JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
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Stereoselective Intermolecular Allylic C−H Trifluoroacetoxylation of Functionalized Alkenes

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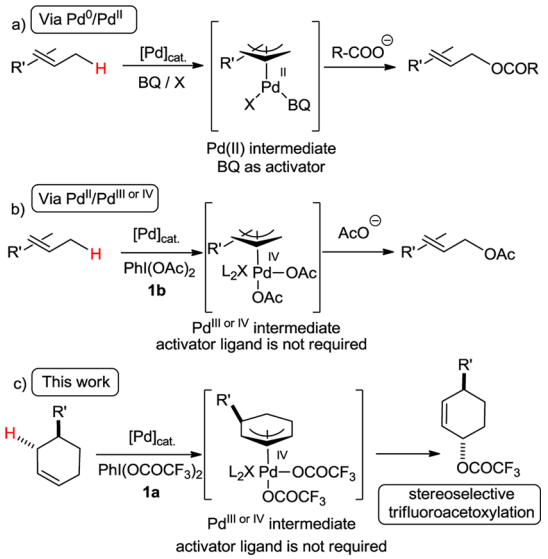
Supporting Information

ABSTRACT: Pd-catalyzed allylic C−H trifluoroacetoxylation of substituted alkenes was performed using $PhI(OCOCF_3)_2$ as the oxidant and acyloxy source. Trifluoroacetoxylation of monosubstituted cyclopentenes and cyclohexenes proceeds with excellent regio- and diastereoselectivity. Studies with one of the possible (η^3-allyl)Pd(II) intermediates suggest that the reaction proceeds via stereoselective formation of Pd(IV) intermediates and subsequent stereo- and regioselective reductive elimination of the product.

Palladium-catalyzed allylic C−H acyloxylation reactions represent one of the first and most widespread applications in C−H functionalizations.[1] This research field was established in the 1990s by the work of Tsuji,[2] Åkermark,[3] Bäckvall,[4] and McMurry and Kocovsky.[5] These early studies described useful protocols and mechanistic studies for the conversion of simple, often symmetrical alkenes to allylic acetates using Pd catalysts in the presence benzoquinone (BQ) as a crucial additive. More recently, efforts have focused on the development of C−H acyloxylations for the functionalization of more complex organic molecules, as exemplified in the work by White,[6] Stahl,[1c,e,f,7] Muzart,[8] Kaneda,[9] Stambuli,[10] Bercaw,[11] and us.[12] This pursuit has raised a number of challenges, including two key aspects of selectivity: (i) in the C−H activation step, when several nonequivalent allylic C−H bonds are available; and (ii) in the nucleophilic attack of the acyloxy group, when nonequivalent carbons can be functionalized, such as in (η^3-allyl)palladium species. If a high level of selectivity control cannot be achieved for both of these steps, an intractable mixture of product regio- and stereoisomers may be formed. One major strategy is to use ligand control to govern the selectivity. For example, White and co-workers[6c−f] employed serial ligand catalysis (SLC) based on the application of sulfoxide and BQ ligands for highly selective C−H acyloxylation reactions. Many other creative ideas to replace BQ with alternative ligand/oxidant combinations, thereby increasing the reactivity and selectivity, have been reported.[7,8,10,11] Although many basic synthetic problems have been solved by the recent advances in catalytic C−H acyloxylation, notorious selectivity and reactivity issues persist. In this communication, we focus on two important questions: (a) the realization of allylic C−H trifluoroacetoxylation reactions, which have never been reported and are probably difficult to achieve through traditional Pd(0)/Pd(II) manifolds; and (b) the achievement of highly stereoselective intermolecular C−H acyloxylation of functionalized cyclic alkenes. Herein we describe how these challenges were met using an approach based on the application of hypervalent iodines, which are able to oxidize the Pd catalyst to the Pd(III) or Pd(IV) oxidation state.[13] When Pd(II) is the highest possible oxidation state in the C−H functionalization, activator ligands (e.g., BQ) are required for the creation of electron deficiency on Pd, which is necessary to induce reductive elimination (e.g., Scheme 1a).[1c,4,14] On the basis of our previous work[12a] and recent studies by Hou and co-workers[15] on oxidative C−H trifluoroacetoxylation, we envisaged that reductive elimination of the trifluoroacetate from electron-deficient Pd(III) or Pd(IV) could be realized without the use of BQ or other activator ligands.

Scheme 1. Basic Strategies for Selective Allylic C−H Acyloxylation of Alkenes

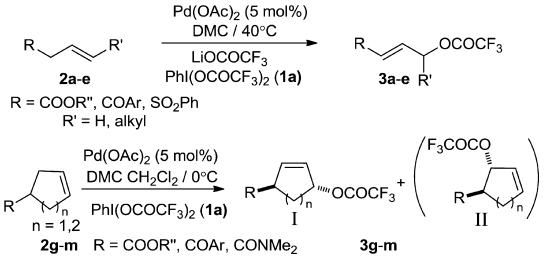


As mentioned above, White and co-workers have presented a number of spectacular applications of stereoselective cyclization via allylic C−H acyloxylation reactions.[6c,e] There are, however, very few studies demonstrating diastereoselective intermolecular allylic C−H acyloxylations.[3a] We predicted that the use of highly oxidized species should enable allylic C−H functionalization at reaction temperatures low enough to permit high diastereoselectivity. We,[12a] and subsequently the Stambuli group,[10b] showed that $PhI(OAc)_2$ (**1b**) can be used as an

Received: March 13, 2012
Published: May 15, 2012

   dx.doi.org/10.1021/ja302457p | J. Am. Chem. Soc. 2012, 134, 8778−8781

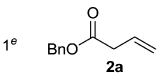
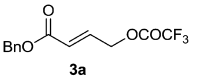
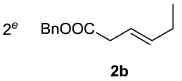
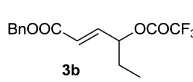
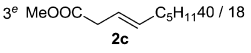
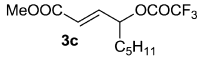
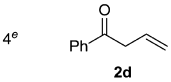
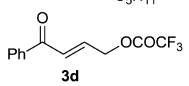
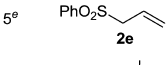
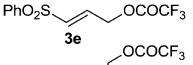
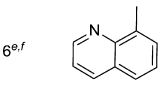
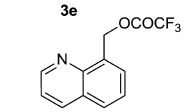
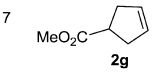
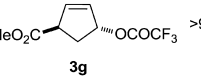
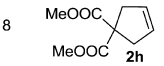
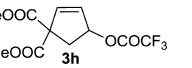
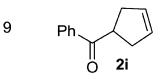
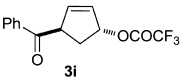
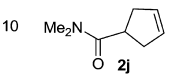
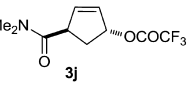
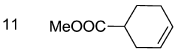
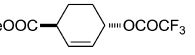
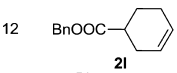
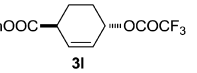
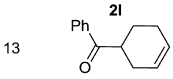
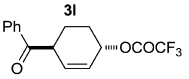
Scheme 2. Scope and Reaction Conditions



oxidant in C−H acyloxylation reactions instead of BQ or other activator ligands (Scheme 1b). We have now found that even stronger oxidants, such as $PhI(OCOCF_3)_2$ (**1a**, also called PIFA), can also be used, further extending the synthetic scope of the Pd-catalyzed C−H acyloxylation to the synthesis of allylic trifluoroacetates from alkenes. Moreover, in line with our prediction, this makes possible the diastereoselective C−H acyloxylation of functionalized cyclic alkenes (Schemes 1c and 2). Thus, alkene substrates (**2**) were reacted with **1a** in the presence of catalytic amounts (5 mol %) of $Pd(OAc)_2$ in dimethyl carbonate (DMC) (Scheme 2) to afford allylic trifluoroacetates in good to excellent yields (Table 1). Our choice of DMC as the solvent was based on its high polarity and stability toward **1a** (which can oxidize possible alternatives such as tetrahydrofuran and dimethyl sulfoxide). Allylic trifluoroacetates are more reactive substrates in Pd(0)-catalyzed allylic substitution than allylic acetates.[1a,b,16] As Pd(0) does not form under the strongly oxidative conditions, product degradation via oxidative addition can be avoided. Both terminal (**2a**, **2d**, and **2e**) and internal (**2b** and **2c**) alkenes reacted with high regioselectivity when **1a** was used as the oxidant and source of the nucleophile, comparable to previously published reactions using **1b**.[10b,12a] With acyclic substrates **2a**−**e**, the reaction proceeded faster in the presence of $LiOCOCF_3$. The reactions were typically conducted at 40 °C in the presence of carboxylate and sulfonate substituents (entries 1−3 and 5), while phenyl ketone **2d** was more reactive, allowing full conversion to be achieved at 25 °C (entry 4). Even benzylic trifluoroacetoxylation could be performed with **2f**, but the reaction required much harsher conditions than for its allylic counterparts. It was shown[13b] that **2f** can be smoothly acetoxylated by **1b**.

The most interesting results were observed for C−H trifluoroacetoxylation of the cyclic substrates **2g**−**m**. The cyclic alkenes reacted much faster than the acyclic analogues. Thus, the reaction temperature for monosubstituted substrates **2g** and **2i**−**m** could be lowered to 0 °C. In fact, it is very unusual that C−H functionalization reactions can be performed under such mild conditions. As the melting point of DMC is above 0 °C, we conducted these reactions in 10:1 DMC/CH_2Cl_2. Disubstitution at the same carbon (**2h**) led to a drop in reactivity (compare the reaction temperatures in entries 7 and 8), probably due to steric effects on the C−H activation step. To our delight, the trifluoroacetoxylation reactions proceeded with very high regio- and diastereoselectivity. Since in substrates **2g** and **2i**−**m** four nonequivalent C−H bonds could be functionalized and there was the possibility of allylic rearrangement, at least six different regio- and stereoisomers could be expected. Hence, the reaction proceeded with high stereoselectivity, and the major product was a 1,4-regioisomer (type I in Scheme 2), while the 1,2-regioisomer (type II) was

Table 1. Pd-Catalyzed C−H Trifluoroacetoxylation by 1a[a]

Entry	Substrate	Conditions[b]	Product	I / II[c]	Yield[d]
1[e]	 **2a**	40 / 15	 **3a**	-	52
2[e]	 **2b**	40 / 18	 **3b**	-	66
3[e]	 **2c**	40 / 18	 **3c**	-	88
4[e]	 **2d**	25 / 24	 **3d**	-	70
5[e]	 **2e**	40 / 18	 **3e**	-	94
6[e,f]	 **2f**	100 / 24	 **3f**	-	(92)[g]
7	 **2g**	0 / 6	 **3g**	>95:5	75
8	 **2h**	25 / 18	 **3h**	-	86
9	 **2i**	0 / 24	 **3i**	11:1	49
10	 **2j**	0 / 8	 **3j**	3:1	59
11	 **2k**	0 / 6	 **3k**	5:1	53
12	 **2l**	0 / 15	 **3l**	10:1	51
13	 **2m**	0 / 6	 **3m**	15:1	49

[a]Substrate **2** (0.3 mmol) was dissolved in DMC, and **1a** (0.45 mmol) and $Pd(OAc)_2$ (0.015 mmol, 5 mol %) were then added. The mixture was then stirred using the temperatures and times indicated. For reactions conducted at 0 °C, a 10:1 DMC/CH_2Cl_2 mixture was used as the solvent. [b]Reaction conditions: temperature/time = °C/h. [c]Ratio of the obtained regioisomers (see Scheme 2). [d]Isolated yields (%). [e]$LiOCOCF_3$ (0.6 mmol) was used as an additive. [f]$(CF_3CO)_2O$ (3.0 mmol) was used as an additive. [g]NMR yield.

formed as a minor product. An exception was the trifluoroacetoxylation of **2g**, which gave only a single regio- and stereoisomer, **3g** (entry 7). The regioselectivity (see the I/II ratio in Table 1) depended on the ring size and the ring substituents. The allylic C−H trifluoroacetoxylation was more selective for cyclopentene than for cyclohexene derivatives (entry 7 vs 11 and 12). Significantly higher regioselectivity was obtained in the presence of the ester functionality than with the amide functionality (entry 7 vs 10). A drop in the regioselectivity of C−H allylation reactions in the presence of amide functionality was also reported by Stambuli and co-workers.[10a] Interestingly, we also observed some difference in regioselectivity between the methyl (**2k**) and benzyl (**2l**) ester functionalities (entry 11 vs 12). The high regio- and stereoselectivity for the intermolecular C−H functionalization of monosubstituted cyclopentenes and cyclohexenes is a very

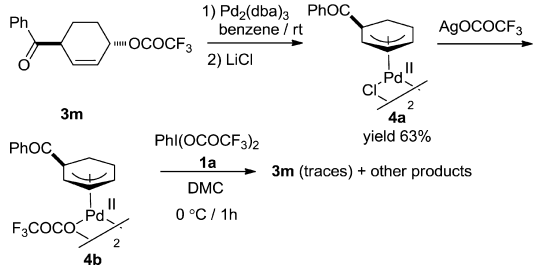
dx.doi.org/10.1021/ja302457p | J. Am. Chem. Soc. 2012, 134, 8778−8781

important synthetic advantage of our method (Scheme 2). To best of our knowledge, very few, if any, examples have been reported in the literature. For example, Åkermark and co-workers[3a] reported the Pd-catalyzed acetoxylation of **2k** using BQ (Scheme 1a-type reaction) at 50 °C to give five regio- and stereoisomers, with the main regioisomers being formed in nearly a 1:1 ratio. Our new system permits the use of considerably lower operating temperatures, granting access to much-improved selectivity.

Surprisingly, when **1a** was replaced with **1b** in reactions with cyclic substrates (e.g., **2g** or **2l**) no reaction occurred at 0 °C or elevated temperatures (up to 35 °C). Thus, it seems likely that the highly selective acyloxylation of monosubstituted cyclic alkenes can be performed only with trifluoroacetate reagent **1a**. Moreover, we found that $Pd(OAc)_2$ and $Pd(OCOCF_3)_2$ showed similar activity as catalysts but that only trifluoroacetoxylated products were observed with $Pd(OAc)_2$. No reaction occurred in the absence of Pd catalyst.

The stereochemistry of the reactions (entries 7−13) and our previous studies[12a] with **1b** (Scheme 1b) suggest that the reaction probably proceeds via (η^3-allyl)palladium species. However, an interesting mechanistic question is whether the reaction starts with the formation of an (η^3-allyl)palladium(II) species that is subsequently oxidized to (η^3-allyl)palladium(IV) or whether oxidation of the Pd(II) catalyst precedes formation of an (η^3-allyl)palladium(IV) complex [i.e., without prior formation of the corresponding (η^3-allyl)palladium(II) species]. It is well-established that (η^3-allyl)palladium(II) complexes can be formed from alkenes and Pd(II) precursors,[17] and therefore, we studied the possible formation of such complexes under catalytic conditions. Complex **4a** was prepared from **3m** and $Pd_2(dba)_3$ in benzene, the resulting complex was then treated with LiCl (Scheme 3). Kurosawa and co-workers have shown that allyl chlorides undergo stereoselective cis oxidative addition with $Pd_2(dba)_3$ when noncoordinating solvents such as benzene are used.[18], We also obtained a single stereoisomeric complex **4a** from product **3m** with $Pd_2(dba)_3$ in benzene at room temperature. Chloro complex **4a** was stable enough for purification by silica-gel chromatography and was obtained in 63% yield. After purification, ligand exchange was performed by halogen abstraction using $AgOCOCF_3$ to give complex **4b**, which is a conceivable reaction intermediate in the catalytic C−H trifluoroacetoxylation of **2m** (entry 13). Notably, complex **4b**

Scheme 3. Synthesis and Reactivity of the Presumed (η^3-Allyl)palladium(II) Intermediate of the Reaction



was very stable under ambient conditions, and we did not observe reductive elimination to **3m**. We hypothesized that **4b** could be oxidized and subsequently undergo reductive elimination to form **3m** upon addition of **1a**. Therefore, **4b** was reacted with **1a** for 1 h at 0 °C in DMC. In this process, **4b** was completely consumed, resulting in a complex mixture in which only a trace of **3m** was observed. However, the catalytic reaction proceeds very cleanly at 0 °C, so we conclude that **4b** is not a true reaction intermediate in the catalytic C−H trifluoroacetoxylation of **2m**. As mentioned above, BQ (or another activator ligand) is necessary to induce reductive elimination (Scheme 1a) in the classical Pd(0)/Pd(II)-based process to generate the allylic product.[1c,4,14] As expected for (η^3-allyl)palladium(II) complexes,[14a] **4b** in the presence of BQ undergoes smooth reductive elimination to afford **3m**.

On the basis of the above observations (Scheme 3) and the results of the catalytic reactions described herein, we propose the catalytic cycle in Figure 1, as exemplified by the **2m** → **3m**

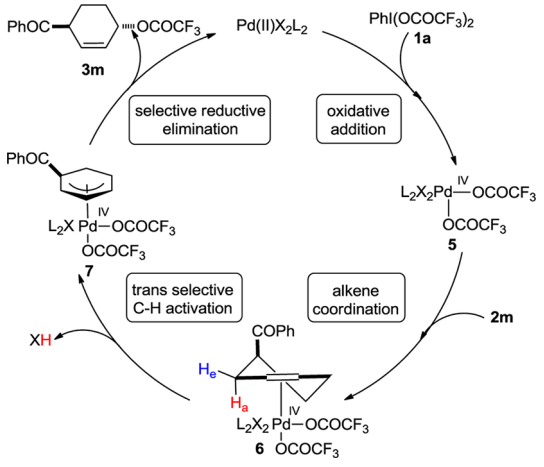


Figure 1. Proposed catalytic cycle.

transformation (entry 13). In the first instance, $Pd(OAc)_2$ is directly oxidized by **1a** to give complex **5**. The observed acceleration of the reaction upon addition of $LiOCOCF_3$ (entries 1−6) may be explained by the formation of anionic Pd species, which are easy to oxidize. Muzart and co-workers[8] reported that $Pd(OAc)_2$ may form such complexes in the presence of lithium salts. We also suppose that coordination of DMC (i.e., L = DMC) may stabilize the formed Pd(IV) species **5**. Coordination of **2m** is followed by stereoselective C−H activation of H_a (colored in red) in complex **6**. A possible mechanism would be deprotonation[19] by an acetate (X = OAc) or trifluoroacetate ligand. The driving force of the formation of (η^3-allyl)palladium(IV) complex **7** is the relief of the electron deficiency at the Pd(IV) center by π-donation from the allyl moiety. Formation of allylpalladium complexes from alkenes with a cis double bond, such as in cyclic substrates **2g−m**, might be easier than the same process with acyclic alkenes **2a−e**. This would explain the above finding that the cyclic substrates are more reactive than the acyclic ones. The Pd atom in **7** is strongly electron-deficient, which allows a rapid reductive elimination involving the trifluoroacetate ligand. Thus, an activator ligand (e.g., BQ; Scheme 1a) is not needed to effect reductive elimination, as the high oxidation state of Pd itself is sufficient.The regioselectivity is probably governed by the hyperconjugative interaction between the polar C−C(OPh) σ bond and the π-allyl system.[20] Thus, the C−H activation (**6** → **7**) is stereoselective and the reductive elimination (**7** → **3m**) is both stereo- and regioselective, imparting an exceptionally high selectivity to the entire allylic C−H functionalization process. The cis counterpart of **3m** might have formed by external attack of the trifluoroacetate on **7**.[14a] However, the lack

dx.doi.org/10.1021/ja302457p | J. Am. Chem. Soc. 2012, 134, 8778−8781

of cis products shows that the allyl moiety is attacked by the trifluoroacetate coordinated to Pd and not an external one. An alternative explanation of the trans selectivity is that the C−H bond of **6** involving H_e (colored in blue) is activated by Pd to form the cis isomer of **7**, which subsequently undergoes external attack by a trifluoroacetate ion to afford **3m**. Of course, the formation of bimetallic Pd(III)−Pd(III) instead of Pd(IV) species is also plausible, as with arylpalladium analogues of **7**.[13d,21] Since the metal centers of Pd(III) complexes are also electron-deficient, similar reductive elimination processes as for the **7** → **3m** process described above may operate. A further possibility is that the reaction proceeds via stereoselective formation of Pd(II) complex **4b** followed by oxidation to **7**. However, our findings do not support this route, and it is known that (η^3-allyl)palladium(II) trifluoroacetate complexes under C−H activation conditions are usually unstable.[17b,22] A further mechanistic alternative might be that Pd(II) serves as a Lewis acid to activate **1a** and also to coordinate to the carbonyl or ester functionality of the substrate. However, this possibility seems unlikely. For example, the reaction of various Lewis acids (e.g., $AlCl_3$,$TiCl_4$, and BF_3) with **1a** and **2g** did not give even traces of **3g**, which was formed cleanly under the same reaction conditions using $Pd(OAc)_2$ (entry 7).

In summary, we have demonstrated the first catalytic allylic C−H trifluoroacetoxylation reaction, which was achieved using Pd catalysis in the presence of $PhI(OCOCF_3)_2$. The reaction proceeds with remarkably high regio- and stereoselectivity and is synthetically useful for the generation of stereodefined cycloalkenes from monosubstituted precursors. As allylic trifluoroacetates are more reactive substrates in allylic substitutions than allylic acetates, we envision that our method will prove to be a selective route to the generation of valuable synthons. Development of the asymmetric version of the reaction (with substrates **2b**, **2c**, and **2g**−**j**) and studies of the possibilities for chirality transfer (with optically pure forms of **2k**−**m**) are ongoing projects in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the Swedish Research Council and the Knut and Alice Wallenberg Foundation via the Center of Molecular Catalysis at Stockholm University for financial support. A postdoctoral stipend from the Carl Tryggers Stiftelse for L.T.P. is gratefully acknowledged. The authors also thank Robert Pendrill for help with some NMR experiments.

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