C–O Bond Formation

DOI: 10.1002/anie.201101088

$C(sp^3)$–O Bond-Forming Reductive Elimination of Ethers from Bisphosphine-Ligated Benzylpalladium(II) Aryloxide Complexes**

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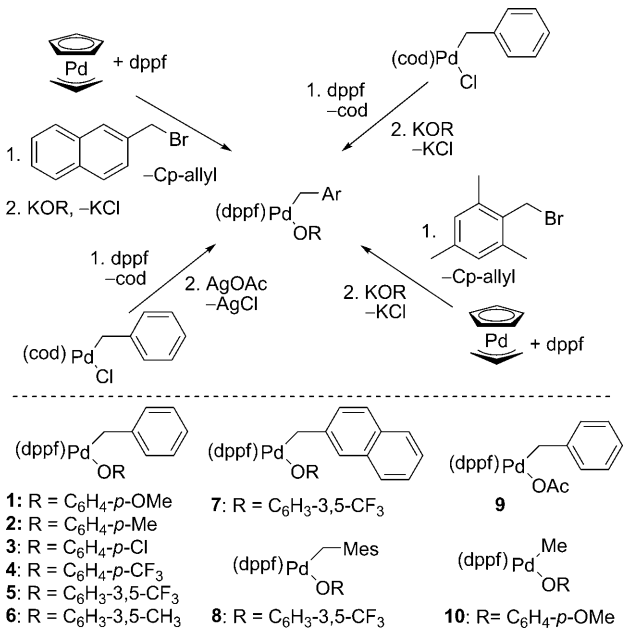
Reductive elimination to form aryl ethers and arylamines from arylpalladium(II) alkoxide or amido complexes has been documented, but the formation of alkyl ethers or alkylamines by the same process is less common. The formation of $C(sp^2)$–O or $C(sp^2)$–N bonds occurs by concerted reductive elimination from arylpalladium(II) complexes as stoichiometric reactions and during catalytic processes,[1–8] but analogous reactions of palladium alkoxide complexes to form $C(sp^3)$–O bonds is unknown.[9]

Instead, all of the known $C(sp^3)$–O reductive elimination reactions from alkoxide or aryloxide complexes occur from metal centers in oxidation states higher than palladium(II), despite the diversity of reductive elimination processes that occur from palladium(II). For example, reductive eliminations to form alkyl acetates and alkyl aryl ethers is documented from methylplatinum(IV) centers.[10,11] Reductive eliminations from the methylplatinum acetate and aryloxide complexes occur by a mechanism involving ionic intermediates, while reductive eliminations from platinum(IV) metallaoxetanes to form epoxides are proposed to occur by a concerted pathway.[12] Reductive eliminations of tetrahydrofuran and tetrahydropyran from metallacyclic Ni^{II} alkylalkoxide complexes also has been reported. These reductive eliminations occur after initial reaction with an oxidant, presumably to generate a Ni^{III} intermediate.[13–15]

We recently reported reductive eliminations to form the $C(sp^3)$–N bond in *N*-benzyl diarylamines and provided evidence that these reactions occur by a stepwise process through ionic intermediates.[16] Because of the differences in stabilities of alkoxide and amide anions, differences in abilities of low and high-valent complexes to cleave to form ion pairs, differences in nucleophilicities of alkoxides and amides, and differences in the stabilities of nitrogen- and oxygen-centered radicals, the relationship between the mechanisms of reductive eliminations to form $C(sp^3)$–N and $C(sp^3)$–O bonds from low-valent and high-valent metal centers are difficult to predict. Thus, we sought to identify palladium(II) complexes that would undergo reductive elimination to form $C(sp^3)$–O bonds in ethers and to gain mechanistic information that would allow comparisons to be made to the mechanisms of other types of reductive eliminations.

Here, we report thermal reductive eliminations from palladium(II) aryloxide complexes to form a $C(sp^3)$–O bond and a series of experiments that provide detailed mechanistic insight. In short, our data show that the mechanism of this reaction is more akin to reductive eliminations to form $C(sp^3)$–N bonds from palladium(II) than those that form $C(sp^2)$–O bonds from palladium(II) or any type of C–O or C–N bond from higher-valent metal centers, but indicate that substantial differences exist between reductive eliminations to form the $C(sp^3)$ bonds in ethers and amines from palladium(II). The stereochemical outcome of the reaction indicates an ionic pathway, but the process lacks many of the effects of electronic and solvent perturbations that typically signal an ionic intermediate.

After a survey of complexes containing different phosphine ligands, we found that benzylpalladium aryloxide complexes ligated by dppf (1,1′-Bis(diphenylphosphino)ferrocene) displayed the appropriate balance of stability, reactivity, and synthetic accessibility to observe reductive eliminations that form $C(sp^3)$–O bonds from fully characterized complexes. The dppf-ligated palladium aryloxide complexes **1**–**10** were synthesized as shown in Scheme 1. Benzyl com-



Scheme 1. Synthesis of palladium aryloxide complexes.

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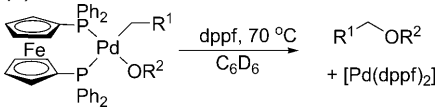
[**] This work was supported by the NSF as part of the Center for Enabling New Technologies through Catalysis (CENTC), CHE-0650456. We thank Luc Boisvert and Karen Goldberg at the University of Washington for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201101088.

plexes **1–6** were prepared by allowing the known [(cod)Pd(Bn)Cl][17] (cod = cyclooctadiene) to react with dppf, followed by the potassium aryloxide in THF. Naphthylmethyl and mesitylmethyl complexes **7** and **8** were synthesized by allowing [CpPd(η^3-allyl)][18] to react with dppf, followed by naphthylmethyl or mesitylmethyl bromide. These bromide precursors were then converted to the aryloxide complexes by reaction with the potassium aryloxide in diethyl ether or THF. The acetate complex **9** was prepared by allowing [(cod)Pd(Bn)Cl] to react with dppf, followed by the addition of silver acetate in THF. Methylpalladium aryloxide complex **10** was synthesized by the reaction of [(cod)Pd(Me)Cl][19] with dppf, followed by addition of the potassium aryloxide. Complexes **1–10** were characterized by conventional one-dimensional NMR spectroscopic methods and elemental analysis.

To assess the ability of complexes **1–10** to undergo reductive elimination, benzene solutions of these complexes were heated with excess dppf to trap the Pd^0 product. As shown in Table 1, benzyl complexes **1–6** and naphthylmethyl

Table 1: C(sp^3)–O bond reductive elimination.



Complex	R^1	R^2	k_{obs} [s^{-1}] 10^4	Yield [%][a]	$t_{1/2}$ [min]
1	Ph	C_6H_4-*p*-OMe	2.4	94	48
2	Ph	C_6H_4-*p*-Me	2.8	73	41
3	Ph	C_6H_4-*p*-Cl	3.3	84	35
4	Ph	C_6H_4-*p*-CF_3	2.6	92	44
5	Ph	C_6H_3-3,5-CF_3	2.6	79	44
6	Ph	C_6H_3-3,5-CH_3	1.7	75	68
7	Naphthyl	C_6H_3-3,5-CF_3	3.8	99[b]	31[b]
8	Mesityl	C_6H_3-3,5-CF_3	14	100[c,d]	8[c]
9	Ph	Ac	0.68	64	170
10	H	C_6H_4-*p*-OMe	–	0[e]	–

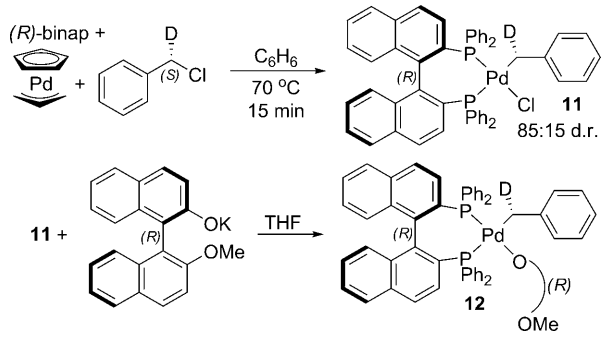
[a] Yields were determined by ^{1}H NMR spectroscopy, relative to trimethoxybenzene as an internal standard on reactions conducted in [D_6]benzene at 70 °C, unless otherwise noted. [b] Reaction conducted at 30 °C. [c] Reaction conducted at 55 °C. [d] The products were a mixture of the 2,4,6-trimethylbenzyl ether and the 2,3,5-trimethylbenzyl ether. [e] Hexamethylbenzene was used as an internal standard.

complex **7** underwent reductive elimination in high yields. The mesitylmethyl complex **8** also underwent reductive elimination, in this case to form a mixture of the 2,4,6-trimethylbenzyl ether (65%) and the isomeric 2,3,5-trimethylbenzyl ether (35%). The acetate complex **9** underwent reductive elimination more slowly than did any of the other complexes studied. The observed reductive elimination of complex **9** contrasts with the previously described oxidative addition of benzyl trifluoroacetate to Pd^0.[20] The less hindered methyl complex **10** did not form products from reductive elimination when heated for extended reaction times at 70 °C; instead methane and free phenol (95%) were observed. The source of the protons and electrons remains unclear at this time.[21]

To distinguish between reductive elimination from complexes **1–9** through a concerted, radical or ionic pathways, we studied reactions in the presence of a trap for a phenoxy radical[22] and prepared a diastereomeric benzylpalladium aryloxide complex that enabled us to determine the relative configuration of the benzylic carbon atom in the reactant and product. Reductive elimination from complex **2** in the presence and absence of 2 equiv of BHT (butylated hydroxytoluene) as a radical trap occurred with indistinguishable rate constants ($2.8\times10^{-4}\,s^{-1}$ and $2.9\times10^{-4}\,s^{-1}$). The rate of reaction of BHT with another phenoxy radical is expected to be about $10^7\,M^{-1}s^{-1}$.[22] Although rapid trapping of a potential phenoxy radical with the metal complex could be occurring, these data and stereochemical data (see below) argue against the intermediacy of a phenoxy radical.

To determine the relative configuration of the palladium-bound carbon in the reactant and product, we prepared a monodeuterated benzylpalladium aryloxide complex containing a chiral, non-racemic aryloxide and bisphosphine. The presence of a chiral, non-racemic bisphosphine allowed us to determine the relative ratio of benzylpalladium halide precursors having the *R* and *S* configurations at the benzylic position. The inclusion of a chiral, non-racemic aryloxide in the complex allows determination of the configuration of the benzylic carbon in the benzyl aryl ether formed by reductive elimination. This strategy is based on the one we developed for determining the stereochemical outcome of the reductive elimination of benzylamines.[16]

The required materials for this analysis were prepared as shown in Scheme 2. The monodeuterio benzylpalladium chloride complex **11** was synthesized in an 85:15 diastereo-

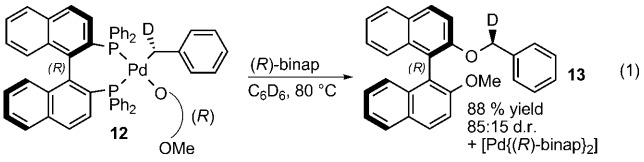


Scheme 2. Synthesis of the monodeuterated complex; binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl.

meric ratio enriched in the R_a,R_C isomer from [CpPd(η^3-allyl)], (*R*)-binap, and (*S*)-monodeuterio benzylchloride. Complex **11** was converted to the corresponding R_a,R_a,R_C-benzylpalladium binaphthylaryloxide complex (**12**) by addition of potassium R_a-binaphthylaryloxide in THF. Complex **12** was characterized using conventional NMR spectroscopic methods and elemental analysis.

Complex **12** underwent reductive elimination of the *O*-benzyl binaphthyl ether **13** in 88% yield after 4 h at 80 °C, as determined by ^{1}H NMR spectroscopy relative to an internal standard [Eq. (1)]. ^{1}H NMR spectroscopy indicated that the

product **13** consisted of the same 85:15 ratio of diastereomers as was present in the reactant **12**. Comparison of the ^{1}H NMR spectrum of the ether product **13** to that of the ether product prepared independently indicated that the reductive elimination occurred with inversion of configuration to form predominately R_a,S_C-**13** (see Supporting Information). We envision the stereochemical outcome results from dissociation of the aryloxide, followed by nucleophilic attack of the aryloxide anion on the benzylic carbon. Reactions that occur by dissociation of aryloxide ligands to form ionic intermediates during organometallic processes in nonpolar solvents are unusual. Nucleophilic attack of phenoxide onto a π-bound allyl ligand is known,[23–26] but none of the reported reactions begin with an allylalkoxide complex.



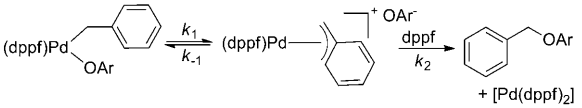
(1)

Several experiments were conducted to probe the effect of parameters that typically stabilize ionic species and accelerate reactions that occur by ionization of the reactant. The effect of the electronic properties of the aryloxide ligand on the rate of the reductive elimination from complexes **1**–**4** are shown in Table 1. Reductive elimination from complex **4** containing an electron-withdrawing *p*-CF_3 group occurred with a rate constant that is indistinguishable from that of reductive elimination from the *p*-tolyl complex **2**, and the rate constant for reductive elimination from complex **1** containing an electron-donating *p*-OMe group was nearly identical to that for reductive elimination from complexes **2** and **4**. The *p*-chloro complex **3** reacted somewhat faster than the other *para*- substituted complexes **1**, **2**, and **4**, but the magnitude of these differences was small. Thus, the rate of reductive elimination is not significantly influenced by the electronic properties of the aryloxide ligand. This result contrasts with the accelerating effect of electron-withdrawing substituents on reductive elimination to form C(sp^3)–O bonds from Pt^{IV},[10,11] and the modest but measurable effect of substituents on the rate of reductive elimination to form C(sp^3)–N bonds from benzylpalladium diarylamido complexes.[16] This lack of an electronic effect on reductive elimination even contrasts with the strong effect of the properties of the aryloxide group on concerted reductive elimination from arylpalladium aryloxide complexes.[27]

Like the effect of substituents, the effect of solvent polarity on the rate of reductive eliminations from the benzylpalladium phenoxide complexes was small. The reaction of complex **1** in [D_5]nitrobenzene occurred with a rate constant of 4.6×10^{-4} s^{-1} at 55 °C, whereas the reaction of **1** in [D_6]benzene at the same temperature occurred with a rate constant of 1.8×10^{-4} s^{-1}. Although the reaction is faster in the more polar solvent, the magnitude of this effect of solvent polarity is small for a reaction occurring through an ionic intermediate. Moreover, the difference in rate that is observed is not likely due to the stability of the anion alone because a similar small (2.8 times) difference in rate of reductive elimination to form a benzylamine in polar and non-polar solvents was observed previously.[16] In contrast, reactions to form methyl aryl ethers from Pt^{IV} complexes were an order of magnitude faster in nitrobenzene than in benzene.[10] This solvent effect for reaction of Pt^{IV} complexes parallels the classic prediction by Hughes and Ingold[28] of faster rates in more polar solvents for elementary reactions that generate two ions from a neutral species.

Protic additives that stabilize dissociated anions are known to increase the rate of reductive eliminations that occur through ionic intermediates.[10,29] Consistent with this trend, the reaction of complex **2** in the presence of 2.6 equiv of cresol occurred with a rate constant (5.1×10^{-4} s^{-1} at 30 °C) that is about 100 times larger than that for reaction of complex **2** in the absence of added cresol (5×10^{-6} s^{-1} at 30 °C). Hydrogen bonding between phenols and phenoxide ligands has been observed in solution and in the solid state,[30,31] and stabilization of the phenoxide ion by phenol likely leads to this large increase in rate. This effect of the conjugate acid of the nucleophilic anion differs from that of reductive eliminations to form benzylamines. Reactions from related diarylamido complexes were unaffected by added diarylamine, presumably because the greater steric hinderance of the diarylamide and the lower acidity of a diarylamine hydrogen-bond donor weakens this association.[16]

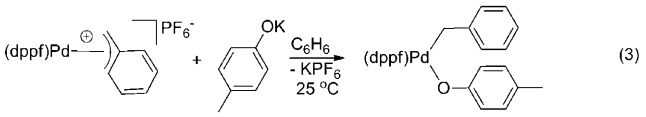
The small effect of the electronic properties of the phenoxide and the small effect of solvent polarity on the rate of reductive elimination from benzylpalladium phenoxide complexes can be rationalized by the combination of reversible dissociation of the aryloxide from the benzylpalladium aryloxide complex and irreversible collapse of the charge-separated pair to form the benzyl ether product [Eq. (2)]. The first equilibrium step would be favored by electronic[10,32,33] and solvent effects[10,34] that stabilize ion pairs, but the second step (k_2) would be disfavored by factors that stabilize ion pairs.[35] Thus, the overall effect of substituents and solvent on the reaction rate is complex and would depend on the relative effects of the properties of the system on these two steps, including the effects of these properties on the partitioning of the ionic intermediate for attack of the aryloxide at the metal to reform the starting complex and attack at the benzyl group to form the ether product.



(2)

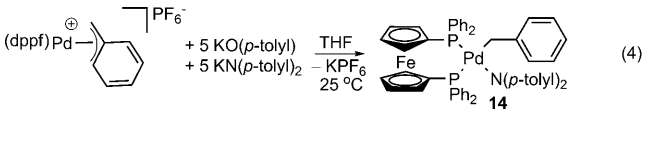
To test our proposal that dissociation of the aryloxide group is reversible, we allowed [(dppf)Pd(η^3-Bn)]PF_6] to react with a suspension of KO-*p*-tolyl in C_6H_6 at room temperature [Eq. (3)]. This reaction cleanly formed benzylpalladium aryloxide complex **2**. No observable benzyl ether was formed. Although this system contains potassium and PF_6^- counterions that are not present in the reactions of **1**–**9**, this result is consistent with our proposal that dissociation of the

phenoxide from the benzylpalladium aryloxide complex is reversible because collapse of the ion pair to regenerate the benzylpalladium aryloxide complex is faster than nucleophilic attack of the aryloxide anion on the benzylpalladium cation to form the benzyl ether product.

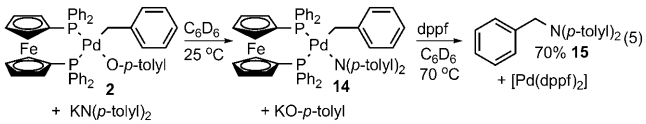


(3)

Considering the strong evidence that reductive elimination occurs through ion pairs, we probed whether reductive elimination to form C–O or C–N bonds would be faster under two sets of conditions that would generate alkoxide and amide ions. First, we conducted a reaction in which the system would contain both alkali metal diarylamides and phenoxides. The reaction of 5 equiv of KN(*p*-tolyl)$_2$ and KO-*p*-tolyl in THF with [(dppf)Pd(η^3-Bn)]PF$_6$, formed amido complex **14** [Eq. (4)] as the only species observed by ^{31}P NMR spectroscopy. Heating this mixture formed *N*-benzyldiarylamine **15** and no benzyl ether **16** [Eq. (5)]. Second, we conducted a reaction in which the ions would be generated from the palladium complex or from the conjugate acid of the anions. The combination of [(dppf)Pd(Bn){N(*p*-tolyl)$_2$}] and 1 equiv of HO(*p*-tolyl) formed phenoxide complex **2**. Heating this mixture led to the formation of benzyl ether **16** in 71 % yield without formation of benzylamine [Eq. (6)], as determined by ^{1}H NMR spectroscopy. These studies are consistent with the greater nucleophilicity of the diarylamide under the aprotic conditions of the first experiment, but greater population of the phenoxide anion under the protic conditions of the second experiment, and signal the fine balance between the population and reactivity of the anions in the systems that undergo reductive elimination.



(4)



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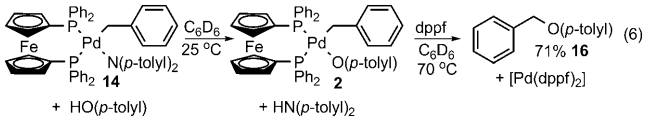

(6)

Finally, the difference between the propensity of benzylpalladium complexes **1**–**9** to undergo reductive elimination and the reluctance of methylpalladium aryloxide complex **10** to undergo the same process likely results from a combination of several factors. For example, a benzyl group is more electrophilic than a methyl group and a benzyl group would promote dissociation of the aryloxide anion because it can stabilize the cationic intermediate through an η^3 binding mode and it is more hindered than a methyl group. Analogous methylpalladium(II) complexes containing a more nucleophilic amido ligand also did not undergo reductive elimination, indicating that the electronic or steric properties of the methyl ligand are most strongly affecting the propensity of these complexes to undergo reductive elimination.[16]

Indeed, the coordinating ability and steric properties of the benzyl group had a large influence on the rate of reductive elimination. Consistent with the proposed ionic mechanism, naphthylmethyl complex **7** underwent reductive elimination much faster than benzyl complex **5**. The naphthylmethyl ligand should bind in an η^3-fashion more strongly than the benzyl ligand, and nucleophilic attack on an η^3-naphthylmethyl complex is known to occur faster than attack on an analogous η^3-benzyl complex.[36] In addition, the mesitylmethyl complex **8** reacted faster than the benzyl complex **5**.[37] A similar trend of faster reductive elimination from naphthylmethyl and mesitylmethyl palladium amido complexes was observed.[16] Thus, further studies are needed to define the role of the hydrocarbyl ligand in these reactions, but these preliminary data imply that several properties of the hydrocarbyl group affect the rate of reductive elimination.

In summary, we report reductive eliminations to form the C(sp^3)–O bond in an ether from a low-valent group 10 metal center without oxidation to form a higher valent intermediate. A combination of kinetic studies and analysis of the stereochemical outcome of the reaction indicate that this process occurs in a stepwise fashion by reversible dissociation of an aryloxide anion, followed by irreversible nucleophilic attack of the aryloxide on the resulting cationic benzylpalladium complex.

The data we gained allow comparisons of the elementary reactions of this system to those of other systems that that undergo reductive elimination to form carbon–heteroatom and carbon–carbon bonds. This pathway we revealed contrasts the concerted mechanism for coupling of aryl and aryloxide ligands[3,4] and the coupling of two alkyl ligands,[38] and the lack of electronic effect of the aryloxide ligand on the reaction rate contrasts the effect of the anionic ligand on reductive eliminations from platinum(IV) or arylpalladium(II) systems. These studies also show that the basic steps of the reductive eliminations to form benzylamines and benzyl ether are similar, but the rates of the elementary steps of the process differ such that reductive eliminations to form ethers are less sensitive to the electronic properties of the heteroatom ligand and to the solvent polarity. Finally, the reductive elimination to form ethers is much more strongly dependent on the concentration of free phenol than is the elimination of amine on the presence of free amine, presumably due to differences in self-association of the anions and conjugate acids. Studies to delineate the origins of these differences further and to extend these reactions to reductive eliminations from purely alkyl complexes are in progress.

Experimental Section

Typical procedure for the synthesis of bisphosphine benzylpalladium aryloxide complexes (Scheme 1): In a 20 mL scintillation vial, [(cod)Pd(Bn)Cl] (110 mg, 0.323 mmol) was dissolved in THF (5 mL). In another vial dppf (179 mg, 0.323 mmol) was dissolved in THF (5 mL) and added to the stirred solution of [(cod)Pd(Bn)Cl] in a nitrogen-filled glovebox resulting in an orange solution. After 10 min KOAr (0.33 mmol) dissolved in THF (5 mL) was added to the orange solution, and the resulting mixture was stirred for a further 10 min. The THF was evaporated in vacuo, and the residue was dissolved in benzene. The benzene solution was filtered through a plug of Celite, which was then rinsed with benzene until the color has dissipated. The filtrate was concentrated in vacuo to a volume of about 3 mL, and then pentane (15 mL) was added. The mixture was cooled to −35 °C for 12 h to complete precipitation. The solid was filtered from the solution and washed with pentane (3 × 10 mL) and then dried in vacuo.

Received: February 13, 2011
Published online: June 17, 2011

Keywords: aryloxides · benzyl complexes · nucleophilic attack · palladium · reductive elimination

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[27] The substitution pattern of the aryloxide group had a minor impact on the rate of the reductive elimination reaction. Complex **4** and **5** underwent reductive elimination with rates that were identical to each other. However, complex **6**, containing 3,5-dimethyl substitution on the phenoxide reacted more slowly than the analogous complex **5** containing 3,5-bistrifluoromethyl substituents. In contrast, C(sp^3)–N reductive elimination reactions exhibited a significant dependence on the substitution pattern of the diarylamido ligands. The complexes containing 3,5-disubstituted amido ligands underwent reductive elimination much more slowly than complexes containing the analogous *para* substituent.[16] The difference between the effect of the substituents in the aryloxide and diarylamido groups is likely due to the 3,5-disubstituted aryloxide ligands being less sterically demanding than 3,5-disubstituted diarylamide ligands.
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