Palladium Catalysis

DOI: 10.1002/anie.201103500

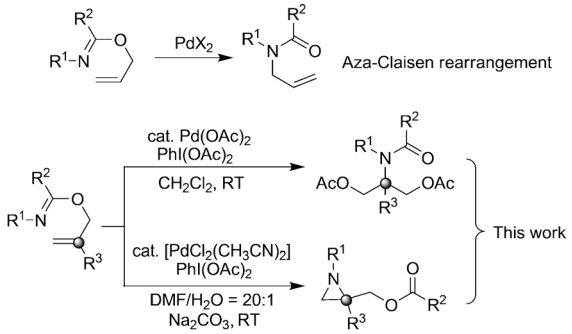
Palladium-Catalyzed Tunable Functionalization of Allylic Imidates: Regioselective Aminodiacetoxylation and Aziridination**

*Sunliang Cui, Lukasz Wojtas, and Jon C. Antilla**

Recently, palladium-catalyzed reactions that appear to involve Pd^{II}/Pd^{IV} catalytic cycles have proven to be interesting and attractive to synthetic chemists. These transformations offer access to novel organic products, complementing those obtained by conventional Pd^{0}/Pd^{II}-catalyzed processes.[1] The Pd-catalyzed oxidative difunctionalization of alkenes is captivating because it is utilized to access diamination,[2] aminooxygenation,[3] dioxygenation,[4] aminofluorination,[5] and cyclopropanation products.[6] One common feature of these reactions is the use of $PhI(OAc)_2$ as an oxidant to intercept the Pd–C bond of the intermediate to facilitate C–X (X = C, N, O, F) bond formation.[7] Despite these advancements, Pd^{II}/Pd^{IV}-catalyzed and tunable functionalization to provide divergent C–X bond formation remains elusive.[8]

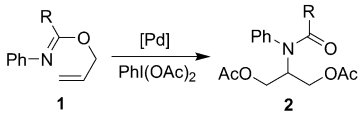
The Pd^{II}-catalyzed aza-Claisen rearrangement of allylic imidates, involving an alkyl palladium intermediate, is a well known process for the synthesis of allylic amines.[9] During our current study, we reasoned that the alkyl palladium intermediate formed in the aza-Claisen rearrangement of allylic imidates could be further transformed by oxidation to the Pd^{IV} species, using $PhI(OAc)_2$ as an oxidant, to provide new C–X bonds. Herein, we report a novel and general palladium-catalyzed tunable functionalization of allylic imidates, thus demonstrating regioselective aminodiacetoxylation and aziridination under mild reaction conditions (Scheme 1).

Our initial investigations began with allyl *N*-phenylbenzimidate (**1a**). Treatment of **1a** with 10 mol% $Pd(OAc)_2$ and 3 equivalents of $PhI(OAc)_2$ in CH_2Cl_2 at room temperature afforded an unexpected 2-amino-1,3-diacetoxylation product **2a** in 62% yield (Table 1, entry 1). The reaction was highly regioselective, with no additional functionalized isomers detected. Control experiments indicated that in the absence of $Pd(OAc)_2$ aminodiacetoxylation was not observed. The use of other Pd^{II} sources and different solvents uniformly failed to improve the yield (Table 1, entries 2–5). Based on an initial mechanistic hypothesis for this reaction, we believed that electron-donating substituents could stabilize a postulated intermediate, thus facilitating this transformation. Indeed,



Scheme 1. DMF = *N*,*N*-dimethylformamide.

Table 1: Optimization of the Pd-catalyzed aminodiacetoxylation of allylic imidate **1**.[a]



1 **2**

Entry	R	Catalyst	Solvent	Product	Yield [%][b]
1	Ph (**1a**)	$Pd(OAc)_2$	CH_2Cl_2	**2a**	62
2	**1a**	$Pd(OAc)_2$	CH_3CN	**2a**	61
3	**1a**	$Pd(OAc)_2$	toluene	**2a**	42
4	**1a**	$Pd(OAc)_2$	AcOH	**2a**	trace
5	**1a**	$[PdCl_2(CH_3CN)_2]$	CH_2Cl_2	**2a**	56
6	4-$CH_3C_6H_4$ (**1b**)	$Pd(OAc)_2$	CH_2Cl_2	**2b**	77
7[c]	PMP (**1c**)	$Pd(OAc)_2$	CH_2Cl_2	**2c**	89
8	**1c**	$[PdCl_2(CH_3CN)_2]$	CH_2Cl_2	**2c**	78
9	**1c**	$[PdCl_2(PhCN)_2]$	CH_2Cl_2	**2c**	65
10	**1c**	$Pd(OAc)_2$	CH_3CN	**2c**	80
11	**1c**	$Pd(OAc)_2$/1,10-phenanthroline (10%)	CH_2Cl_2	**2c**	trace

[a] Reaction conditions: **1** (0.30 mmol), catalyst (10 mol%), $PhI(OAc)_2$ (0.90 mmol), solvent (1 mL), at RT. [b] The yield of isolated product calculated with **1** as the limiting reagent. [c] PMP = *para*-methoxyphenyl.

when **1b** and **1c** were subjected to these reaction conditions (Table 1, entries 6 and 7), **2b** and **2c** were obtained in 77% and 89% yield respectively. These remarkable improvements demonstrated that electron-rich substituents could enhance reactivity. With this result in hand, we attempted to further optimize the reaction conditions using **1c** as a model substrate, and found other combinations of Pd sources and solvents did not promote the process (Table 1, entries 8–10). Addition of 1,10-phenanthroline as a ligand inhibited the reaction (Table 1, entry 11). Notably the reaction proceeds smoothly at room temperature under an atmosphere of air

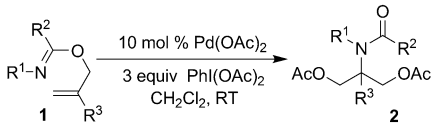
[*] Dr. S. Cui, Prof. Dr. J. C. Antilla
Department of Chemistry, University of South Florida
4202 E. Fowler Avenue, Tampa, FL 33620 (USA)
E-mail: jantilla@usf.edu
Dr. L. Wojtas
Department of Chemistry X-Ray Facility, University of South Florida
4202 E. Fowler Avenue, Tampa, FL 33620 (USA)

[**] We thank the University of South Florida for financial support.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201103500.

with high regioselectivity. Additional control reactions under an argon atmosphere gave identical results.

2-Amino-1,3-diol subunits constitute an important triad pattern found in many natural molecules of biological interest and attract much synthetic attention.[10] Encouraged by our results, we applied the aminodiacetoxylation protocol to a variety of allylic imidates, which are readily available from the respective allyl alcohol and imidoyl chloride.[11] As summarized in Table 2, electron-rich *N*-aryl allylic imidates furnished

Table 2: Pd-catalyzed aminodiacetoxylation of allylic imidates.[a]



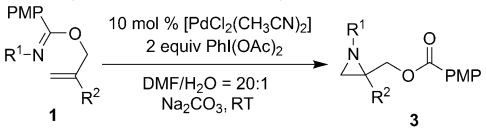
Entry	R^1	R^2	R^3	Product	Yield [%][b]
1	Ph	PMP	H	**2c**	89
2	4-$CH_3C_6H_4$	PMP	H	**2d**	81
3	4-$CH_3OC_6H_4$	PMP	H	**2e**	86
4	4-ClC_6H_4	PMP	H	**2f**	76
5	4-BrC_6H_4	PMP	H	**2g**	75
6	4-$CH_3O_2CC_6H_4$	PMP	H	**2h**	78
7	4-NCC_6H_4	PMP	H	**2i**	56
8	3-$CF_3C_6H_4$	PMP	H	**2j**	63
9	2,6-$(CH_3)_2C_6H_3$	PMP	H	**2k**	92
10	isopropyl	PMP	H	**2l**	88
11	cyclohexyl	PMP	H	**2m**	92
12	$Cl(CH_2)_3$	PMP	H	**2n**	65
13	Ph	Ph	CH_3	**2o**	72
14	Ph	PMP	CH_3	**2p**	88
15	4-$CH_3C_6H_4$	PMP	CH_3	**2q**	89
16	4-BrC_6H_4	PMP	CH_3	**2r**	74
17	isopropyl	PMP	CH_3	**2s**	92
18	Ph	PMP	Et	**2t**[c]	53
19	4-$CH_3C_6H_4$	PMP	Et	**2u**[d]	52

[a] Reaction conditions: **1** (0.30 mmol), $PhI(OAc)_2$ (0.90 mmol), CH_2Cl_2 (1 mL), RT, 1–5 h. [b] The yield of isolated product calculated with **1** as the limiting reagent. [c] The aza-Claisen rearrangement product was detected and ^1H NMR analysis of the reaction mixture showed a ratio of 1:1.54 versus **2t**. [d] The aza-Claisen rearrangement product was detected and ^1H NMR analysis of the reaction mixture showed a ratio of 1:1.62 versus **2u**.

the regioselective *N*-arylaminodiacetoxylation products in good to excellent yields (Table 2, entries 1–3 and entry 9), while electron-deficient *N*-aryl substrates afforded the products in moderate to good yields (Table 2, entries 4–8). The reaction could also be performed with various *N*-alkyl allylic imidates, giving *N*-alkylaminodiacetoxylation products in moderate to excellent yields (Table 2, entries 10–12). A number of disubstituted allylic imidates were also employed to investigate the scope of the aminodiacetoxylation. The transformation afforded the corresponding tetrasubstituted carbon-tethered aminodiacetoxylation products in moderate to excellent yields (Table 2, entries 13–19), with generality in both *N*-aryl and *N*-alkyl substitution. Notably, tetrasubstituted carbon-tethered amines are difficult to synthesize by conventional methods,[12] and this Pd-catalyzed functionalization gives facile access to these compounds in a general and efficient manner, therefore displaying valuable synthetic utility. The reaction is tolerant of various functional groups, e.g., -CN, $-CO_2CH_3$, -Cl, -Br, $-CF_3$, thus showing a broad substrate scope. Interestingly, aryl–bromide bonds were unaffected by the reaction conditions (Table 2, entries 5 and 16). The general structure of the products was confirmed by X-ray single-crystal analysis of compound **2k** (see the Supporting Information), in addition to standard characterization.

Furthermore, we discovered that the addition of water to this reaction could lead to a rather surprising formation of aziridine products. Optimization of the reaction conditions showed that the use of $[PdCl_2(CH_3CN)_2]$ as a catalyst, DMF/H_2O (20:1) as cosolvent, and Na_2CO_3 as an additive led to divergent reactivity of the allylic imidate, exclusively promoting the aziridination (for optimization, see the Supporting Information). The generality of the reaction was then established, with various functionalized aziridines synthesized in moderate to good yields (Table 3). The structure of the products was further confirmed by X-ray single-crystal

Table 3: Pd-catalyzed aziridination of allylic imidates.[a]

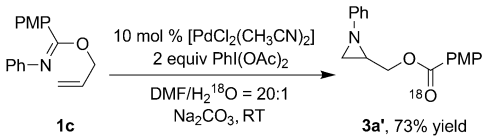


Entry	R^1	R^2	Product	Yield [%][b]
1	Ph	H	**3a**	78
2	4-$CH_3C_6H_4$	H	**3b**	79
3	4-$TsOC_6H_4$	H	**3c**	64
4	4-ClC_6H_4	H	**3d**	69
5	4-BrC_6H_4	H	**3e**	71
6	4-$CH_3O_2CC_6H_4$	H	**3f**	66
7	4-NCC_6H_4	H	**3g**	58
8	3-$CF_3C_6H_4$	H	**3h**	55
9	3-$NO_2C_6H_4$	H	**3i**	58
10	2,6-$(CH_3)_2C_6H_3$	H	**3j**	73
11	Ph	CH_3	**3k**	46

[a] Reaction conditions: **1** (0.30 mmol), $PhI(OAc)_2$ (0.60 mmol), DMF (3 mL), Na_2CO_3 (4 M aqueous solution, 150 μL), RT, 2–8 h. [b] The yield of the isolated product calculated with **1** as the limiting reagent.

analysis of compound **3g** (see the Supporting Information), in addition to standard characterization. Aziridines are versatile substances for the synthesis of useful nitrogen-containing compounds. Therefore, we believe this method to be of potential synthetic utility.[13,14]

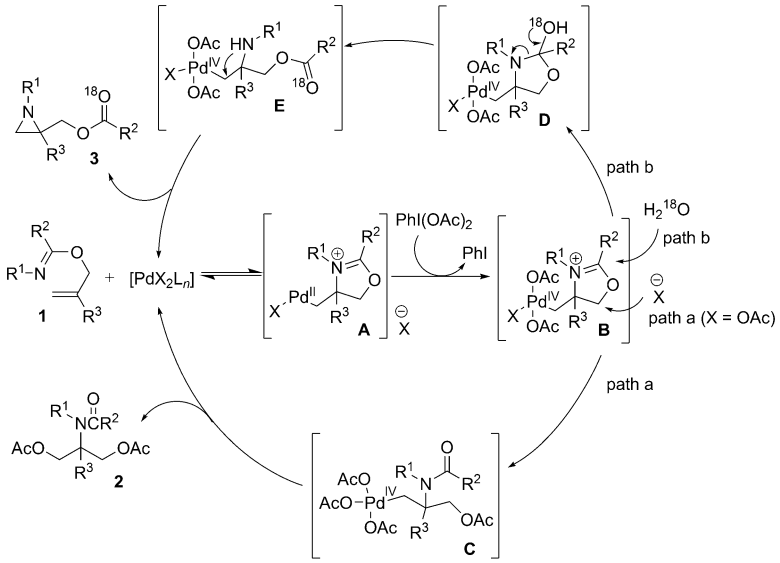
Control experiments were conducted to gain insight into the reaction mechanism. Interestingly, no aminodiacetoxylation or aziridination was observed when various Pd^0/Pd^{II} oxidants, such as $Cu(OAc)_2$, $CuCl_2$, and benzoquinone were used in place of $PhI(OAc)_2$. On this basis, we believe these transformations are less likely to proceed through a traditional Pd^0/Pd^{II} catalytic cycle. Indeed, when stoichiometric $[PdCl_2(CH_3CN)_2]$ was used in the absence of $PhI(OAc)_2$, aziridination was not observed. Furthermore, an isotope labeling experiment was conducted to probe the aziridination mechanism, using $H_2{}^{18}O$ (97 atom % ^{18}O; Scheme 2). HRMS showed an ^{18}O atom was incorporated in the product **3a′**



Scheme 2. Isotopic labeling experiment.

(90% ^{18}O enriched, $[M+H]^+$ 286.1317) and IR spectroscopy showed that the C=O bond frequency shifted from 1708 to 1682 cm^{-1}.[15] These results confirm the C=O group of **3a′** is ^{18}O labeled, and the ^{18}O atom was delivered from $H_2{}^{18}O$.

On the basis of these results, a possible catalytic cycle for this tunable transformation is proposed (Scheme 3). First, the



Scheme 3. Proposed $Pd^{II/IV}$-catalyzed tunable functionalization of allylic imidates.

Pd^{II}-mediated reversible 5-*exo*-trig aminopalladation of the allylic imidate forms the oxazolinium-substituted alkyl palladium species **A**,[16] which is oxidized by $PhI(OAc)_2$ to produce Pd^{IV} intermediate **B**.[17] Intermediate **B** shows divergent reactivity: 1) Under reaction conditions for aminodiacetoxylation, **B** is nucleophilically attacked by acetate, leading to oxazolinium fragmentation to give **C**, a subsequent reductive elimination furnishes the final product **2** and regenerates the Pd^{II} catalyst (path a). 2) Under conditions for aziridination, **B** is hydrolyzed to **D** and a subsequent ring opening gives amine intermediate **E**,[18,19] followed by an intramolecular cyclization/reductive elimination to furnish the aziridination product **3** and the Pd^{II} catalyst (path b).[14a] Therefore, the functionalization is tunable, depending on the reaction conditions. Moreover, when R^2 is an electron-rich group, such as PMP, the initial aminopalladation is enhanced to facilitate this transformation.

In summary, we have successfully developed a novel palladium-catalyzed tunable functionalization of allylic imidates, including regioselective aminodiacetoxylation and aziridination with switchable reactivity toward divergent C–N and C–O bond formation. This method opens up a new avenue for the functionalization of allylic imidates under mild reaction conditions and with broad substrate scope and high efficiency. Isotope labeling experiments provide evidence for two possible mechanistic pathways involving a proposed Pd^{II}/Pd^{IV} catalytic cycle. Further study of the scope of the reaction and extension of the method are in progress.

Experimental Section

Typical procedure for aminodiacetoxylation: $Pd(OAc)_2$ (6.8 mg, 0.03 mmol) and $PhI(OAc)_2$ (290 mg, 0.9 mmol) were added to a vial. CH_2Cl_2 (0.9 mL) was added, followed by the addition of allylic imidate **1c** (80.1 mg, 0.3 mmol) by using a microsyringe. The microsyringe was washed with CH_2Cl_2 (0.1 mL) and this solution was added to the reaction solution. The mixture was kept at room temperature under air. After completion of the reaction, the solution was purified by flash column chromatography on silica gel using ethyl acetate/hexanes (v/v, 1:2) as eluent to give product **2c** as a colorless oil (102.8 mg, 89% yield). ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 7.17$ (m, 5H), 7.02 (m, 2H), 6.57 (d, $J = 7.5$ Hz, 2H), 4.87 (t, $J = 7.5$ Hz, 1H), 4.35 (d, $J = 7.5$ Hz, 4H), 3.64 (s, 3H), 1.95 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 170.9$, 170.5, 160.6, 142.1, 130.6, 129.2, 129.1, 128.2, 127.4, 113.0, 62.2, 57.3, 55.1, 20.8 ppm; HRMS (ESI) (*m*/*z*): calcd for $C_{21}H_{23}NO_6$ $[M+H^+]$ 386.1598; found 386.1599.

Typical procedure for aziridination: $[PdCl_2(CH_3CN)_2]$ (7.8 mg, 0.03 mmol), $PhI(OAc)_2$ (193.2 mg, 0.6 mmol) were added to a vial. DMF (2.5 mL) and Na_2CO_3 (4 M aqueous solution, 150 μL) were added, followed by the addition of allylic imidate **1c** (80.1 mg, 0.3 mmol) by using a microsyringe. The microsyringe was washed with DMF (0.5 mL) and this solution was added to the reaction mixture. The mixture was kept at room temperature under air. After completion, the solution was decanted into a separatory funnel, diluted with 15 mL Et_2O and 5 mL water. The two layers were separated and the aqueous layer was extracted with Et_2O (3 × 15 mL). The combined ether layers were washed with brine (20 mL), dried (Na_2SO_4), concentrated in vacuo, and purified by flash column chromatography on Al_2O_3 using ethyl acetate/hexanes (v/v, 1:4) as eluent to give aziridine **3a** as a colorless oil (66 mg, 78% yield). ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 8.01$ (d, $J = 10.0$ Hz, 2H), 7.16 (m, 2H), 6.91 (m, 5H), 4.58 (dd, $J_1 = 12.5$ Hz, $J_2 = 5.0$ Hz, 1H), 4.11 (dd, $J_1 = 10.0$ Hz, $J_2 = 7.5$ Hz, 1H), 3.80 (s, 3H), 2.48 (m, 1H), 2.24 (d, $J = 2.5$ Hz, 1H), 2.13 ppm (d, $J = 7.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 166.3$, 163.7, 153.9, 131.9, 129.2, 122.8, 122.5, 120.8, 113.9, 66.8, 55.6, 37.8, 31,7 ppm; HRMS (ESI) (*m*/*z*): calcd for $C_{17}H_{17}NO_3$ $[M+Na^+]$ 306.1101; found 306.1110.

Received: May 22, 2011
Published online: August 10, 2011

Keywords: allylic imidates · aziridination · oxidation · palladium · synthetic methods

[1] For reviews, see: a) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196–5217; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094–5115; b) K. Muñiz, *Angew. Chem.* **2009**, *121*, 9576–9588; *Angew. Chem. Int. Ed.* **2009**, *48*, 9412–9423; c) P.

Sehnal, R. J. K. Taylor, I. J. S. Fairlamb, *Chem. Rev.* **2010**, *110*, 824 – 889; d) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147 – 1169; e) L.-M. Xu, B.-J. Li, Z. Yang, Z.-J. Shi, *Chem. Soc. Rev.* **2010**, *39*, 712 – 733; f) K. M. Engle, T.-S. Mei, X. Wang, J.-Q. Yu, *Angew. Chem.* **2011**, *123*, 1514 – 1528; *Angew. Chem. Int. Ed.* **2011**, *50*, 1478 – 1491.

[2] a) J. Streuff, C. H. Hövelmann, M. Nieger, K. Muñiz, *J. Am. Chem. Soc.* **2005**, *127*, 14586 – 14587; b) K. Muñiz, *J. Am. Chem. Soc.* **2007**, *129*, 14542 – 14543.

[3] a) E. J. Alexanian, C. Lee, E. J. Sorensen, *J. Am. Chem. Soc.* **2005**, *127*, 7690 – 7691; b) G. Liu, S. S. Stahl, *J. Am. Chem. Soc.* **2006**, *128*, 7179 – 7181; c) L. V. Desai, M. S. Sanford, *Angew. Chem.* **2007**, *119*, 5839 – 5842; *Angew. Chem. Int. Ed.* **2007**, *46*, 5737 – 5740.

[4] Y. Li, D. Song, V. M. Dong, *J. Am. Chem. Soc.* **2008**, *130*, 2962 – 2964.

[5] T. Wu, G. Yin, G. Liu, *J. Am. Chem. Soc.* **2009**, *131*, 16354 – 16355.

[6] a) X. Tong, M. Beller, M. K. Tse, *J. Am. Chem. Soc.* **2007**, *129*, 4906 – 4907; b) L. L. Welbes, T. W. Lyons, K. A. Cychosz, M. S. Sanford, *J. Am. Chem. Soc.* **2007**, *129*, 5836 – 5837; c) T. Tsujihara, K. Takenaka, K. Onitsuka, M. Hatanaka, H. Sasai, *J. Am. Chem. Soc.* **2009**, *131*, 3452 – 3453.

[7] a) A. R. Dick, K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2004**, *126*, 2300 – 2301; b) L. V. Desai, K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2004**, *126*, 9542 – 9543; c) A. R. Dick, J. W. Kampf, M. S. Sanford, *J. Am. Chem. Soc.* **2005**, *127*, 12790 – 12791; d) L. V. Desai, K. Stowers, M. S. Sanford, *J. Am. Chem. Soc.* **2008**, *130*, 13285 – 13293; e) J. M. Racowski, A. R. Dick, M. S. Sanford, *J. Am. Chem. Soc.* **2009**, *131*, 10974 – 10983; f) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074 – 1086; g) X. Wang, Y. Lu, H.-X. Dai, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 12203 – 12205; h) D. C. Powers, D. Y. Xiao, M. A. L. Geibel, T. Ritter, *J. Am. Chem. Soc.* **2010**, *132*, 14530 – 14536.

[8] a) C. F. Rosewall, P. A. Sibbald, D. V. Liskin, F. E. Michael, *J. Am. Chem. Soc.* **2009**, *131*, 9488 – 9489; b) P. A. Sibbald, C. F. Rosewall, R. D. Swartz, F. E. Michael, *J. Am. Chem. Soc.* **2009**, *131*, 15945 – 15951.

[9] a) T. G. Schenck, B. Bosnich, *J. Am. Chem. Soc.* **1985**, *107*, 2058 – 2066; b) M. Calter, T. K. Hollis, L. E. Overman, J. Ziller, G. G. Zipp, *J. Org. Chem.* **1997**, *62*, 1449 – 1456; c) Y. Donde, L. E. Overman, *J. Am. Chem. Soc.* **1999**, *121*, 2933 – 2934; d) C. E. Anderson, L. E. Overman, *J. Am. Chem. Soc.* **2003**, *125*, 12412 – 12413; e) A. Moyano, M. Rosol, R. M. Moreno, C. López, M. A. Maestro, *Angew. Chem.* **2005**, *117*, 1899 – 1903; *Angew. Chem. Int. Ed.* **2005**, *44*, 1865 – 1869; f) E. J. Yoo, I. Bae, S. H. Cho, S. Chang, *Org. Lett.* **2006**, *8*, 1347 – 1350.

[10] a) S. Kim, N. Lee, S. Lee, T. Lee, Y. M. Lee, *J. Org. Chem.* **2008**, *73*, 1379 – 1385; b) J. Cho, Y. M. Lee, D. Kim, S. Kim, *J. Org. Chem.* **2009**, *74*, 3900 – 3904; c) A. Voituriez, A. Pérez-Luna, F. Ferreira, C. Botuha, F. Chemla, *Org. Lett.* **2009**, *11*, 931 – 934.

[11] R. N. Ram, N. Kumar, N. Singh, *J. Org. Chem.* **2010**, *75*, 7408 – 7411.

[12] For a review, see: J. Clayden, M. Donnard, J. Lefranc, D. J. Tetlow, *Chem. Commun.* **2011**, *47*, 4624 – 4639.

[13] a) P. Müller, C. Fruit, *Chem. Rev.* **2003**, *103*, 2905 – 2920; b) *Aziridines and Epoxides in Organic Synthesis* (Ed.: A. K. Yudin), Wiley-VCH, Weinheim, **2006**; c) I. D. G. Watson, L. Yu, A. K. Yudin, *Acc. Chem. Res.* **2006**, *39*, 194 – 206.

[14] For Pd^{II}/Pd^{IV}-mediated aziridination, see: a) J.-E. Bäckvall, *J. Chem. Soc. Chem. Commun.* **1977**, 413 – 414; b) A. M. M. Antunes, S. J. L. Marto, P. S. Branco, S. Prabhakar, A. M. Lobo, *Chem. Commun.* **2001**, 405 – 406.

[15] For IR analysis of a carbonyl group containing an ^{18}O atom, see: K. B. Hong, M. G. Donahue, J. N. Johnston, *J. Am. Chem. Soc.* **2008**, *130*, 2323 – 2328.

[16] For 5-*exo*-trig aminopalladation, see: Ref. [2] and Ref. [3a].

[17] For a similar oxidation of an alkyl Pd^{II} species to Pd^{IV} using other oxidants, see: a) V. G. Zaitsev, D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* **2005**, *127*, 13154 – 13155; b) G. Yin, G. Liu, *Angew. Chem.* **2008**, *120*, 5522 – 5525; *Angew. Chem. Int. Ed.* **2008**, *47*, 5442 – 5445; c) A. Wang, H. Jiang, H. Chen, *J. Am. Chem. Soc.* **2009**, *131*, 3846 – 3847; d) M.-K. Zhu, J.-F. Zhao, T.-P. Loh, *J. Am. Chem. Soc.* **2010**, *132*, 6284 – 6285; e) D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* **2010**, *132*, 3965 – 3972.

[18] For hydrolysis of oxazolinium ions, see: L. Engman, *J. Org. Chem.* **1993**, *58*, 2394 – 2401.

[19] For a similar hydrolysis of oxocarbenium ions in Au-catalyzed homogeneous oxidative reactions, see: a) Y. Peng, L. Cui, G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2009**, *131*, 5062 – 5063; b) G. Zhang, Y. Peng, L. Cui, L. Zhang, *Angew. Chem.* **2009**, *121*, 3158 – 3161; *Angew. Chem. Int. Ed.* **2009**, *48*, 3112 – 3115.

