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An Aryl to Imidoyl Palladium Migration Process Involving Intramolecular C−H Activation

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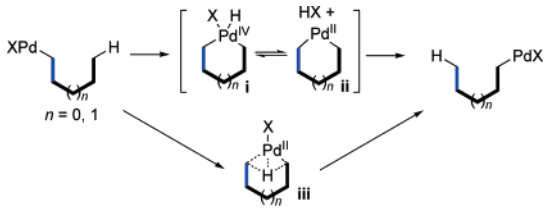
Abstract: Biologically interesting fluoren-9-one and xanthen-9-one derivatives have been prepared by a novel aryl to imidoyl palladium migration, followed by intramolecular arylation. The fluoren-9-one synthesis appears to involve both a palladium migration mechanism and a C−H activation process proceeding through an unprecedented organopalladium(IV) hydride intermediate. The results from deuterium labeling experiments are consistent with the proposed dual mechanism.

Introduction

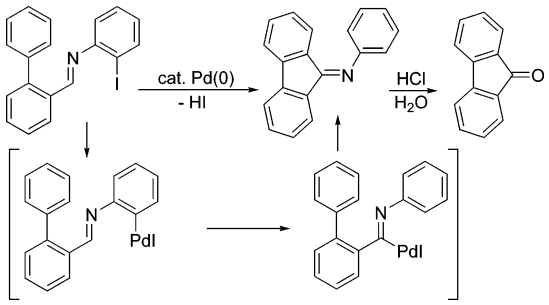
Transitional-metal-catalyzed reactions are widely used in organic synthesis. Recently, the through-space shift of a metal has been disclosed for both palladium- and rhodium-catalyzed reactions.[1] It appears that palladium migration is a fairly general rearrangement that has been observed to occur in a wide variety of systems. The through-space shift of palladium generally involves an intramolecular C−H activation process.[2] Specifically, vinylic to aryl,[3] aryl to aryl,[4] alkyl to aryl,[5] vinylic to aryl to allylic,[6] and aryl to benzyl[7] palladium migration processes have been reported. Palladium migration is synthetically useful because it affords an alternative way to introduce a palladium moiety into a specific position of an organic molecule, which may not be readily accessible by conventional methods. Indeed, palladium migration chemistry has been utilized to prepare a number of structurally diverse fused polycycles.[3−5]

In the reported palladium migration processes, a five- or six-membered palladacycle intermediate is generally involved, as shown in Scheme 1. Although the mechanism of palladium migration is still under investigation, the evidence obtained from our previous work on the vinylic to aryl to allylic palladium migration appears to favor a mechanism which involves a palladacycle(IV) hydride **i** or a palladacycle(II) intermediate **ii**,

Scheme 1



Scheme 2



which also successfully explains the H−D exchange observed.[6]A recent theoretical study suggests a one-step proton-transfer mechanism for a related palladium migration process in which an energetically favored transition state **iii** is presumably involved.[3d] However, this mechanism fails to account for the hydrogen−deuterium exchange observed in many of our migration processes, when such processes are run in the presence of D_2O.

We recently briefly communicated the synthesis of fluoren-9-ones by an aryl to imidoyl palladium migration process (Scheme 2).[8] Herein, we wish to report a full account of this novel palladium migration process, which affords a fairly general and efficient synthesis of biologically interesting fluoren-9-ones and xanthen-9-ones, plus we also wish to provide evidence with regard to the reaction mechanism, which appears to involve both

(1) For a recent review on 1,4-metal migration, see: Ma, S.; Gu, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 7512.
(2) (a) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992. (b) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. (c) Li, C.-J. *Acc. Chem. Res.* **2002**, *35*, 533. (d) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731.
(3) (a) Zhao, J.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 5340. (b) Zhao, J.; Larock, R. C. *Org. Lett.* **2005**, *7*, 701. (c) Larock, R. C.; Tian, Q. *J. Org. Chem.* **2001**, *66*, 7372. (d) Bour, C.; Suffert, J. *Org. Lett.* **2005**, *7*, 653.
(4) (a) Karig, G.; Moon, M. T.; Thasana, N.; Gallagher, T. *Org. Lett.* **2002**, *4*, 3115. (b) Huang, Q.; Campo, M. A.; Yao, T.; Tian, Q.; Larock, R. C. *J. Org. Chem.* **2004**, *69*, 8251. (c) Campo, M. A.; Larock, R. C. *J. Am. Chem. Soc.* **2002**, *124*, 14326. (d) Campo, M. A.; Huang, Q.; Yao, T.; Tian, Q.; Larock, R. C. *J. Am. Chem. Soc.* **2003**, *125*, 11506.
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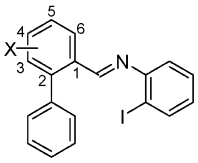
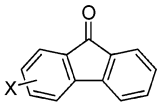
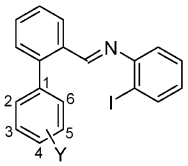
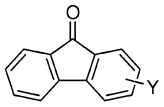
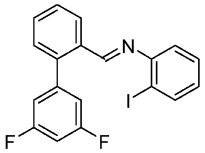
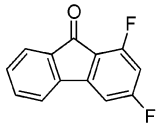
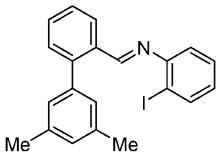
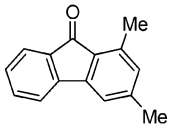
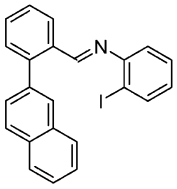
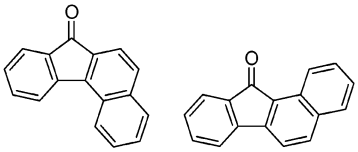
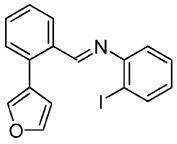
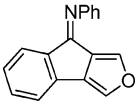
10.1021/ja070657l CCC: $37.00

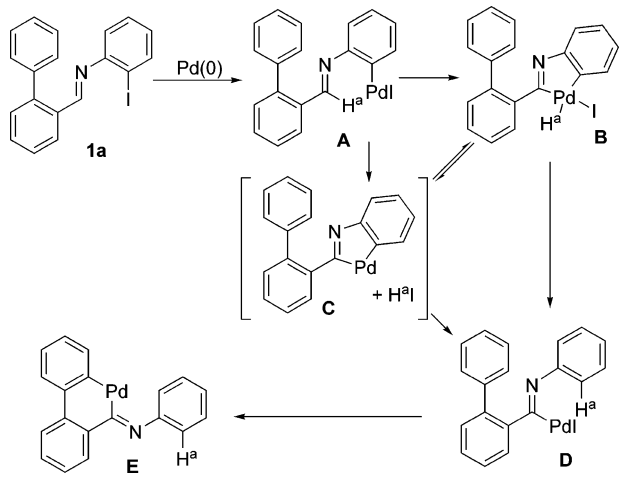
Table 1. Synthesis of Fluoren-9-ones[a]

entry	imine		time (h)	product(s)		% yield
						
1	X = H	**1a**	12		**2a**	95
2	5-OMe	**1b**	12		**2b**	90
3	4-Me	**1c**	24		**2c**	56
4	5-F	**1d**	12		**2d**	80
						
5	Y = 4-Me	**1e**	4		**2e**	97
6	4-OMe	**1f**	2		**2b**	100
7	4-CO_2Me	**1g**	12		**2f**	100
8	4-NO_2	**1h**	12		**2g**	100
9	2-Cl	**1i**	48		**2h**	65
10		**1j**	6		**2i**	95
11		**1k**	24		**2j**	92
12		**1l**	4		**2k, 2l**	91 (9:1)[b]
13		**1m**	2		**2m**	82[c,d]

[a] The reaction was carried out employing 0.25 mmol of the imine, 5 mol % of $Pd(OAc)_2$, 5 mol % of $(Ph_2P)_2CH_2$ (dppm), and 2 equiv of CsO_2CCMe_3 (CsPiv) in DMF (4 mL) at 100 °C unless otherwise noted. [b] The ratio of products **2k**:**2l** was determined by GC analysis. [c] The reaction was run at 110 °C. [d] Compound **2m** is not stable under our usual hydrolysis conditions; omitting the hydrolysis step, the imine intermediate **2m** was isolated in an 82% yield.

the usual palladium migration mechanism and an unprecedented mechanism proceeding through an organopalladium(IV) hydride intermediate. To the best of our knowledge, although imines have been widely employed in Pd-mediated reactions, especially chelation-assisted reactions, the direct activation of imidoyl C−H bonds by catalytic palladium is unknown. In the past,

Scheme 3. Plausible Palladium Migration Mechanism (Route A)



imidoyl palladium complexes have generally been obtained by the oxidative addition of imidoyl halides to Pd(0) species.[9]

Results and Discussion

Synthesis of Fluoren-9-ones via Aryl to Imidoyl Palladium Migration. Fluoren-9-ones are the core structures of many biologically interesting and pharmaceutically important compounds.[10] The most useful syntheses of fluoren-9-ones include Friedel−Crafts ring closures of biarylcarboxylic acids,[11] intramolecular [4 + 2] cycloaddition reactions of conjugated enynes,[12] the oxidation of fluorenes,[13] the remote metalation of 2-biphenylcarboxamides or 2-biphenyloxazolines,[14] and the palladium-catalyzed cyclocarbonylation of *o*-halobiaryls.[15] Those methods generally suffer from the use of strong acids, strong bases, toxic CO gas, or harsh reaction conditions. Recently, the first intramolecular arene acylation reaction by aryl-substituted aldehydes has been reported to cyclize biphenyl-2-carbaldehydes to fluoren-9-ones, but the reaction efficiency is only moderate and only a few fluoren-9-ones have been prepared this way.[16]

Our previous work indicated that the aryl-[3,4] or alkyl palladium[5] intermediates generated by palladium migration processes can be readily trapped by intramolecular arylation to afford a variety of polycyclic structures. Therefore, we envisioned that an imidoyl palladium intermediate generated from an aryl to imidoyl palladium migration process might also undergo facile intramolecular arylation to afford biologically interesting fluoren-9-one derivatives. To examine this possibility, we first treated imine **1a** (0.25 mmol) with 5 mol % of Pd(OAc)$_2$, 5 mol % of bis(diphenylphosphino)methane (dppm), and 2 equiv of CsO_2CCMe_3 (CsPiv) in DMF (4 mL) at 100 °C (Table 1, entry 1). After 12 h reaction, the crude imine product obtained was hydrolyzed by aqueous HCl in acetone to afford a 95% yield of the desired fluoren-9-one **2a** after flash chromatography. It appears that the "optimal" palladium migration conditions, which have been successfully employed in a number of previously reported palladium migration reactions, work well in this fluoren-9-one synthesis.

We next investigated the scope and limitations of this process, as shown in Table 1. The effect of substituents on the arene which would bear the imidoyl palladium moiety was first examined. A 5-methoxy-substituted imine **1b** was prepared and allowed to react in the usual fashion, and a 90% yield of the fluoren-9-one **2b** was obtained (entry 2). However, imine **1c** bearing a methyl group on the 4 position of the arene only affords a 56% yield of the desired product **2c** (entry 3). In this case, the electron density on the imidoyl group is presumably increased by the *para*-methyl group, which apparently retards imidoyl C−H activation. The 5-fluoro-substituted imine **1d** affords an 80% yield of the fluoren-9-one product **2d** (entry 4).

We then investigated the effect of substituents on the arene, which undergoes the cyclization reaction. Surprisingly, almost quantitative yields of fluoren-9-ones have been obtained for both electron-rich and electron-poor functionally substituted substrates, which raises some question as to whether the intramolecular arylation step proceeds via electrophilic aromatic substitution as usually assumed (entries 5−8). These results also suggest that the palladium migration could be the rate-determining step in this overall transformation. The only exception to the high yields was the reaction employing the substrate **1i** with a 2-chloro group, where only a 65% yield of the fluoren-9-one **2j** was obtained, possibly due to competing oxidative addition of the aryl chloride or perhaps hindered reaction of the aromatic ring or simply reduction in the number of *ortho* positions available for reaction (entry 9). Imines **1j** and **1k** afforded 95 and 92% yields of the expected fluoren-9-ones, respectively (entries 10 and 11). Once again, neither electron-donating nor electron-withdrawing groups on the ring undergoing substitution seem to have a significant effect on the yield. When the naphthalene substrate **1l** was prepared and allowed to react under our usual reaction conditions, arylation took place in both the 3 and 1 positions of the naphthalene in a 91% overall yield, with the less hindered product **2k** predominant (9:1) (entry 12). The furan-containing ring present in imine **1m** facilitates electrophilic aromatic substitution, and within 2 h, the reaction was complete (entry 13). However, because the resulting 8*H*-indeno[2,1-*b*]furan-6-one was not stable under our hydrolysis conditions, we were only able to isolate a 50% yield of the ketone. Omitting the hydrolysis step, the corresponding imine **2m** was obtained in an 82% yield.

Mechanistic Studies of the Fluoren-9-one Synthesis. After we investigated the reaction scope and limitations, we examined the reaction mechanism of this fascinating process. In fact, it appears that this reaction proceeds through a rather unusual mechanism. Presumably, Pd(0) first undergoes oxidative addition to the aryl iodide **1a** to generate intermediate **A**. The palladium moiety may then undergo further oxidative addition of the imidoyl C−H bond to afford a palladacycle(IV) intermediate **B**, which can undergo reductive elimination to form palladacycle(II) **C** or the imidoyl palladium intermediate **D**. Alternatively, palladacycle(II) **C** may be directly generated from

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(12) Danheiser, R. L.; Gould, A. E.; Pradilla, R. F.; Helgason, A. L. *J. Org. Chem.* **1994**, *59*, 5514.
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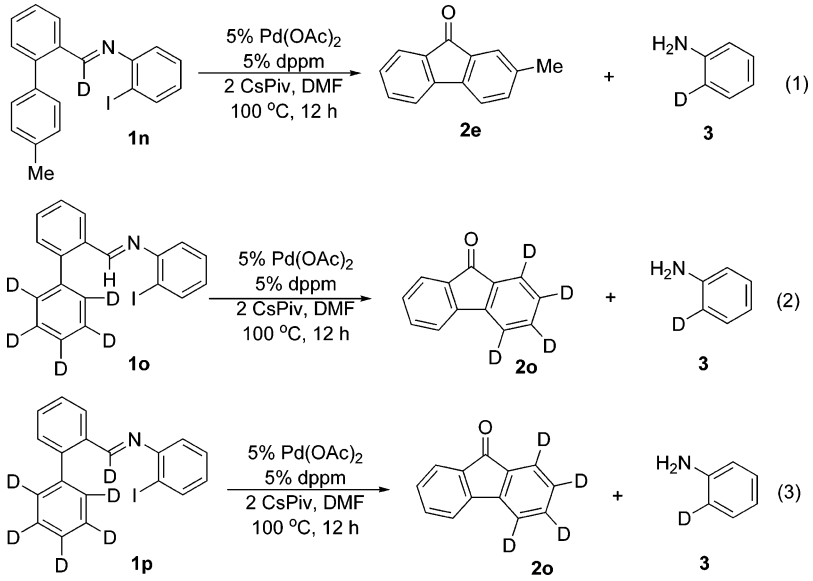
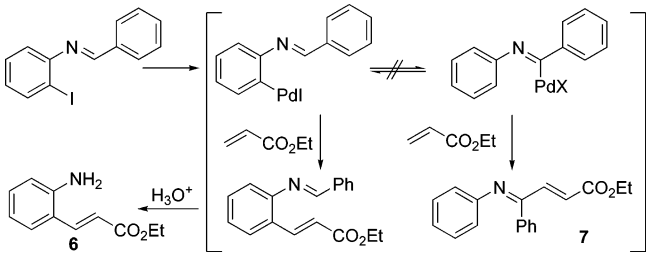
(14) (a) Ciske, F.; Jones, W. D., Jr. *Synthesis* **1998**, 1195. (b) Wang, W.; Snieckus, V. *J. Org. Chem.* **1992**, *57*, 424.
(15) Campo, M. A.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 5616.
(16) Barluenga, J.; Trincado, M.; Rubio, E.; Gonzalez, J. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3140.

Scheme 4. Deuterium Labeling Experiments



Scheme 5



A or it may be formed through the intermediacy of **B**, where an equilibrium between **B** and **C** may be involved. A similar equilibrium has been demonstrated in a previously reported example of a consecutive vinylic to aryl to allylic palladium migration.[6] Intermediate **C** can also lead to intermediate **D**, which then undergoes intramolecular arylation to afford the cyclization product **E**, and the imine product after reductive elimination. According to this proposed mechanism, the imidoyl hydrogen (H^a) shifts to the *ortho* position of the aniline when the palladium moiety migrates from the aryl position to the imidoyl position. By observing the movement of H^a, we should be able to detect the through-space shift of the palladium moiety. This proton shift should be readily determined by an appropriate isotope labeling experiment (Scheme 4). Indeed, deuterium-substituted imine **1n** was allowed to react under our "optimal" reaction conditions, and the aniline (**3**) obtained upon hydrolysis of the resulting imine was isolated (eq 1). Thirty five percent deuterium incorporation was observed in one of the two *ortho* positions of the aniline as determined by ^{1}H NMR spectroscopy and GC−MS analysis. This reaction was repeated in the presence of 10 equiv of D_2O hoping that higher deuterium incorporation could be observed in the aniline (**3**). However, only slightly higher 45% deuterium incorporation was observed, which is apparently inconsistent with the proposed mechanism (route A). If the aryl to imidoyl palladium migration is a reversible process as observed with the analogous aryl to aryl palladium migrations,[4,17] we should be able to observe deuterium incorporation in both of the *ortho* positions when the reaction is conducted in the presence of a deuterium source. However, incorporation of only one deuterium was observed.

We have also attempted to trap the aryl and imidoyl palladium intermediates by a Heck reaction (Scheme 5) as we did in our aryl to aryl palladium migration chemistry.[4,17] Analogous Heck reactions of acyl palladium intermediates are well-known.[18] However, after a 24 h reaction, only ester **6** was observed by GC−MS analysis, and ester **7**, which presumably should be generated from the Heck reaction of the postulated imidoyl palladium intermediate, was not evident. This is inconsistent with the involvement of **C** in route A (Scheme 3). These results also indicate that the aryl to imidoyl palladium migration process is probably not a reversible process in the absence of intramolecular arylation as a driving force. Indeed, the whole process appears to be rather unusual compared with previously reported examples of palladium migration. Although H−D exchange occurs during the course of the palladium migration, this leads to low deuterium incorporation. It is difficult to attribute all of the deuterium loss to H−D exchange since the yield of deuterated product was only slightly improved when the reaction was conducted in the presence of an additional deuterium source.

An alternative pathway for generation of the fluoren-9-one product without invoking an imidoyl hydrogen shift is proposed in Scheme 6. In this mechanism, the aryl palladium intermediate **A** undergoes intramolecular C−H activation to afford palladacycle(IV) **B**; subsequent reductive elimination could generate palladacycle(II) **C**. It is also possible that palladacycle(II) **C** could be generated directly from aryl palladium intermediate **A**. At this point, the palladium moiety might insert into the C−H bond of the neighboring arene to afford an unprecedented palladacycle(IV) intermediate **F**. Such a palladacycle might be expected to undergo reductive elimination to afford palladacycle **E**, which after a second reductive elimination would generate the expected imine product. In this mechanism, H^a is lost to the solution when forming intermediate **C**, but H^b shifts from

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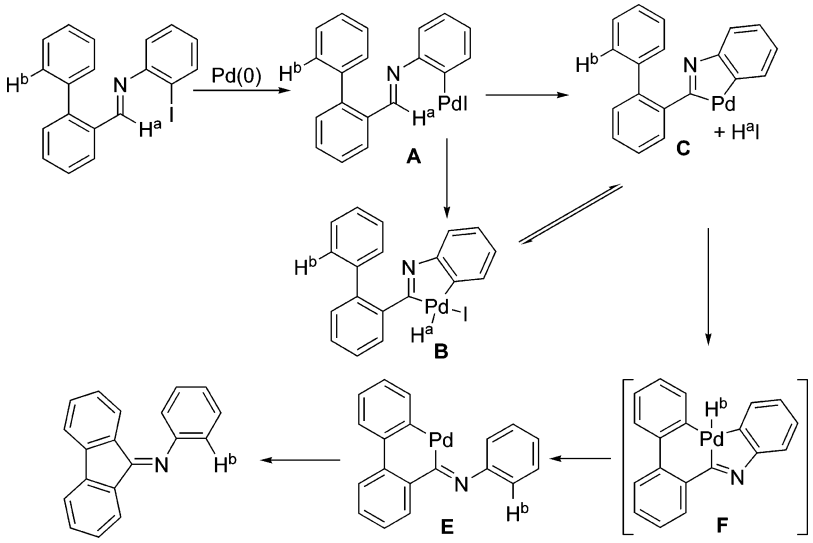
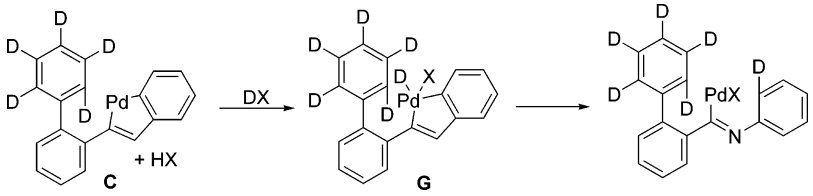
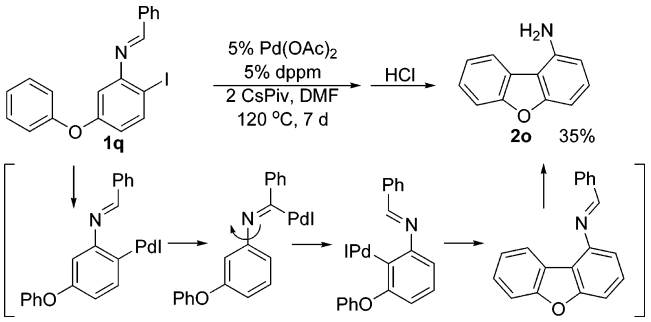
Scheme 6. Plausible C−H Activation Mechanism (Route B)



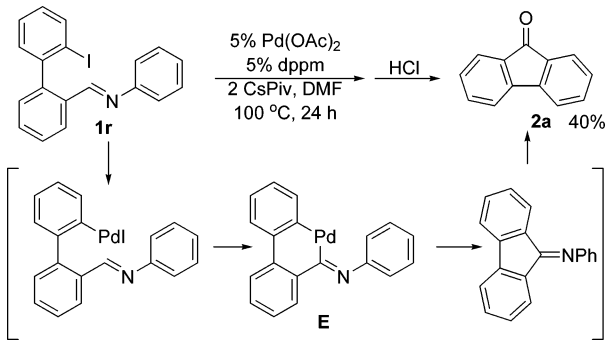
Scheme 7



Scheme 8



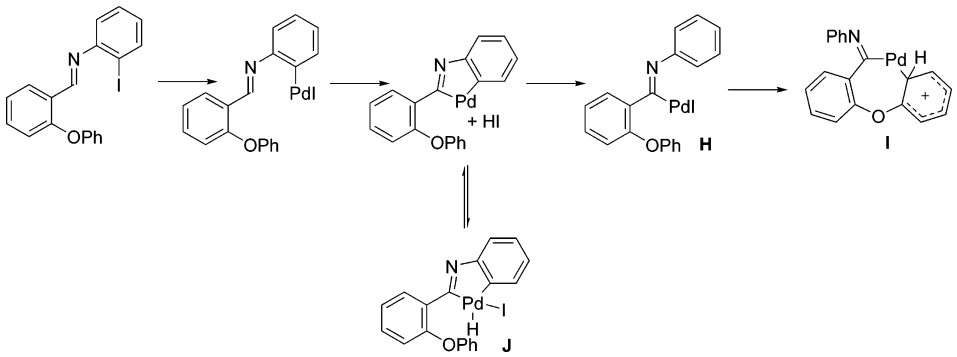
Scheme 9



the biphenyl moiety to one of the two *ortho* positions of the aniline. Deuterium-labeled substrate **1o** (Scheme 4, eq 2) was prepared and allowed to react under the standard reaction conditions. If this mechanism is in force, we expect to see some deuterium at one of the two *ortho* positions of the resulting aniline if the reaction goes through route B. Indeed, we observed 35% deuterium incorporation in one of the two *ortho* positions of the resulting aniline. At this point, we reasoned that this fluoren-9-one synthesis actually goes through a dual mechanism, a palladium migration mechanism (Scheme 3, route A excluding involvement of **C**) and an unprecedented intramolecular C−H activation mechanism (Scheme 6, route B involving **C**). On the basis of this assumption, one would expect that higher deuterium incorporation would be obtained if both H^a and H^b are labeled with deuterium. Indeed, when substrate **1p** (Scheme 4, eq 3) was employed in this reaction, 75% deuterium incorporation in the aniline ring was observed, which is consistent with our hypothesis.

The final intramolecular arylation step of route A (Scheme 3) would release 1 equiv of HX or DX into solution, which might add to palladacycle(II) **C** to afford a new palladacycle-(IV) intermediate **G**. Subsequent reductive elimination could afford the *ortho* deuterated aniline product (Scheme 7). This can also explain the deuterium incorporation into the aniline observed in the experiment described in Scheme 4, eq 2. However, if 1 equiv of DX can afford as much as 35% deuterium incorporation, even when the concentration of DX is quite low because it is gradually released into the solution, the analogous reaction run in the presence of 10 equiv of D_2O should afford very high deuterium incorporation, at least comparable to the results obtained from the experiments described in Scheme 4, eq 3, in which 2 equiv of DX is released. However, we did not observe a significant increase in deuterium incorporation when 10 equiv of D_2O was present; only 45% deuterium incorporation was observed. Remember that these migration reactions have been conducted in the presence of 2 equiv of CsPiv base, which should quickly neutralize the DX acid generated by the final arylation step. Thus, this pathway

Scheme 10. Plausible Mechanism for the Synthesis of Xanthones



for the introduction of deuterium into the aniline in the reaction reported in Scheme 3, eq 2, is highly unlikely.

It has been shown previously that palladium can migrate more than once in these migration reactions.[4,6] Thus, an interesting question is whether the imidoyl palladium intermediate can migrate the palladium to a second aryl position. As shown in Scheme 8, imine **1q** was prepared and allowed to react under our usual reaction conditions, but this reaction failed to afford any of the desired product. By heating the reaction to 120 °C, after 7 days, we were able to obtain a 35% yield of the desired 1-aminodibenzo[*b*,*d*]furan (**2o**).[8] In this case, palladium must have migrated from the aryl to the imidoyl position solely through the migration mechanism shown in Scheme 3. According to our study of the vinylic to aryl palladium migration chemistry,[3a] the palladium moiety tends to migrate to the more electron-rich arene during the course of the migration. The palladium migration from the phenoxy-substituted arene to the imidoyl position is probably not a very favorable process, but palladium migration from the imidoyl position back to the aryl position of this arene, which is *ortho* to the phenoxy group is quite possibly a favorable process.

Activation of the imidoyl C−H bond in this fluoren-9-one synthesis proceeds through a five-membered ring intermediate. One might wonder whether palladium can activate an imidoyl C−H bond by a six-membered ring intermediate. Indeed, substrate **1r** has been prepared and allowed to react under our usual reaction conditions. After 24 h of reaction at 100 °C, only a 40% yield of the desired fluoren-9-one product was obtained (Scheme 9). Although it appears that six-membered ring activation is feasible, the reaction efficiency is not high.

Synthesis of Xanthones via Aryl to Imidoyl Palladium Migration. After developing a general and efficient synthesis of fluoren-9-one derivatives, we attempted to extend this protocol to the synthesis of six-membered ring heterocycles, such as xanthones, thioxanthones, and acridones. Xanthones are secondary metabolites found in higher plant families, fungi, and lichens exhibiting interesting pharmaceutical properties.[19] Most common syntheses of the xanthone skeleton typically involve a multistep procedure, which generally proceeds through the intermediacy of a benzophenone or a diaryl ether.[20] Recently, we reported a one-step synthesis of xanthones by a tandem coupling−cyclization of 2-hydroxybenzoates and arynes.[21]

In our fluoren-9-one synthesis, palladium migrates from an aryl position to an imidoyl position and then undergoesintramolecular arylation through a six-membered ring intermediate. We envisioned that an imidoyl palladium intermediate might also undergo intramolecular arylation by a seven-membered ring intermediate to afford six-membered ring heterocycles, as shown in Scheme 10. Indeed, imine **4a** was allowed to react under our optimal conditions, and a 72% yield of the xanthone product **5a** was obtained by flash chromatography.

The reaction scope and limitations of this new xanthone synthesis are shown in Table 2. We first investigated the effect of the substituent on the arene bearing the imine group. Methyl-substituted substrate **4b** affords an 80% yield of the xanthone **5b** (entry 2), and methoxy-substituted imine **4c** affords a 77% yield of product **5c** (entry 3). Imines bearing an electron-withdrawing group have also been prepared and subjected to the usual reaction conditions. The imines **4d** and **4e** substituted with NO_2 and CF_3 groups afforded 56 and 38% yields of the xanthone products **5d** and **5e**, respectively (entries 4 and 5). Note that a higher temperature is required here. Substrates bearing a functional group Y on the arene, which undergoes substitution, have also been prepared. The methoxy-, chloro-, alkyl-, and aryl-substituted imines **4f**−**j** have been allowed to react under our usual reaction conditions, and 56−77% yields of the substituted xanthones **5f**−**j** have been obtained (entries 6−10). However, the reaction was very sluggish when imine **4k** bearing an electron-withdrawing ester group was allowed to react. After 1 day of reaction at 120 °C, only about 10% of the desired product was observed by GC−MS analysis (entry 11). This intramolecular arylation presumably proceeds via an electrophilic aromatic substitution,[22] although some evidence points toward a proton-transfer mechanism.[23] Thus, an electron-withdrawing substituent might be expected to disfavor the

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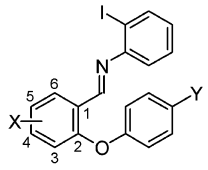
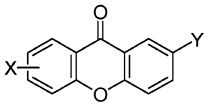
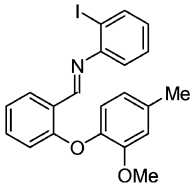
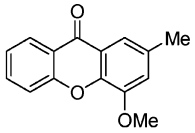
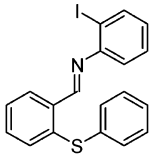
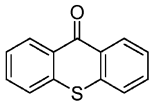
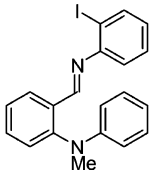
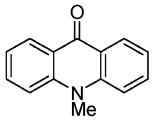
Table 2. Synthesis of Xanthones[a]

entry	imine			temp (°C)	product		% yield
							
1	X = H	Y =	**4a**	100		**5a**	72
2	5-Me	H	**4b**	100		**5b**	80
3	5-OMe	H	**4c**	100		**5c**	77
4	5-CF_3	H	**4d**	120		**5d**	56
5	5-NO_2	H	**4e**	120		**5e**	38
6	H	OMe	**4f**	100		**5c**	77
7	H	Cl	**4g**	100		**5f**	73
8	H	*i*-Pr	**4h**	100		**5g**	56
9	H	Ph	**4i**	100		**5h**	63
10	H	*t*-Bu	**4j**	100		**5i**	61
11	H	CO_2Me	**4k**	120		**5j**	10
12			**4l**	100		**5k**	79
13			**4m**	120		**5l**	0[b]
14			**4n**	100		**5m**	20

[a] The reaction was carried out employing 0.25 mmol of the imine, 5 mol % of $Pd(OAc)_2$, 5 mol % of $(Ph_2P)_2CH_2$ (dppm), and 2 equiv of CsO_2CCMe_3 (CsPiv) in DMF (4 mL) under Ar for 24 h. [b] Starting materials were recovered.

cyclization step, especially for this cyclization proceeding by a difficult seven-membered ring intermediate **I**. Note, however, that cyclization to form a fluoren-9-one was not impeded by the presence of strong electron-withdrawing groups (see Table 1, entries 7 and 8). Introducing a methoxy group *ortho* to the oxygen atom of the phenoxy group could facilitate electrophilic aromatic substitution, but might introduce some steric hindrance at the same time, as well as reducing statistically the number of positions available for cyclization. In fact, the reaction of imine **4l** affords a 79% yield of the xanthone product, which indicates that electronic factors apparently predominate (entry 12). We have also attempted to extend this protocol to the synthesis of thioxanthones, an important class of potential anticancer drugs.[24] When imine **4m** was treated under the reaction conditions used in our xanthone synthesis, we did not observe any cyclization product, and we recovered most of the starting material (entry 13). Repeating this reaction at 120 °C afforded similar results. The presence of the larger sulfur atom apparently disfavors cyclization through the now larger

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seven-membered ring intermediate or perhaps the sulfur chelates the intermediate imidoyl palladium species preventing cyclization.

Acridones are also naturally occurring compounds exhibiting a variety of interesting biological activities. They are important anti-leishmanial, anti-fungal, anti-tumor, and DNA-intercalating anti-cancer drugs.[25] We prepared imine **4n** from the corresponding aldehyde and treated it under our standard palladium migration conditions. After 1 day of reaction at 100 °C, a 20% yield of the acridone **5m** was obtained (entry 14). We have also conducted this reaction at 120 °C but failed to observe any improvement in the reaction efficiency.

Conclusions

In summary, we have established a novel 1,4-Pd migration from an aryl position to an imidoyl position, which affords a general synthesis of the biologically interesting fluoren-9-one and xanth-9-one ring systems. Both electron-rich and electron-poor substrates have been screened in this process, and generally good yields of the desired product have been obtained. The fluoren-9-one synthesis appears to involve both a standard palladium migration mechanism (route A) and a C−H activation mechanism (route B), which proceeds through an unprecedented organopalladium(IV) hydride intermediate. The results from the deuterium labeling experiments are consistent with the proposed dual mechanism.

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Supporting Information Available: General experimental procedures and spectroscopic characterization of aldehydes, fluoren-9-ones and xanth-9-ones. This material is available free of charge via the Internet at http://pubs.acs.org.

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