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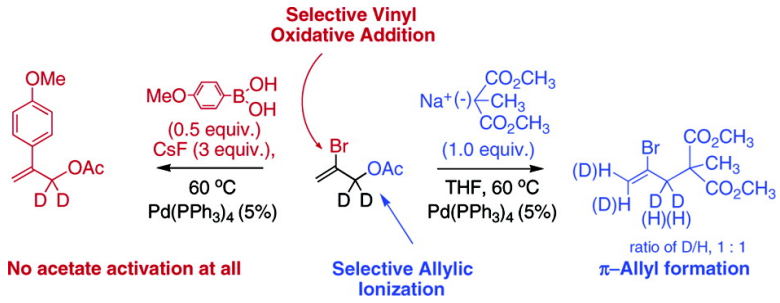

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Allylic Ionization versus Oxidative Addition into Vinyl C−X Bonds by Pd with Polyfunctional Olefin Templates

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Abstract: The chemoselectivity of activation by a $(PPh_3)_4Pd$ catalyst on a series of small, olefin-based compounds that were substituted with a variety of allylic and vinylic functional groups was studied. Of particular note, the allylic acetate of 1-acetoxy-2-bromo-2-propene (**7**) was selectively ionized by Pd in the presence of a malonate nucleophile, while oxidative addition of the C−Br bond to Pd occurred exclusively in the presence of a boronic acid nucleophile. When the acetate nucleophile was used, no ionization of the acetate leaving group occurred at all, which was proven by the use of deuterium-labeled substrates (e.g., **11**). This report demonstrates that the nucleophile interacts in some way with Pd *prior* to catalyst activation of the substrate. Certainly in the case of the malonate nucleophile, this is without precedent and contradicts the central dogma of how these proposed catalytic cycles operate.

Introduction

We have been working for some time on the development of small, densely functionalized olefin building blocks (olefin templates) whose functional groups can be activated selectively and sequentially using metal catalysts for convergent, modular organic synthesis.[1] There are two principal functional group activations possible by Ni or Pd catalysts involving olefins: allylic ionization and oxidative addition.[2] In a competitive situation, allylic ionization will generally happen first because of the bond energies involved and the stability of the resultant π-allyl complex, relative to that of the corresponding σ-complex resulting from oxidative addition of the vinyl halide.[3] Providing this selectivity is reliable; such substituted olefin templates can be modified systematically into products by activating allylic halides or pseudohalides first in the presence of vinylic ones.[1] For example, the allylic Br in **1a** (Figure 1) is activated cleanly by Pd at room temperature, and allylic substitution can then be followed by cross-coupling at the vinyl position.[1a]

If an olefin template could be designed that had a vinylic functional group that could be activated in the presence of an allylic one, and then the allylic site activated readily later, complementary synthetic routes could be considered that offer considerable advantages. To this end, we have demonstrated that certain allylic phenoxide-based leaving groups are stable to Suzuki reaction conditions, and that these phenoxide groups can later be ionized by changing the reaction conditions in situ (e.g., Figure 1, **1b**).[4]

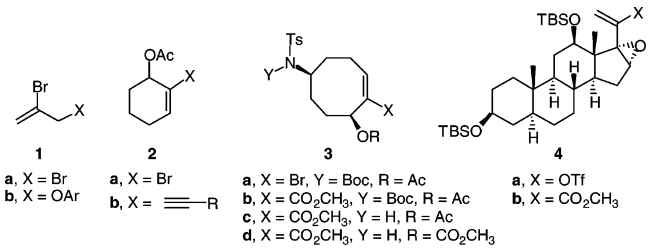


Figure 1. Some examples of polyfunctionalized olefins, which are substrates for Pd-catalyzed reactions.

We were intrigued by the few reports in the literature of selective activation of a vinyl halide or pseudohalide by Pd in the presence of a good allylic leaving group. The bromides in **2a**[5] and **3a**[6] were activated selectively by Pd, which then underwent Sonogashira coupling or carbonylation to provide **2b** and **3b**, respectively (Figure 1). Similarly, the vinyl triflate in **4a** was activated cleanly in the presence of the epoxide to provide **4b** by carbonylation.[7]

It is our contention that the lack of reactivity of the allylic functional groups in these examples was the result of conformational, not electronic, considerations as proposed originally by Nwokogu[5] and later supported by Heathcock.[7] Indeed, Pd failed to activate the acetate in **3c** with the Br gone.[6] Thus, on the basis of these experimental data, it cannot be said that the

(1) (a) Organ, M. G.; Cooper, J. T.; Rogers, L. R.; Soleymanzadeh, F.; Paul, T. *J. Org. Chem.* **2000**, *65*, 7959−7970. (b) Organ, M. G.; Mayhew, D.; Cooper, J. T.; Dixon, C. E.; Lavorato, D. J.; Kaldor, S. W.; Siegel, M. G. *J. Comb. Chem.* **2001**, *3*, 64−67. (c) Organ, M. G.; Bilokin, Y. V.; Bratovanov, S. *J. Org. Chem.* **2002**, *67*, 5176−5183. (d) Organ, M. G.; Antunes, L. M. *Tetrahedron Lett.* **2003**, *44*, 6805−6808. (e) Organ, M. G.; Ghasemi, H. *J. Org. Chem.* **2004**, *69*, 695−700.

(2) For general discussions of these two processes, see: Tsuji, T. *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*; John Wiley and Sons Ltd.: Chichester, England, 1995.

(3) (a) Rahaman, A.; Raff, L. M. *J. Phys. Chem. A* **2001**, *105*, 2156−2172. (b) Tsang, W. *J. Phys. Chem.* **1984**, *88*, 2812−2817.

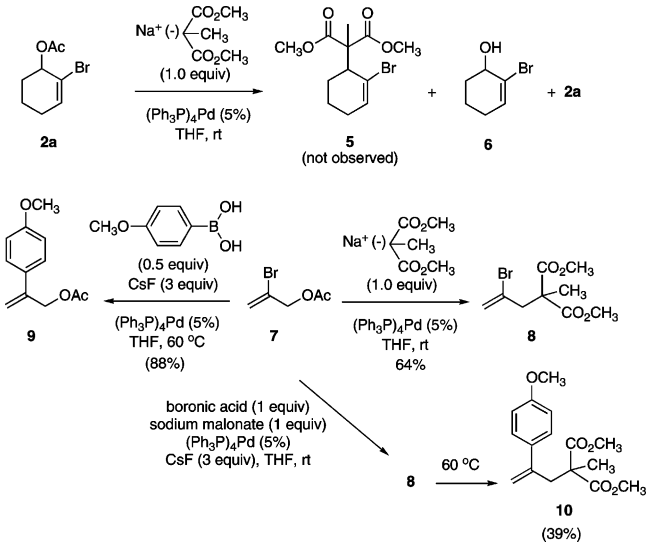
(4) Organ, M. G.; Arvanitis, E. A.; Dixon, C.; Cooper, J. T. *J. Am. Chem. Soc.* **2002**, *124*, 1288−1294.

(5) (a) Nwokogu, G. C. *Tetrahedron Lett.* **1984**, *25*, 3263−3266. (b) Nwokogu, G. C. *J. Org. Chem.* **1985**, *50*, 3900−3908.

(6) Trost, B. M.; Oslob, J. D. *J. Am. Chem. Soc.* **1999**, *121*, 3057−3064.

(7) Yamamoto, K.; Heathcock, C. H. *Org. Lett.* **2000**, *2*, 1709−1712.

Scheme 1



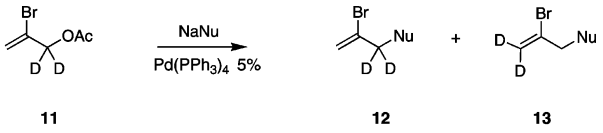
Br is "electronically deactivating" the olefin in allylic substitution. Once converted to the carbonate (**3d**), the allylic group ionized, albeit, at 100 °C. Such a reactive group should activate well below this temperature, and in fact, allylic carbonates on suitable substrates ionize with Pd at −78 °C.[8] We propose that the principal reason the allylic leaving groups in **2**−**4** did not activate is that these groups could not adopt the requisite antiperiplanar relationship between the carbon−leaving group bond and the coordinate Pd−olefin bond that precedes allylic ionization.[9] Thus, if these conformational restrictions were removed, these same allylic groups would activate readily and selectively in the presence of the vinyl halide or pseudohalide groups.

Results and Discussion

To explore the results seen by Nwokogu,[5] we prepared **2a** and treated it to Pd-catalyzed allylic alkylation with sodium dimethyl methylmalonate, an excellent nucleophile for such substitution reactions (Scheme 1). Only starting material (**2a**) and the product corresponding to hydrolyzed acetate (**6**) were recovered. Thus, similar to the findings of Nwokogu, no product resulting from apparent allylic activation of the acetate (e.g., **5**) was isolated with this cyclic system. However, when **7**, an acyclic variant of **2a**, was reacted under the same conditions, the transformation proceeded smoothly under very mild conditions to provide **8**. This seemed to support our hypothesis that the Br is not necessarily electronically deactivating the olefin. Conversely, it would, in fact, support the notion that the compounds in Figure 1 may not have ionized due to conformational constraints.

Interestingly, treatment of **7** with anhydrous Suzuki conditions did not lead to allylic coupling as anticipated,[10] but rather, the product of vinyl cross-coupling (**9**) was obtained in excellent recovery as the sole product. Treatment of **7** with both malonate nucleophile and 4-methoxyphenylboronic acid under competition conditions at room temperature led initially to the exclusive formation of **8**. Heating the reaction mixture at this stage, that is, following the allylic substitution, led to the cross-coupled product **10**.

Scheme 2



11 **12** **13**

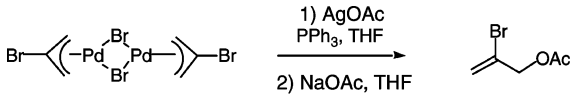
a) Nu = acetate, THF, rt	only product	not observed
b) Nu = acetate, THF, reflux	only product	not observed
c) Nu = acetate, DMF, rt	only product	not observed
d) Nu = acetate, DMF, 70 °C	only product	not observed
e) Nu = dimethyl methylmalonate, $Pd(PPh_3)_4$ (1 equiv) THF, rt	1	1
f) Nu = dimethyl methylmalonate, THAB, THF, 55°C (THAB = tetrahexylammonium bromide)	1	1

If one considers the presently accepted mechanistic dogma of metal-catalyzed allylic substitution and cross-coupling reactions, following Pd−olefin docking, the first step in either cycle is the activation of the halide (or pseudohalide) by the metal, that is, allylic ionization or oxidative addition, respectively. This being the case, meaningful interactions that lead to product between Pd and **7** should take place first, irrespective of the other reaction partners present. If the acetate is the most reactive functional group present on **7**, it should activate first. The results in Scheme 1 are suggestive that something other than the accepted simplified mechanisms for these processes is operating. It is possible that one of (at least) three scenarios is affecting the chemoselectivity of the catalyst. (1) Ionization of the acetate is happening first in every case, but the reverse reaction is kinetically faster than transmetalation with the boronic acid to facilitate allylic cross-coupling whereas most/all insertions of Pd into the vinyl C−Br bond lead to product. (2) Functional group activation is temperature-dependent. (3) Oxidative addition of the vinyl bromide occurs preferentially, except in the presence of the malonate where the catalyst is interacting in some way with this reagent, and this is affecting the catalyst's chemoselectivity. To investigate these possibilities, a series of experiments were carried out with deuterium-labeled substrates to track functional group activation.

Reversibility of Acetate Ionization by Pd in Compound 7. To see whether the allylic acetate was being reversibly ionized, compound **11** was prepared and treated with Pd and sodium acetate nucleophile at room temperature (reaction a, Scheme 2) and then at reflux (reaction b). In neither case was compound **13** formed, suggesting that **11** did not ionize and either the leaving group or the nucleophile (which are the same in this case) attack the Pd π-allyl complex. Mechanistic studies on allyl acetate ionization by Amatore and co-workers[11] suggest that formation of the Pd π-allyl complex occurs with complete ion pairing in THF (i.e., no free acetate ions were produced), while in DMF, no significant ion pairing occurred. This could mean that ionization does occur, but that tight ion pairing in THF is resulting in a "memory effect"[12] for the leaving group;

(8) Organ, M. G. Unpublished results.
(9) (a) Collins, D. J.; Jackson, W. R.; Timms, R. N. *Tetrahedron Lett.* **1976**, 495−496. (b) Matsushita, H.; Negishi, E. *Chem. Commun.* **1982**, 160−161. (c) Temple, J. S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310−1315. (d) Trost, B. M.; Schmuff, N. R. *J. Am. Chem. Soc.* **1985**, *107*, 396−405. (e) Heumann, A.; Reglier, M. *Tetrahedron* **1995**, *51*, 975−1015. (f) Enders, D.; von Berg, S.; Jandeleit, B. *Synlett* **1996**, 18−20.
(10) Treatment of 1-acetoxy-2-propene with the identical reaction conditions smoothly converted the allylic acetate to the corresponding aryl derivative in 70% isolated yield.
(11) Amatore, C.; Jutand, A.; Gilbert, M.; Mottier, L. *Chem.−Eur. J.* **1999**, *5*, 466−473.
(12) Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 235−236.

Scheme 3



14 **7**

thus, the double bond position does not scramble. To this end, **11** was treated with sodium acetate in DMF (reactions c and d), and only starting material was recovered. This demonstrates that simple ion pairing cannot explain the nonappearance of product **13**. Carboxylates are known to be suitable, albeit, modest nucleophiles for Pd-catalyzed allylic substitution.[13]

It is difficult to argue that ionization did occur in the above situations and that the acetate ion simply did not re-add. That is, in the presence of catalytic Pd, the acetate ionized and Pd remained trapped as a π-allyl complex in a small and, therefore, undetectable amount. Even if one argued that sodium acetate is too insoluble to act as a nucleophile, the ionized acetate itself, which forms at least a close ion pair with the π-allyl cation, should re-attack, and this would scramble the position of the double bond, at least to some degree. To put this possibility to rest, the Pd π-allyl complex derived from dimer **14**[14] was prepared and treated with sodium acetate in THF (Scheme 3). Compound **7** was produced, proving that sodium acetate does indeed react well with the Pd π-allyl complex. Therefore, it would appear that under the Suzuki conditions used in Scheme 1, the allylic acetate in **7** did not ionize at all and the bromide was activated selectively.

When **11** was reacted with sodium dimethyl methylmalonate at 55 °C (reaction e), the expected products of nucleophilic attack were obtained, proving that **11** does ionize readily in the presence of a "strong and suitable" nucleophile for Pd-catalyzed allylic alkylation.[15] The same result was the case when the more soluble tetrahexylammonium counterion was used (reaction f). Of particular note, the fact that alkylation products **12** and **13** were obtained in a 1:1 ratio further demonstrates that no memory effect due to tight ion pair formation is operating in these systems.[11,12]

Temperature Studies. In a competition experiment similar to the one in Scheme 1, a suspension of **11**, 4-methoxyboronic acid, CsF, and the sodium dimethyl methylmalonate was warmed to reflux, and then a solution containing the catalyst was added (Scheme 4). The progress of the reaction was then followed by ^{1}H NMR spectroscopy. The premise is to ensure that if oxidative addition of the C−Br bond to Pd is temperature-dependent (i.e., requires heat), relative to ionization of the acetate, that the reaction's conditions are such that both processes could happen when the Pd is added. The products show selective addition of the malonate to the allylic position, while the boronic acid added only to the central bromine-bearing carbon *after* allylic substitution took place. This, at least in part, demonstrates that temperature is not a factor in the selectivity of functional group activation by Pd, and this is addressed further in Scheme 6.

In a related experiment, the same boronic acid was reacted alongside sodium phenoxide, which is known to be a much poorer nucleophile for Pd-catalyzed allylic substitution than is malonate (Scheme 5).[16] All the products obtained (i.e., **18**−**20**) resulted from ionization of the acetate moiety and attack by the phenoxide nucleophile on the central carbon of the 2-bromo-π-allyl Pd complex.[1717−18] These results also support the notion that ionization of the acetate is not temperature-dependent, and that it ionizes readily in the presence of a suitable nucleophile, even if it is a weak one. Furthermore, this ionization occurs equally well in the presence or absence of the vinyl bromide.

What remained to be investigated more deeply was the effect of reaction temperature on vinyl bromide oxidative addition to Pd. All of the Suzuki reactions required heating, presumably to facilitate metal−metal exchange and reductive elimination. So, it remained unclear as to whether this was impacting on reactivity. To this end, compound **7** was reacted under Sonogashira conditions with TMS acetylene, and enyne **21** was obtained in suitable recovery at room temperature (Scheme 6). Thus, either the allylic acetate or the vinyl bromide can be activated selectively at room temperature or at elevated temperature based solely on the nature of the reacting partner in the reaction.

Effect of Halide and Olefin Structure on Selectivity of Pd Activation. Next, a Suzuki coupling was performed on **11** at 65 °C to see if any apparent ionization of the acetate was occurring under these conditions (Scheme 7). No product of simple allylic coupling was observed (i.e., **26** or **27**). While we cannot say with certainty that products **22**−**25** did not arise from reversible ionization of the acetate first, earlier observations with **7** and **11** and those in Scheme 8 involving **25** (vide infra) do not support it.

We prepared **25** from the corresponding alcohol (**28**) and treated it with $(PPh_3)_4Pd$ and sodium acetate at reflux (Scheme 8). In this case, the products of ionization were observed, suggesting that the formation of **24** and **25** in Scheme 7 proceeds first by cross-coupling of the Br followed by ionization of the acetate, which scrambles the position of the double bond. This result clearly demonstrates that while the bromide is not tolerated at the 2-position during ionization for allylic cross-coupling, other substituents, even ones as large as phenyl, do not hinder ionization.

We then prepared a variety of labeled allyl acetates and treated them with Pd catalyst in the presence of 1.0 equiv of sodium acetate or tetrahexylammonium bromide (Scheme 9). In the case of dibromide **31**, ionization occurred readily, demonstrating that in the presence of a superior leaving group, such as Br, the Pd π-allyl complex will form regardless of the reaction conditions (e.g., the presence of malonate, acetate, or boronic acid nucleophiles). In the absence of the vinyl bromide (i.e., **29**), acetate, in fact, does ionize readily. When compared to earlier results

(13) (a) Deardorff, D. R.; Myles, D. C. *Org. Synth.* **1988**, *67*, 114−120. (b) Deardorff, D. R.; Myles, D. C.; MacFerrin, K. D. *Tetrahedron Lett.* **1985**, *26*, 5616−5619. (c) Trost, B. M.; Organ, M. G. *J. Am. Chem. Soc.* **1994**, *116*, 10320−10321.

(14) (a) Castano, A. M.; Aranyos, A.; Szabó, K. J.; Bäckvall, J.-E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2551−2553. (b) Aranyos, A.; Szabó, K. J.; Castano, A. M.; Bäckvall, J.-E. *Organometallics* **1997**, *16*, 1058−1064.

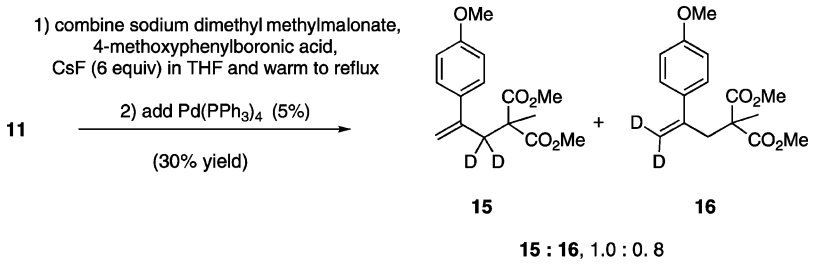
(15) In a control experiment with no Pd present, no reaction took place, proving that nucleophilic attack by malonate is Pd-catalyzed.

(16) In a competition experiment, 1 equiv each of malonate and phenoxide nucleophiles was reacted with 1-acetoxy-2-propene and $(PPh_3)_4Pd$. Only the product of malonate substitution was obtained, and the starting acetate reacted fully: Organ, M. G.; Arvanitis, E. A.; Hynes, S. J. *Tetrahedron Lett.* **2002**, *43*, 8989−8992.

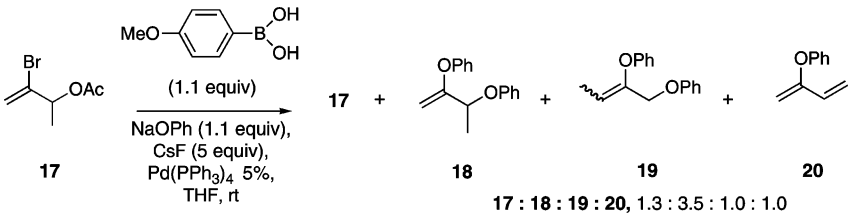
(17) For a discussion pertaining to the attack of the phenoxide nucleophile at the central position of Pd π-allyl complexes, see: (a) Organ, M. G.; Miller, M.; Konstantinou, Z. *J. Am. Chem. Soc.* **1998**, *120*, 9283−9290. (b) Organ, M. G.; Miller, M. *Tetrahedron Lett.* **1997**, *38*, 8181−8184. (c) Kadota, J.; Katsuragi, H.; Fukumoto, Y.; Murai, S. *Organometallics* **2000**, *19*, 979−983.

(18) Organ, M. G.; Arvanitis, E. A.; Hynes, S. J. *J. Org. Chem.* **2003**, *68*, 3918−3922.

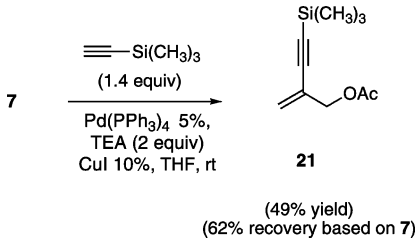
Scheme 4



Scheme 5



Scheme 6

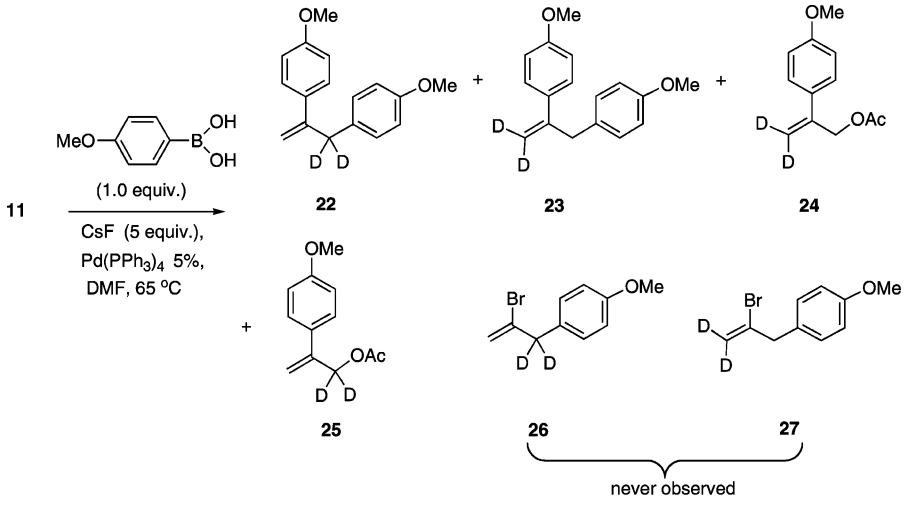


with **7** or **11**, this result shows that acetate ionization does not take place in the presence of the vinyl bromide *without a suitable nucleophile for Pd* (e.g., malonate) *being present*. This effect could be due either to the electronegativity of the bromide, which deactivates acetate toward ionization, or to the preferential oxidative addition of the vinyl bromide bond to Pd.

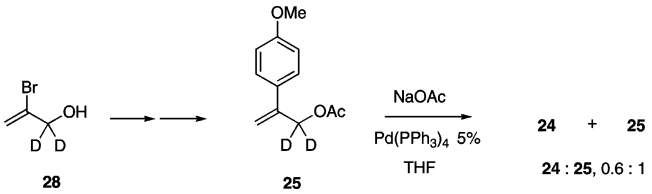
To test the former hypothesis, iodoacetate **30** was prepared and treated to standard allylic substitution conditions with sodium acetate, and no ionization products were observed. Significantly, the chloro derivative, **32**, smoothly ionized under similar conditions with the same poor nucleophile. This can also be seen in Scheme 10, where **33b** ionized in the presence of malonate, in this case a good nucleophile, but **33a** did not. These results clearly demonstrate that electronegativity (Cl = 2.9, Br = 2.8, I = 2.2) does not play a role in the ionizing ability of the acetate. Thus, in the presence of a less efficient vinyl oxidative addition partner, the catalyst instead activates the allylic acetate. Additionally, when the iodoacetate **33a** was treated with 1.0 equiv of $Pd(PPh_3)_4$, selective activation of the vinyl halide was observed, and oxidative addition product **35** precipitated from the reaction mixture. These results strongly support the theory that oxidative addition of Pd to the vinyl bromide occurs preferentially to π-allyl formation by acetate ionization in templates such as **7**. Furthermore, this may also shed some light on why no products of ionization were observed in Suzuki reactions with **11** and why **26** and **27** were never obtained during cross-coupling reactions with **11**.

We were curious to see whether there was a special relationship between the position of the halide, relative to the allylic acetate. One could imagine some complexation being possible between the 1- and 2-position of this propene framework via Pd, and that could effect where Pd inserts. To this end, we prepared and treated **37** to Suzuki and allylic substitution

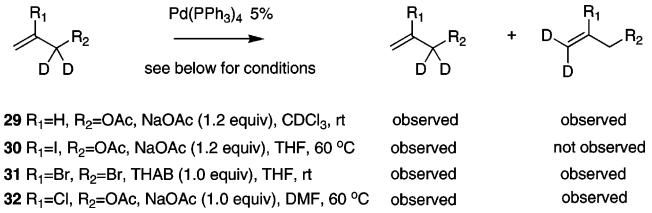
Scheme 7



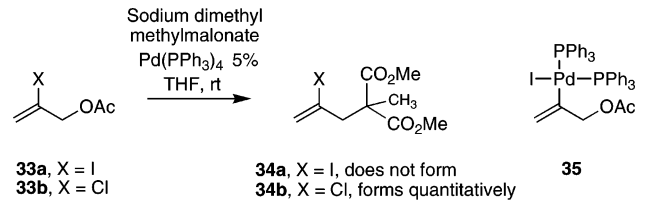
Scheme 8



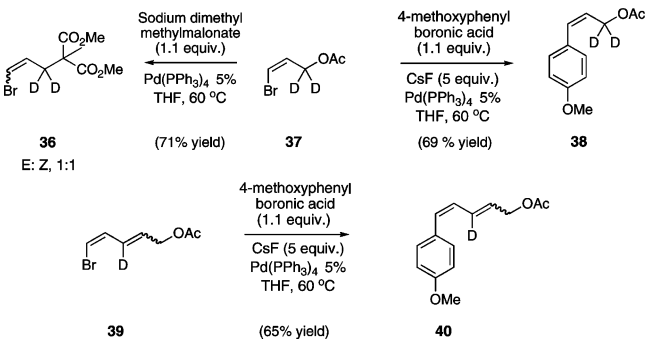
Scheme 9



Scheme 10



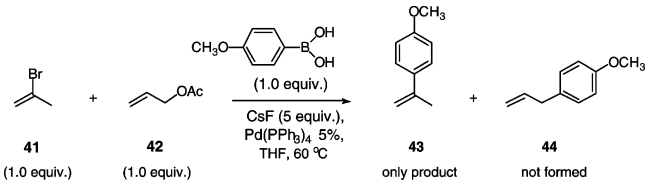
Scheme 11



reaction conditions (Scheme 11). The chemoselectivity of the cross-coupling reaction for the bromide site was maintained as it was for diene **39**. Thus, in the presence of a readily ionizable leaving group, oxidative addition occurred preferentially to π-allyl formation, leading to **38** and **40**. In the case of **37**, which was prepared as a single stereoisomer, the stereochemistry was preserved in the product, proving that ionization of the acetate did not occur in this case, as well. Alternatively, when **37** was treated with malonate nucleophile, the acetate ionized smoothly, leading to substitution product **36**. The scrambling of the stereochemistry of the vinyl bromide proves the intermediacy of a Pd π-allyl complex.

In an attempt to further probe the inherent reactivity of Pd toward a vinyl bromide relative to an allyl acetate, while continuing to try to eliminate any possible effect that the two centers might have on each other, a competition Suzuki experiment was conducted (Scheme 12). Equal portions of 2-bromopropene (**41**) and allyl acetate (**42**) were allowed to react a limiting amount of 4-methoxyphenylboronic acid in the presence of Pd. Only **41** reacted further, proving that the vinyl bromide reacts fastest under these reaction conditions. Once **41** has been consumed, then **42** would be able to react since it is known to be a good substrate for allylic coupling with boronic acids.

Scheme 12



Summary

This study has demonstrated that the cyclic bromo acetate **2a** is deactivated toward allylic alkylation by Pd, even in the presence of malonate nucleophile, relative to its acyclic analogue **7**. We propose this to be the case because the metal cannot adopt the requisite antiperiplanar alignment with the leaving group to facilitate ionization in cyclic, conformationally constrained structures. This result has implications for the findings of Nwokogu[5] (among others)[6,7] who reported selective activation of vinyl bromides in the presence of allylic carbonates or acetate groups. Significantly, the substrates investigated by these groups were either hindered or cyclic, and so the chemoselectivity of Pd activation observed may have been due to conformational rather than electronic factors. With the use of labeling studies, we have shown that the vinyl halogen, in fact, does deactivate the allyl acetate toward ionization in the presence of the Pd catalyst. However, this deactivation is not for the reasons suggested earlier by Nwokogu[5] and Heathcock.[7] Rather, we propose that the "electronic effect" is due to preferential oxidative addition of Pd into the vinyl carbon−halogen bond. This was demonstrated in the absence of a vinyl halogen (**29**) and in the presence of a relatively poor substrate for oxidative addition, such as vinyl chloride **32**, where ionization of the acetate occurred readily. Thus, electronegativity of the vinyl halide, which has been implicated by others in deactivating the allylic leaving group, likely plays no role in the chemoselectivity of Pd activation.

Ionization depends not only on the vinyl moiety but also on the nature of the allyl group. For example, while allyl acetate failed in some cases (e.g., **7**) to ionize when the vinyl bromide was present, the analogous allyl bromide (**31**) ionized readily under all reaction conditions tried. The consequences of these results are that in the presence of a cross-coupling partner, the vinyl Br is activated selectively alongside the allylic acetate. Once the cross-coupling has been completed and the halogen removed from the vinyl position, ionization can occur readily, giving rise to allylic addition products. However, in the presence of a suitable nucleophile (e.g., malonate or phenoxide), our results show clearly that ionization occurs readily and indeed takes preference over vinyl halogen activation. The accepted mechanism of allylic alkylation with stabilized carbanions, such as malonates, stipulates that both ionization and nucleophilic attack proceed anti to the metal−olefin bond so that the metal does not come into contact with the leaving group or the incoming nucleophile.[9] This has been demonstrated with stereochemical studies with chiral allyl acetates, whereby alkylation proceeds with overall retention of configuration via a double inversion process. Our results are highly suggestive that this dogma may not be entirely correct, and that interactions between the certain nucleophiles and Pd take place *prior* to ionization, thereby creating a new catalytic species with different properties that are reflected in catalyst chemoselectivity. At this stage, we

have no direct proof that this is indeed occurring, but the results are suggestive that this is the case. Thus, while the bromine in **7** clearly switches off the allyl acetate toward ionization, the presence of malonate switches this process back on. In other words, the presence of the malonate alters the catalyst chemoselectivity and that there is a clear dependence on, or at least an involvement of, the reaction partner (e.g., a suitable soft nucleophile) in catalyst chemoselectivity with polyfunctional olefins.

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Supporting Information Available: All experimental and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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