JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Pd-Catalyzed Sequential C−C Bond Formation and Cleavage: Evidence for an Unexpected Generation of Arylpalladium(II) Species

So Won Youn,* Byung Seok Kim, and Arun R. Jagdale

Department of Chemistry and Research Institute for Natural Sciences, Hanyang University, Seoul 133-791, Korea

Supporting Information

ABSTRACT: A Pd(II)-catalyzed reaction engaging alkenyl β-keto esters is reported that leads to the formation of 1-naphthols and an unexpected generation of arylpalladium(II) species. Interception of the in situ generated arylpalladium(II) species in a Mizoroki−Heck reaction, together with additional mechanistic studies, provided strong evidence in support of the first *aromatization-driven* β-carbon elimination process. A single Pd catalyst served to promote a series of both C−C bond forming and cleavage events in an unprecedented manner.

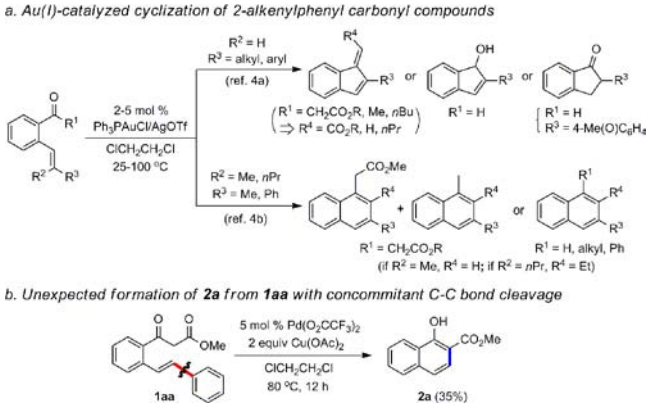
Transition-metal-catalyzed transformations involving the cleavage of chemically inert C−H[1] and C−C[2,3] bonds have received widespread recent attention from the synthetic community. The latter transformations, generally more challenging, have been achieved primarily through oxidative insertion of a transition metal into the C−C bond or β-carbon elimination[3] of a carbon−metal (i.e., M-C-C-C) or heteroatom−metal species (e.g., M-O-C-C). β-Hydride elimination is often a preferred competing pathway over β-carbon elimination, where the driving force to facilitate the latter process usually invokes the release of ring strain or the formation of a relatively more stable intermediate (such as a π-allylmetal intermediate). As such, programmed β-carbon elimination and its potential in organic synthesis remain a challenging area yet to be explored.

As part of our continued interest in transition-metal-mediated C−C bond-forming processes, we recently disclosed a Au(I)-catalyzed cyclization of 2-alkenylphenyl carbonyl compounds to afford a variety of indenes, indenols, indanones, and naphthalenes (Scheme 1a).[4] Early on, we systematically examined various transition metals, and much to our surprise, an unexpected formation of 1-naphthol **2a** was observed when 2-alkenylphenyl β-keto ester **1aa** was exposed to a catalytic amount of Pd(II) under oxidative conditions (Scheme 1b).[5−7] Indeed, on cursory inspection of the skeletal framework of the substrate (**1aa**) and the observed 1-naphthol product (**2a**), we realized the pendent phenyl group of the stilbene starting material had been cleaved during this process. Recognizing the novelty of this process in generating 1-naphthol derivatives, and more intriguingly, the origin of the unexpected C−C bond scission, here we report the findings of our methodological and mechanistic investigations.

We began using **1aa** as the test substrate and soon identified $Pd(O_2CCF_3)_2$−$Cu(OAc)_2$ as the most effective Pd(II)−oxidant combination; no reaction was observed in the absence of either one of these reagents.[8] The use of base or ligand as additives did not improve the production of **2a**, and the addition of BHT or ascorbic acid had no deleterious effect on the reaction, which excludes the presence of propagating radical species. Ultimately, the use of 5 mol % $Pd(O_2CCF_3)_2$ and 2 equiv of $Cu(OAc)_2$ in $ClCH_2CH_2Cl$ (or dioxane) at 100 °C was identified as the optimal reaction protocol, and the reaction could be performed without strict exclusion of moisture and air. The established reaction parameters proved generally effective for a wide variety of substrates, as shown in Table 1. Substrates bearing substituted phenyl rings at R_5 were well-tolerated, with little electronic dependence, whereas R_5 = alkyl afforded only trace amount of the 1-naphthol product (entries 1−10). β-Keto esters bearing alkoxy substituents (entries 12−15) and 1,3-diketones (entries 16 and 17) were all competent substrates, apart from diaryl 1,3-diketone **1ha**. Allylic substrates **1lb** and **1ma** also cyclized smoothly to afford 1-naphthols **2l** and **2m**, respectively (entries 24 and 25), but trisubstituted stilbene **1la** was unsuccessful in this reaction (entry 23).

Having established a workable condition for the conversion of 2-alkenylphenyl β-keto esters (and 1,3-diketones) to the 1-naphthol products, we next pursued in earnest the investigation of the unexpected C−C bond cleavage. As an entry point to this study, and because the conversion from **1** to **2** was generally modest, we set out to account for the mass balance through a series of detailed ^{1}H NMR and GC-MS analyses, together with the isolation of side products. We identified

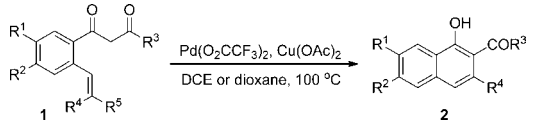
Scheme 1. Transition-Metal-Mediated Cyclization of 2-Alkenylphenyl Carbonyl Compounds

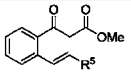
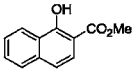
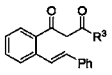
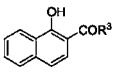
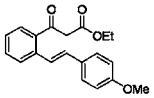
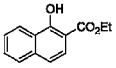
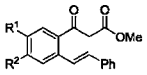
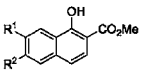
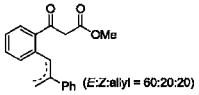
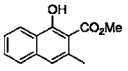
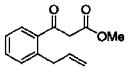
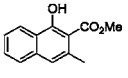
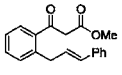
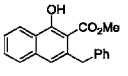


Received: February 17, 2012
Published: June 21, 2012

   dx.doi.org/10.1021/ja304616q | J. Am. Chem. Soc. 2012, 134, 11308−11311

Table 1. Pd-Catalyzed Synthesis of Various 1-Naphthols 2 from Alkenyl 1,3-Dicarbonyl Compounds 1[a]



entry	substrate	time (h)	product	yield (%)[b]
				
1[c]	R^5 = Ph (**1aa**)	7	**2a**	68
2[c]	R^5 = 4-MeC_6H_4 (**1ab**)	4	**2a**	62
3[d]	R^5 = 4-$MeOC_6H_4$ (**1ac**)	6	**2a**	67
4[c]	R^5 = 4-$AcOC_6H_4$ (**1ad**)	1	**2a**	63
5[d]	R^5 = 4-ClC_6H_4 (**1ae**)	10	**2a**	64
6[c]	R^5 = 4-$CF_3C_6H_4$ (**1af**)	12	**2a**	67
7[c]	R^5 = 4-$NO_2C_6H_4$ (**1ag**)	17	**2a**	65
8[c]	R^5 = H (**1ah**)	4	**2a**	62
9[c]	R^5 = *n*Bu (**1ai**)	24	**2a**	trace
10[c]	R^5 = *t*Bu (**1aj**)	24	**2a**	trace
11[d]	R^5 = CO_2Et (**1ak**)	8	**2a**	51
				
12[c]	R^3 = OEt (**1ba**)	8	**2b**	54
13[c]	R^3 = O*n*Bu (**1ca**)	8	**2c**	56
14[c]	R^3 = OcHex (**1da**)	6	**2d**	55
15[c]	R^3 = O*t*Bu (**1ea**)	5	**2e**	40
16[c]	R^3 = Me (**1fa**)	6	**2f**	64
17[c]	R^3 = Et (**1ga**)	6	**2g**	62
18[c]	R^3 = Ph (**1ha**)	24	**2h**	0
19[d]	 **1bb**	2	 **2b**	52
				
20[d]	R^1 = OMe, R^2 = H (**1ia**)	2	**2i**	56
21[c]	R^1 = F, R^2 = H (**1ja**)	7	**2j**	68
22[c]	R^1 = H, R^2 = Me (**1ka**)	4	**2k**	64
23[c]	 **1la**	24	 **2l**	0
24[d]	 **1lb**	4	 **2l**	64
25[c]	 **1ma**	23	 **2m**	64

[a]Reaction conditions: **1** (1 equiv), $Pd(O_2CCF_3)_2$ (5 mol %), and $Cu(OAc)_2$ (2 equiv) in $ClCH_2CH_2Cl$ or dioxane at 100 °C. [b]Isolated yields. [c]In $ClCH_2CH_2Cl$ (0.025 M). [d]In dioxane (0.1 M).

compounds **1aa′**, **3aa**, **3aa′**, and **4aa** as the principal byproducts in the reaction of **1aa** (Figure 1). **1aa′** and **3aa′** (and **4aa**, *vide infra*) were of particular interest due to the incorporation of an additional phenyl group (similar results were obtained for reactions with **1ae**, **1af**, and **1ag**[8]).

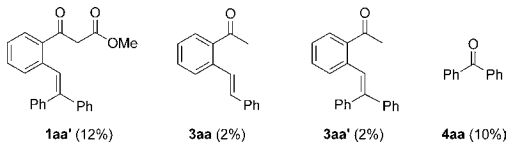


Figure 1. Major side products observed in the reaction of **1aa**.

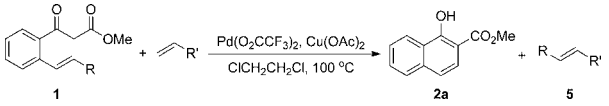
While a clear mechanistic picture was elusive at this juncture, we hypothesized the incorporation of an additional phenyl group could invoke the participation of an Ar−M species generated in the reaction mixture. We further questioned if this Ar−M species could be intercepted with the introduction of a suitable electrophile. To our delight, when methyl acrylate was introduced to our standard reaction conditions using **1aa** as the substrate, cinnamate **5aa** was obtained in 58% yield, alongside the previously described **2aa** (63%, Table 2, entry 1). Depending on the 2-alkenylphenyl *β*-keto ester substrate, different substituted methyl cinnamates could be obtained in respectable yields (entries 1−12). Methyl acrylate could also be replaced with a diverse array of activated olefins (entries 13−21) and styrenes (entries 22−27).

With the successful identification of cinnamate and stilbene derivatives **5**, the involvement of an Ar−M species seems highly plausible. The presence of an Ar−M species (M = Pd) was deemed most likely, since its participation in the Mizoroki−Heck-type cross-coupling[9] with various activated and non-activated olefins is well-precedented. A plausible mechanistic proposal is presented in Scheme 2. We speculate that the O,O′-bound complex **A**, formed initially upon treatment of **1** with Pd(II), first undergoes rearrangement to afford the alkene-coordinated C-bound tautomer **B**,[10] which then engages in a *syn* carbopalladation across the stilbene olefin to generate transient intermediate **C** with concomitant C−C bond formation (**B**→**C**). At this point, intermediate **C**, with *syn*-orientated Pd and Ar substituents, is poised to undergo *β*-carbon elimination, leading to the generation of arylpalladium species **D**. We also speculate that, further to the prerequisite *syn* stereochemical arrangement of the Pd and Ar substituents in **C**, the formation of 1-naphthol (**2**) through *aromatization* provides an *additional and essential* driving force to facilitate the *β*-carbon elimination.[11] Carbopalladation of the external olefin with the newly generated arylpalladium species **D** in a Mizoroki−Heck manner affords the cross-coupling product **5**, where the so-liberated Pd(0) is reoxidized to Pd(II) with the aid of $Cu(OAc)_2$.

Several additional experiments and analysis provided further support for this mechanistic proposal. First, with the speculated arylpalladium species **D** in mind, several attempts to intercept and subsequently isolate the arylpalladium complex by the addition of amino or phosphino ligands proved unrewarding. Reaction of (*Z*)-**1aa** under the same reaction conditions failed to deliver any product **2a**. Although **2a′** could be speculated as the possible product resulting from the alternative *β*-hydride elimination pathway, we believe there is a significant energy barrier that prevents the *cis*-stilbene olefin from being in close enough proximity for the reaction to take place (**B′**, Scheme

dx.doi.org/10.1021/ja304616q | J. Am. Chem. Soc. 2012, 134, 11308−11311

Table 2. Pd-Catalyzed Reactions of Aryl-Substituted Alkenyl β-Keto Esters 1 with Olefins[a]

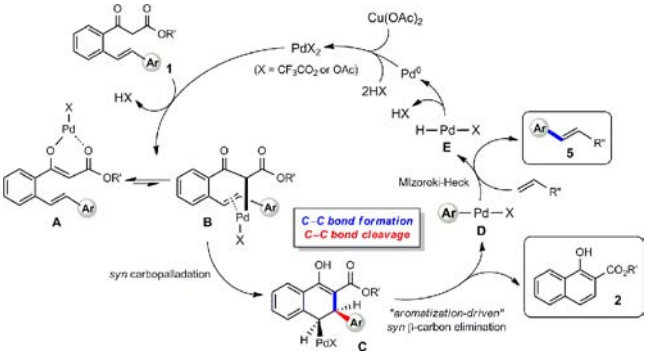


entry	R	R′	time (h)	yield (%)[b] 2a	5
1	Ph (**1aa**)	CO_2Me	8	63	58 (**5aa**)
2[c]	4-MeC_6H_4 (**1ab**)	CO_2Me	2	64	65 (**5ab**)
3[c]	4-$MeOC_6H_4$ (**1ac**)	CO_2Me	2	63	38 (**5ac**)
4	4-$AcOC_6H_4$ (**1ad**)	CO_2Me	1	69	53 (**5ad**)
5	4-ClC_6H_4 (**1ae**)	CO_2Me	2	62	59 (**5ae**)
6[d]	4-$CF_3C_6H_4$ (**1af**)	CO_2Me	4	69	63 (**5af**)
7[d]	4-$NO_2C_6H_4$ (**1ag**)	CO_2Me	5	66	68 (**5ag**)
8	3-$CF_3C_6H_4$ (**1al**)	CO_2Me	2	69	69 (**5ah**)
9	2-$CF_3C_6H_4$ (**1am**)	CO_2Me	3	65	64 (**5ai**)
10[e]	4-PhC_6H_4 (**1an**)	CO_2Me	5	63	42 (**5aj**)
11[e,f]	1-naphthyl (**1ao**)	CO_2Me	6	62	59 (**5ak**)
12[c]	C_6F_5 (**1ap**)	CO_2Me	4	50	45 (**5al**)
13	4-$CF_3C_6H_4$ (**1af**)	CO_2Et	2	75	65 (**5ba**)
14	4-$CF_3C_6H_4$ (**1af**)	CO_2nBu	2	71	69 (**5bb**)
15	4-$CF_3C_6H_4$ (**1af**)	CO_2tBu	2	71	65 (**5bc**)
16	4-$CF_3C_6H_4$ (**1af**)	$CONMe_2$	6	60	63 (**5bd**)
17	4-$CF_3C_6H_4$ (**1af**)	COMe	2	57	64 (**5be**)
18[e,f]	4-$CF_3C_6H_4$ (**1af**)	SO_2Ph	6	57	34 (**5bf**)
19[e,f]	4-$CF_3C_6H_4$ (**1af**)	$PO(OEt)_2$	6	63	54 (**5bg**)
20[f]	4-$CF_3C_6H_4$ (**1af**)		5	61	45[g] (**5bh**)
21[f]	4-$CF_3C_6H_4$ (**1af**)		5	68	48[h] (**5bi**)
22	4-$CF_3C_6H_4$ (**1af**)	Ph	2	62	63 (**5ca**)
23	4-$CF_3C_6H_4$ (**1af**)	4-MeC_6H_4	2	70	66 (**5cb**)
24[e]	4-$CF_3C_6H_4$ (**1af**)	4-$MeOC_6H_4$	8	56[i]	61[i] (**5cc**)
25[c]	4-$CF_3C_6H_4$ (**1af**)	4-ClC_6H_4	2	67	66 (**5cd**)
26	4-$CF_3C_6H_4$ (**1af**)	4-$NO_2C_6H_4$	2	70	68 (**5ce**)
27[e,f]	4-$CF_3C_6H_4$ (**1af**)	1-naphthyl	6	67	51 (**5cf**)

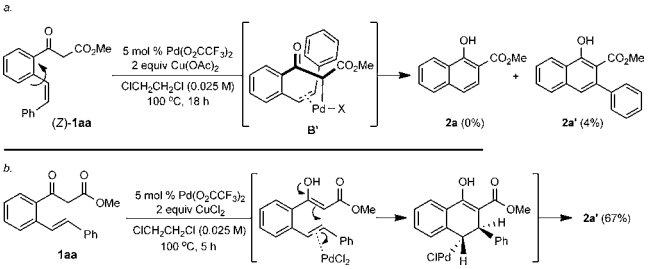
[a]Reaction conditions: **1** (1 equiv), olefin (2 equiv), $Pd(O_2CCF_3)_2$ (5 mol %), and $Cu(OAc)_2$ (2 equiv) in $ClCH_2CH_2Cl$ (0.05 M) at 100 °C. [b]Isolated yields. [c]3 equiv of olefin. [d]1.5 equiv of olefin. [e]10 mol % $Pd(O_2CCF_3)_2$. [f]5 equiv of olefin. [g]Internal olefin and the corresponding *exo* olefin isomer were obtained in 28% and 17% yields, respectively. [h]The inseparable mixture of internal olefin and the corresponding *exo* olefin isomer was obtained in 48% yield and a ratio of 42:58, determined by ^1H NMR. [i]**2a** and **5cc** were not separable; therefore, each yield was calculated from both the weight of the purified mixture of **2a** and **5cc** and their ratio, determined by ^1H NMR.

3a). The same steric argument could also account for the failure of substrate **1la** in this reaction. Interestingly, reaction of **1aa** in the presence of $CuCl_2$ instead of $Cu(OAc)_2$ gave a 3-phenyl-substituted 1-naphthol (**2a′**) as a sole product, which suggests a contrasting outer-sphere *anti* carbopalladation pathway through the in situ generated $PdCl_2$ (Scheme 3b).[5c,6a,b]

Scheme 2. Proposed Mechanism



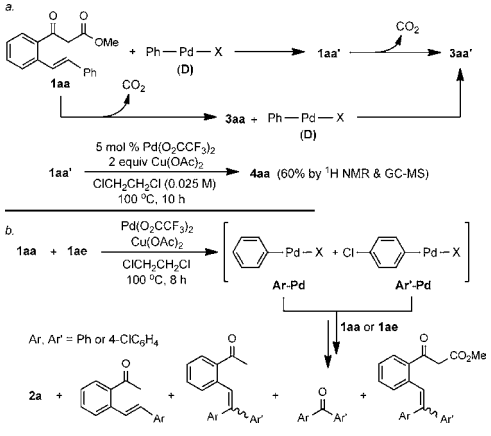
Scheme 3. Reactions of (Z)-1aa and 1aa in the Presence of $CuCl_2$



As alluded to earlier, reaction of **1aa** afforded **1aa′** and **3aa′** as the primary side products in addition to 1-naphthol **2a**. Mechanistically, the formation of **1aa′** and **3aa′** can now be easily rationalized through a Mizoroki–Heck reaction engaging arylpalladium species **D** and **1aa** and subsequent decarboxylation (or through decarboxylated **3aa** and its Mizoroki–Heck reaction with **D**), respectively (Scheme 4a). Crossover experiments between **1aa** and **1ae** afforded the byproduct mixture containing all the possible combinations, which further supports the generation of Ar–Pd (**D**, and Ar′–Pd) during the reaction (Scheme 4b). Pd-mediated oxidative cleavage of substituted stilbene (i.e., **1aa′** or **3aa′**) has also been reported,[12] and has been validated by us experimentally (**4aa**, Scheme 4a).

Finally, in the competition experiments between alkenyl β-keto esters with varying substituents on the departing aryl ring (**1aa**, **1ac**, **1af**, **1ag**), electron-rich substrates generally proceeded significantly faster than their electron-deficient

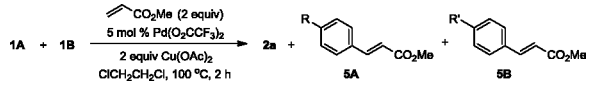
Scheme 4. Formation of Side Products and Crossover Experiments



dx.doi.org/10.1021/ja304616q | J. Am. Chem. Soc. 2012, 134, 11308–11311

counterparts (Table 3). This electronic dependence is in agreement with the migratory aptitude of the aryl group during the β-carbon elimination. Furthermore, the β-carbon elimination is expected to take place much more effectively for M−C−C−C(sp^2) species than M−C−C−C(sp^3) species (cf. substrates **1ai** and **1aj**).

Table 3. Competition Experiments of 4′-Substituted Aryl-Containing Alkenyl β-Keto Esters 1



entry	1A	1B	1A (%)[a]	1B (%)[a]	2a (%)[b]	5A (%)[a]	5B (%)[a]	mass balance[b,c]
1[d,e]	**1aa**	**1ac**	24 (**1aa**)	6 (**1ac**)	42	38 (**5aa**)	32 (**5ac**)	60.5 / 53.5
2	**1aa**	**1af**	0 (**1aa**)	36 (**1af**)	49	51 (**5aa**)	46 (**5af**)	67 / 66.5
3	**1aa**	**1ag**	0 (**1aa**)	36 (**1ag**)	40	50 (**5aa**)	30 (**5ag**)	58 / 58
4[f]	**1ac**	**1ag**	0 (**1ac**)	49 (**1ag**)	39	32 (**5ac**)	11 (**5ag**)	66.5 / 49

[a]Isolated yields of each recovered starting material (**1A** and **1B**) and products (**5A** and **5B**) based on amount used of **1A** or **1B**. [b]Isolated yield of **2a** and mass balance based on total amount of **1A** and **1B**. [c]First and second mass balances based on the amount of recovered **1A**/**1B**, byproduct (if any), and products either **2a** or **5A**/**5B**, respectively. [d]For 6 h. [e]Decarboxylated byproduct **3aa** obtained in 7% isolated yield based on the amount used of **1aa**. [f]Decarboxylated byproduct **3ag** obtained in 6% isolated yield based on the amount used of **1ag**.

In summary, we have developed a novel and concurrent preparation of 1-naphthols and cinnamate/stilbene derivatives through a Pd(II)-catalyzed reaction of 2-alkenylphenyl β-keto esters and 1,3-diketones with olefins. More significantly, we have uncovered an unprecedented catalytic process that operates through a unique mode of C−C bond activation. A single catalytic system enabled intramolecular C−C bond formation through inner-sphere *syn* carbopalladation, C−C bond cleavage via a novel aromatization-driven *syn* β-carbon elimination followed by intermolecular C−C bond formation in a Mizoroki−Heck manner. These new findings may expand the current understanding of Pd(II) reactivity and present new opportunities to broaden the current lexicon of Pd(II)-catalyzed (cascade) transformations. Further investigations to expand this concept together with detailed mechanistic studies are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

■ AUTHOR INFORMATION

Corresponding Author

sowony73@hanyang.ac.kr

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Nos. 2011-0003705 and 2012-0002223). We sincerely thank Professor David Yu-Kai Chen (Department of Chemistry, Seoul National University) for helpful discussions and valuable suggestions as well as editorial assistance.

■ REFERENCES

(1) Selected recent reviews on C−H activation: (a) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094. (b) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (c) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (d) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215.

(2) Selected reviews on C−C activation: (a) Murakami, M.; Matsuda, T. *Chem. Commun.* **2011**, *47*, 1100. (b) Bonesi, S. M.; Fagnoni, M. *Chem.—Eur. J.* **2010**, *16*, 13572. (c) Seiser, T.; Cramer, N. *Org. Biomol. Chem.* **2009**, *7*, 2835. (d) Necas, D.; Kotora, M. *Curr. Org. Chem.* **2007**, *11*, 1566. (e) Jun, C.-H. *Chem. Soc. Rev.* **2004**, *33*, 610. (f) Mitsudo, T.; Kondo, T. *Synlett* **2001**, 309. (g) Murakami, M.; Ito, Y. *Top. Organomet. Chem.* **1999**, *3*, 97. (h) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870.

(3) Reviews on β-carbon elimination: (a) Aïssa, C. *Synthesis* **2011**, 3389. (b) Murakami, M.; Makino, M.; Ashida, S.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1315. (c) Satoh, T.; Miura, M. *Top. Organomet. Chem.* **2005**, *14*, 1. A selected example: (d) Terao, Y.; Wakui, H.; Satoh, T.; Miura, M.; Nomura, M. *J. Am. Chem. Soc.* **2001**, *123*, 10407.

(4) (a) Jagdale, A. R.; Youn, S. W. *Eur. J. Org. Chem.* **2011**, 3904. (b) Jagdale, A. R.; Park, J. H.; Youn, S. W. *J. Org. Chem.* **2011**, *76*, 7204.

(5) Transition-metal-catalyzed intramolecular addition of 1,3-dicarbonyl compounds to alkenes: (a) Zhou, C.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2007**, *129*, 5828. (b) Pei, T.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 11290. (c) Qian, H.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 2056. Intermolecular addition of 1,3-dicarbonyl compounds to alkenes: (d) Cucciolito, M. E.; D'Amora, A.; Vitagliano, A. *Organometallics* **2010**, *29*, 5878. (e) Li, Y.; Yu, Z.; Wu, S. *J. Org. Chem.* **2008**, *73*, 5647. (f) Nguyen, R.-V.; Yao, X.-Q.; Bohle, D. S.; Li, C.-J. *Org. Lett.* **2005**, *7*, 673. (g) Yao, X.; Li, C.-J. *J. Am. Chem. Soc.* **2004**, *126*, 6884.

(6) Pd-catalyzed oxidative cyclization of alkenyl 1,3-dicarbonyl compounds involving β-hydride elimination: (a) Han, X.; Widenhoefer, R. A. *J. Org. Chem.* **2004**, *69*, 1738. (b) Pei, T.; Wang, X.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 648. (c) Trend, R. M.; Ramtohul, Y. K.; Stoltz, B. M. *J. Am. Chem. Soc.* **2005**, *127*, 17778. (d) Trend, R. M.; Ramtohul, Y. K.; Ferreira, E. M.; Stoltz, B. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 2892.

(7) (a) Pd-catalyzed intra- and intermolecular allylic alkylation between 1,3-dicarbonyls and alkenes: Lin, S.; Song, C.-X.; Cai, G.-X.; Wang, W.-H.; Shi, Z.-J. *J. Am. Chem. Soc.* **2008**, *130*, 12901. (b) Selenium-mediated cyclization of alkenyl β-keto esters **1** in the presence of the Lewis acid $FeCl_3$ for the synthesis of naphthols through 1,2-rearrangement of aryl groups: Shahzad, S. A.; Vivant, C.; Wirth, T. *Org. Lett.* **2010**, *12*, 1364.

(8) For details, see the Supporting Information.

(9) Reviews on the Mizoroki−Heck reaction: (a) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146. (b) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.

(10) Related examples of Pd enolates: (a) Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 494. (b) Culkin, D. A.; Hartwig, J. F. *Acc. Chem. Res.* **2003**, *36*, 234. (c) Chernyak, N.; Gorelsky, S. I.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2011**, *50*, 2342. (d) Metz, A. E.; Berritt, S.; Dreher, S. D.; Kozlowski, M. C. *Org. Lett.* **2012**, *14*, 760.

(11) Related examples of aromatization-driven C−C bond cleavage: (a) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222. (b) Halcrow, M. A.; Urbanos, F.; Chaudret, B. *Organometallics* **1993**, *12*, 955.

(12) Wang, A.; Jiang, H. *J. Org. Chem.* **2010**, *75*, 2321.