyl cyclohexyl ether is also cleaved at the benzylic position, but requires an elevated catalyst loading of 3% (Table 1, entry 2). Primary methyl ethers undergo demethylation while secondary methyl ethers are cleaved at the 2° position. Primary secondary ethers show poor reactivity, even with long reaction times and high catalyst loading. In nearly all cases the resulting silvl ethers appear to be stable with respect to further reduction.¹⁷ Although complex 2 is able to cleave MTBE, other tertiary ethers including t-butyl benzyl ether were not reduced (Table 2, entries 6 and 7). Surprisingly, benzylic ether cleavage could be accomplished selectively even in the presence of a methyl ether (Table 1, entry 8). These preliminary observations on the reactivity of complex 2 show significantly attenuated reactivity versus Brookhart's complex 1, validating our hypothesis that more-selective iridium catalysts could be obtained through the use of cationic non-pincer bis(phosphine)iridium complexes.

The rapid and selective cleavage of benzyl ethers suggested that complex 2 could potentially serve as a catalyst for the conversion of benzylic ethers to silyl ethers. Benzylic ethers are typically cleaved by hydrogenolysis under mild conditions with heterogeneous metal catalysts. The ease of benzylic ether formation and subsequent deprotection has led to applications of benzyl ethers as versatile protecting groups for alcohols.¹⁸ Benzyl ether hydrogenolysis over heterogeneous Pd catalysts is compatible with an array of functional groups, but alkenes, alkynes and azides undergo reduction, while alkyl and aryl halides and psuedohalides are also subject to competitive hydrodehalogenation or catalyst poisoning under certain conditions.^{19–22}

	5 7 7			
	R ^{1/O} R	$2 \xrightarrow{\text{HSiEt}_3 (1.6 \text{ equiv})}{\text{Complex } 2 (1 \text{ or } 3 \text{ mol } \%)} \rightarrow \mathbb{R}^1 - \text{OSiEt}_3$ $C_6 D_6, 25 \ ^\circ C$	R ² -H	
Entry	Substrate	Conditions	Silyl ether	NMR yield
1	BnO CH3	1 mol% 1 h	Et ₃ SiO (CH ₃	>98%
2	Ŭ OBn	3 mol% 2 h	OSiEt ₃	70%
3	H ₃ C ^{-O} (Y_{5} -CH ₃	1 mol% 8 h	Et ₃ SiO ₁ CH ₃	75%
4	CTO-CH3	1 mol% 2 h	CH ₃ OSiEt ₃	61%
5	CH3 CH3	3 mol% 48 h	$Et_3SiO_{4}CH_3$	26%
6	Bn ^O ^t Bu	1 mol% 48 h	NR	—
7	^t Bu ^O () ₅ CH ₃	1 mol% 48 h	NR	
8	BnO OCH3	3 mol% 40 min	Et ₃ SiO	>98%

Under our optimized conditions, a variety of alkyl and aryl halides are tolerated (Fig. 2). Benzylic ether cleavage is observed without reduction of an aryl chloride, bromide or iodide. An aryl triflate is similarly untouched under our conditions. Although primary alkyl chlorides, bromides, and iodides all survive benzyl ether silylation in moderate to good yield, somewhat lower yields are obtained for a substrate containing a secondary alkyl bromide. In contrast to our results with 2, complex 1 is a reported hydrodehalogenation catalyst under closely-related conditions.²³

In line with the reported dehydrosilylation activity of related complexes, substrates containing free alcohols undergo dehydrosilylation more rapidly than ether cleavage. We have been able to exploit this property in the selective disilylation of 3-(benzyloxy)propanol (eqn (1)). Sequential treatment with *tert*-butyl(dimethyl)silane (1.1 equiv.) and diethyl(methyl)silane (2.2 equiv.) gives the unsymmetrically silylated 1,3-propanediol.



A survey of the scope of compatible functionality with our silyl ether cleavage conditions also revealed some limitations. As many iridium complexes including **1** are excellent hydrosilylation catalysts for olefins and carbonyl derivatives,^{24,25} substrates containing such functionality were not suitable for ether cleavage by **2**. Similarly, substrates containing Lewis basic functionality including nitriles, amines, thioethers, and azides are totally unreactive under our optimized conditions. Thus substrates which are either more Lewis-basic than ethers or are known to undergo rapid hydrosilylation appear to pose a challenge for this system.²⁶ We suspect further catalyst development may provide solutions for certain substrate classes, but given the kinetic stability of ethers relative to other functionality, these limitations are unsurprising.



Fig. 2 Isolated yields obtained in the conversion of benzyl ethers to silyl ethers by 2.

$$\begin{array}{c} Ph_{3}P \\ H \\ H \\ PPh_{3} \end{array} \xrightarrow{H} H \\ PPh_{3} \end{array} \xrightarrow{HSiEt_{3} (20 \text{ equiv.})} C_{6}D_{6}, 80 \ ^{\circ}C \end{array} \xrightarrow{Ph_{3}P} H \\ Et_{3}Si \\ PPh_{3} \end{array} (2)$$

$$\begin{array}{c} Ph_{3}P \\ H \\ H \\ PPh_{3} \end{array} \xrightarrow{H} H \\ PPh_{3} \end{array} (2)$$

A proposed mechanism for ether cleavage catalyzed by 2 is given in Scheme 2.13 An interesting feature of iridium-catalyzed ether silvlation is its resemblance to the borane-catalyzed reaction.27 The key mechanistic similarity between both iridium and borane-catalyzed ether silvlation is the heterolytic cleavage of the silane to give a silvloxonium ion and a metal hydride or borohydride respectively. When the reduction of benzyl heptyl ether by 2 is monitored by ${}^{31}P{}^{1}H$ NMR, a single major resonance appears at 13.7 ppm. We have found that the same species can be generated by treatment of the neutral iridium pentahydride $(PPh_3)_2IrH_5$ (3) with Et₃SiH, indicating that the major iridium-containing species during the reaction is a neutral complex lacking the BAr^F₄ anion. This complex has been previously characterized as the neutral iridium tetrahydrido silvl complex 4 (eqn (2)).²⁸ Formation of 4 during catalysis likely occurs *via* attack of an ether on a σ -Si-H complex¹³ to give $(PPh_3)_2IrH_3$ (5) followed by oxidative addition of a second equivalent of Et₃SiH (Scheme 2). The presence of 4 as the major iridium-containing species during catalysis is compatible with the general framework for the overall mechanism proposed by Brookhart¹³ and well as studies on a related catalytic reaction by Oestrich.¹²

In both iridium and borane-catalyzed varients of this transformation, hydride attack on the dialkysilyloxonium ion is proposed to be responsible for the C-O bond cleavage step. Brookhart has proposed that a neutral iridium(m)dihydride resulting from silvlium transfer to the ether may be responsible for this step.¹³ Studies on a closely related system by Oestreich have also implicated a neutral iridium(v)silyltrihydride or iridium(m)dihydrido σ -silane, though recent calculations appear to support the hypothesis that the iridium(m) dihydride is competent for ether cleavage.²⁹ Our observation of complex 4 during catalysis is wholly consistent with Oestreich's mechanistic proposal and allows us to tentatively suggest that complex 4 may be responsible for hydride transfer to the silyloxonium ion. Importantly, complex 4 itself does not serve as a catalyst for ether silvlation when generated in situ from 3 (eqn (3)). This observation suggests that a cationic precursor is required for silvloxonium ion formation. On the other hand, complex 4 is extremely active when applied in the presence of equimolar [CPh₃]BAr^F₄ (eqn (4)). For this experiment, [CPh₃]BAr^F₄ was added to a benzene solution of triethylsilane to generate a known triethylsilylium ion equivalent³⁰ which was then treated with substrate ether to give the silyloxonium ion. Subsequent addition of a solution of 4 leads to rapid catalysis (eqn (4)). Alternatively, $[CPh_3]BAr_4^F$ or a triethylsilylium ion generated in situ may serve to abstract a hydride from 4 to give a cationic iridium species related to 2. Indeed treatment of a THF solution of 4 with $[CPh_3]BAr_4^F$ appears to give 2 by ³¹P NMR. In either case, complex 4 alone is clearly



Scheme 2 Proposed mechanism for ether cleavage by 2.

insufficiently electrophilic to transfer an equivalent of triethylsilylium to substrate ether.

$$\begin{array}{c} \text{Complex 4 (3 mol \%)^*} \\ \text{BnO} \underbrace{\swarrow_5}_{\text{CH}_3} \underbrace{\text{HSiEt}_3 (2.2 \text{ equiv.})}_{\text{C}_6\text{D}_6, 60 \ ^\circ\text{C}, 16 \text{ h}} & no \\ \end{array} \tag{3}$$

The efficacy of borane catalysts with structurally similar motifs to the weakly coordinating anions used in this study warrants discussion. B-C cleavage might be expected to generate the triaryl borane BAr^F₃ [tris(3,5-bis(trifluoromethyl) phenyl)borane]. The similarity of BArF₃ to tris(pentafluorophenyl)borane (BCF), a known catalyst for ether hydrosilylation led us to investigate the possibility that anion degradation to an active catalyst could be responsible for our observed reactivity. Under our catalytic conditions the BAr^F₄ anion remains unchanged by ¹⁹F-NMR spectroscopy which precludes the formation of BAr^F₃ at concentrations detectable with this technique. Furthermore, NaBArF4 is inactive for ether cleavage both on its own and in the presence of the neutral tetrahydridosilyliridium complex 4. Finally, we independently prepared the BAr^F₃ borane and compared its reactivity to reactions catalyzed by 2. BAr^F₃ is a poor catalyst for ether reduction under our optimized conditions (Table 2, entry 1), and while it improves in CD₂Cl₂ solvent, catalysis by BAr^F₃ is significantly slower than catalysis by 2. For instance, after 15 minutes we see complete conversion using 2 (>30 turnovers) and only 3 turnovers when BAr^F₃ is used as the catalyst over the same time period. Therefore these results allow us to rule out the possibility that the observed catalytic behavior of 2 results from trace borane generated by anion degradation. In a related experiment we found that catalysis by 2 is not inhibited by the presence of excess Hg metal, providing evidence against degradation of 2 to active iridium(0) nanoparticles in situ (eqn (6)).^{31,32}

Table 2 Comparison of catalysis by 2 versus the borane BAr^F₃

	BnO () CH ₃ HSiEt	vst (3 mol %) i ₃ (2.2 equiv.)	Et ₃ SiO	CH _{3 (5)}
Entry	Catalyst	Solvent	Time	NMR yield
1 2 3 4 5	BAr ^F ₃ Complex 2 BAr ^F ₃ BAr ^F ₃ BAr ^F ₃	$\begin{array}{c} C_6D_6\\ CD_2Cl_2\\ CD_2Cl_2\\ CD_2Cl_2\\ CD_2Cl_2\\ CD_2Cl_2 \end{array}$	2 h 15 m 15 m 1 h 4 h	<1% >98% 9% 39% 85%

$$BnO_{1} \xrightarrow{Complex 2 (3 mol \%)} Hg^{0} (420 mol \%)$$

$$HSiEt_{3} (2.2 equiv.) \xrightarrow{C_{6}D_{6}, 25 °C, 3 h} Et_{3}SiO_{1} \xrightarrow{C_{7}} CH_{3}$$

$$(6)$$

Conclusions

We have demonstrated that a simple cationic non-pincer bis(phosphine)iridium complex is an active catalyst for the conversion of alkyl ethers into silyl ethers. $[(PPh_3)_2IrH_2(THF)_2]$ BAr^F₄ is significantly more selective than the previous reported iridium system for the same transformation, and is able to cleave benzylic ethers in the presence of sensitive alkyl and aryl halide functionality. Unlike the previous pincer-supported system, the product silyl ethers are not subject to complete deoxygenation. Preliminary mechanistic experiments strongly suggest that $[(PPh_3)_2IrH_2(THF)_2]BAr^F_4$ operates according to the accepted mechanism for iridium- and borane-catalyzed ether silylation reactions. Our findings suggest that cationic bis(phosphine)iridium complexes may be a promising catalyst platform for the development of more-selective C–O bond cleavage reactions of functionalized molecules.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research. Funding from Vanderbilt University is gratefully acknowledged.

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