Heterocycles

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Palladium-Catalyzed Reaction of Aryl Iodides with *ortho*-Bromoanilines and Norbornene/Norbornadiene: Unexpected Formation of Dibenzoazepine Derivatives**

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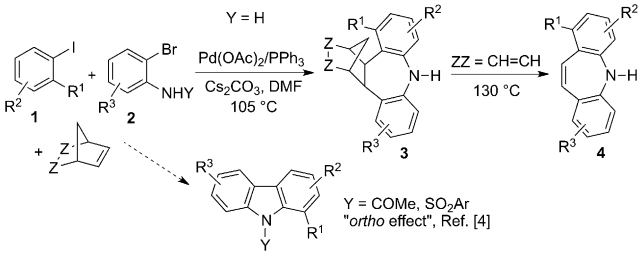
Herein we report a new palladium-catalyzed reaction that leads to dibenzoazepine derivatives when starting with aryl iodides, *ortho*-bromoanilines, and either norbornene or norbornadiene. The resulting products arise from a dramatic deviation from the usually observed carbon–carbon bond formation sequence.[1] According to our general methodology, which allows the selective synthesis of unsymmetrical biaryl units starting from *ortho*-substituted aryl iodides and aryl bromides under the joint catalytic action of palladium and norbornene,[2] the *ortho* substituent in the aryl iodide ensures C_{sp^2}–C_{sp^2} rather than C_{sp^2}–C_{sp^3} coupling.[3] In the accompanying paper,[1] however, it has been shown that certain chelating groups are able to offset the *ortho* effect and direct migration of the palladium-bonded aryl towards the cycloaliphatic carbon atom. In relation to this possibility we attempted to use *ortho*-bromoaniline and found that the resulting product indeed implied aryl–norbornyl or aryl–norbornadienyl coupling. To our surprise, however, a subsequent cyclization led to an unexpected nitrogen-containing seven-membered ring (**3**; Scheme 1). The result is remarkable when compared to our recent report on the formation of N-substituted carbazoles, which involves aryl–aryl coupling in accordance with the *ortho* effect when using the same reagents having acetylated or sulfonylated amino groups (Scheme 1, dashed arrow).[4] As shown, the use of norbornene with **1** and **2** leads to the dihydrodibenzoazepine derivatives **3**, whereas with norbornadiene a subsequent retro-Diels–Alder reaction affords the dibenzoazepines **4**.



Scheme 1. Palladium-catalyzed reactions of *ortho*-substituted aryl iodides and *ortho*-bromoanilines: norbornene (ZZ = CH_2–CH_2) or norbornadiene (ZZ = CH=CH) incorporation into dihydrodibenzoazepine or dibenzoazepine derivatives, respectively. The dashed arrow indicates previously reported carbazole synthesis. DMF = *N*,*N*′-dimethylformamide.

Dibenzoazepines as well as dihydrodibenzoazepines are important building blocks for the synthesis of antidepressant and antiepileptic drugs.[5] Various methods to synthesize these compounds have been reported in the literature.[6] Nevertheless, the development of new and efficient procedures for the selective synthesis of these seven-membered rings continues to represent an important and challenging goal. The methodology proposed herein is based on the ordered assembly of three simple and readily available components under mild catalytic conditions. It affords satisfactory yields and offers a significant alternative to previously reported procedures.

The addition of triarylphosphines to the palladium catalyst was crucial to the success of the reaction and the best one proved to be PPh_3 when used in a 2.5:1 molar ratio relative to $Pd(OAc)_2$. Among the bases examined, Cs_2CO_3 gave the highest yields. Thus, by heating *ortho*-iodotoluene (**1**) and *ortho*-bromoaniline (**2**) with norbornene in the presence of $Pd(OAc)_2$, PPh_3, and Cs_2CO_3 in DMF at 105 °C for 6 hours under nitrogen, the compound **3a** (ZZ = CH_2-CH_2; R^1 = Me; R^2, R^3 = H) was isolated in 74% yield (Table 1, entry 1). The use of norbornadiene in place of norbornene leads to similar results to give compounds **3** (ZZ = CH=CH), which then undergo a retro-Diels–Alder reaction that easily occurs with norbornadiene at 130 °C and allows the direct synthesis of dibenzoazepines **4** in one pot (Table 2).

It can be observed from the results in Table 1 that a variety of substituents can be present on different positions of the aryl iodide and bromide. As expected on the basis of previous knowledge,[2a,3] even aryl iodides not bearing *ortho* substituents react with *ortho*-bromoaniline to give the desired products **3** (Table 1, entries 16–19). However, yields are not as good as those for aryl iodides bearing *ortho*-substituents, which under the reaction conditions strongly reduce the formation of by-products.[7] 4-Chloro-2-bromoaniline (entries 5, 11, and 15), behaves better than other substituted

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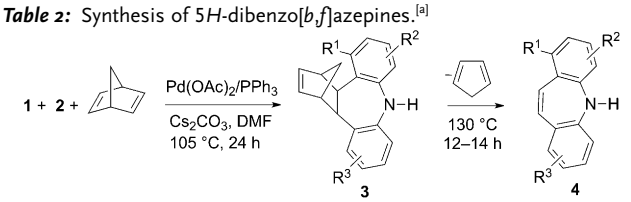
Table 1: One-pot synthesis of dihydrodibenzoazepine derivatives: *cis*,*exo*-1,2,3,4,4*a*,13*b*-hexahydro-1,4-methano-9*H*-tribenzo[*b*,*f*]azepines.[a]

Entry	Product	*t* [h]	Yield [%][b]
1	**3a**: R^2, R^3 = H	6	74
2	**3b**: R^2 = 7-Me, R^3 = H	6	67
3	**3c**: R^2 = 7-OMe, R^3 = H	21	76
4	**3d**: R^2 = 6-CO_2Me, R^3 = H	6	76
5	**3e**: R^2 = H, R^3 = Cl	24	81
6	**3f**: R^2 = H, R^3 = F	16	77
7	**3g**: R^2, R^3 = H	18	85
8	**3h**: R^2 = 7-OMe, R^3 = H	44	88
9	**3i**: R^2 = H, R^3 = 11-Me	72	74
10	**3j**: R^2 = H, R^3 = 12-Me	28	83
11	**3k**: R^2 = H, R^3 = 12-Cl	24	90
12[c]	**3l**: R^2 = H, R^3 = 11-F	98	56
13	**3m**: R^2 = H, R^3 = 12-F	30	82
14	**3n**: R^3 = H	20	79
15	**3o**: R^3 = Cl	24	94
16	**3p**: R^2 = H	20	46
17[d]	**3q**: R^2 = 6-CO_2Me	64	72
18	**3r**: R^2 = 7-Me	24	60
19	**3s**: R^2 = 7-OMe	21	64

[a] Reaction conditions: aryl iodide (1.1 equiv), aryl bromide (1.0 equiv), norbornene (1.2 equiv), $Pd(OAc)_2$ (5 mol%), PPh_3 (12.5%), Cs_2CO_3 (2.25 equiv) in DMF at 105°C under N_2, for the time needed for palladium black precipitation; 0.2×10^{-2} mmol $Pd(OAc)_2$/mL DMF. [b] Yield of isolated product. [c] Conversion of **1** (R^1 = OMe) and **2** (R^3 = 5-F) is 75 and 69%, respectively. [d] K_2CO_3 as base; *o*-iodoaniline in place of *o*-bromoaniline.

Table 2: Synthesis of 5*H*-dibenzo[*b*,*f*]azepines.[a]



Entry	Product	Yield [%][b]
1	**4a**: R^2, R^3 = H	61
2	**4b**: R^2 = H; R^3 = 7-Me	66
3	**4c**: R^2 = 3-Me; R^3 = H	63
4	**4d**:R^2 = 2-CO_2Me, R^3 = H	66
5	**4e**: R^2 = 3-OMe, R^3 = H	72
6	**4f**:R^2 = 2-CO_2Me;R^3 = 8-Cl	78
7	**4g**: R^2 = 2,3-OMe; R^3 = H	72
8[c]	**4h**: R^3 = H	59
9[c]	**4i**: R^3 = Me	65
10[c]	**4j**: R^3 = Cl	74
11[c]	**4k**: R^3 = F	66
12	**4l**: R^3 = H	70
13	**4m**: R^3 = 9-Me	65
14	**4n**; R^3 = 10-Cl	50
15[d]	**4o**; R^2 = H	45
16	**4p**: R^2 = 1-Et	58
17[d]	**4q**: R^2 = 3-F	54

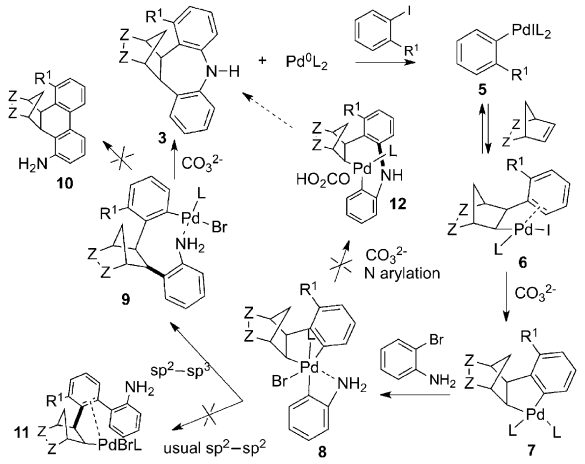
[a] Reaction conditions as in Table 1 using norbornadiene (2.0 equiv) in place of norbornene at 105°C (24 h) and then at 130°C (12–14 h). [b] Yield of isolated product. [c] K_2CO_3 as base. [d] Bromobenzene and 4-fluorobromobenzene in place of the corresponding iodides.

or unsubstituted *ortho*-bromoanilines. NHMe as well as acetylated and sulfonylated NH anilines prevent the formation of **3**, with the former being unreactive and the latter leading to carbazole (Scheme 1).[4] The substituent effect, in both the iodides and bromides, is not easy to rationalize because more than one step can be affected by each substituent.

The results in Table 2 show a similar trend to that seen in Table 1, but yields are lower and a higher ratio of norbornadiene to palladium is needed because of the higher reactivity of norbornadiene. The higher reactivity of norbornadiene leads to by-products by reaction with aryl iodides according to previously described pathways.[2a,7] Some reactions shown in Table 2 (entries 8, 10, and 11) were carried out for 24 hours at 105°C without additional heating to 130°C. Compounds **3h**, **3j**, and **3k** (ZZ = CH=CH) were isolated in 45, 61, and 40% yield, respectively, together with their corresponding dibenzoazepines **4h**, **4j** and **4k** in 20, 20, and 33% yield, respectively. The retro-Diels–Alder reaction of compound **3h** (ZZ = CH=CH; R^1 = OMe, R^2, R^3 = H) was carried out separately in DMF at 130°C for 14 hours to give product **4h** in almost quantitative yield.

The reaction pathway, proposed on the basis of both experimental and DFT calculations, is depicted in Scheme 2 for an *ortho*-substituted aryl iodide and *ortho*-bromoaniline.

As previously shown through stoichiometric reactions, the formation of the palladacycle **7**[8] readily takes place through: a) oxidative addition of the aryl iodide to $[Pd^0L_2]$;[9] b) norbornene or norbornadiene stereoselective insertion to give the *cis*,*exo*-palladacycle precursor **6**;[10] c) intramolecular C–H bond activation.[11] Oxidative addition of *ortho*-bromoaniline to palladacycle **7** affords **8**.[12] Our proposal of a Pd^{IV} intermediate has recently been substantiated by Vicente and co-workers who isolated and characterized a Pd^{IV} aryl complex, which was obtained by oxidative addition of the chelating *ortho*-iodobenzoate to Pd^{II}.[12e] The newly formed complex **8** undergoes reductive elimination by C_{sp^2}–C_{sp^3} coupling to give **9**. This step is in contrast to the aryl group migration to the aryl site of the palladacycle—C_{sp^2}–C_{sp^2} coupling to give the intermediate **11**—which is invariably observed in the absence of the amino group when the palladacycle contains an *ortho* substituent ($R^1 \neq H$; see below for a proposed rationalization of this behavior). The Pd^{II} complex **9** thus formed contains the two aryl groups in a *cis*,*exo* arrangement, which forces them into a close prox-



Scheme 2. Possible reaction pathway.

imity,[10,13] thus making possible the coordination of the NH_2 group to palladium. The subsequent steps involve NH_2 deprotonation by the base and final seven-membered ring closure through C–N coupling[14] to give compound **3**. This pathway represents a deviation from the intramolecular aromatic substitution leading to the six-membered ring compound **10** as reported in the accompanying paper.[1] C_{sp^2}–N bond formation directly from the Pd^{IV} complex **8** leading to **12**, as modeled by DFT calculations is also energetically precluded. Formation of the C_{sp^2}–C_{sp^3} instead of C_{sp^2}–C_{sp^2} bond, as well as the seven-membered ring closure mentioned above are key features of the mechanism.

It is worth noting in this context that addition of water has been shown by Malacria and co-workers to counteract the chelating effect of the CH_2CONH_2 functionality,[1] thus driving the reaction back to the usual C_{sp^2}–C_{sp^2} bond formation. In our case water addition turns out not to be able to cause a significant change of the reaction course.

Further insight into the nature of the intermediates of the reaction comes from theoretical calculations carried out on norbornane-containing palladacycles. On the basis of our previous studies[3a] we anticipated that *ortho*-substituted aryl halide/Pd^{IV} complexes would be formed. The calculated barrier for the oxidative addition of *ortho*-bromoaniline to deliver **8** (R = Me, ZZ = CH_2-CH_2) upon ligand displacement is lower by 9.9 kcal mol^{-1} in ΔG compared to an C_{sp^2}–C_{sp^3} reductive elimination from a bimetallic intermediate alternative leading to Pd^{IV} (see Figures S1 and S2 in the Supporting Information). We also considered a possible chelation by the *ortho*-arylbromide at the Pd^{II} stage and its effect on oxidative addition. By displacing both ligands L from **7**, the barrier is similar ($\Delta\Delta G = +3.0$ kcal mol^{-1} at 278 K, -0.7 kcal mol^{-1} at 378 K). Upon facile ligand association at the Pd^{IV} stage, this pathway leads to the same intermediate **8**, which contains the halide *trans* to the aryl ring of the metallacycle. Higher barriers are obtained to form its isomeric complex **8a**, ($\Delta G = +4.5$ kcal mol^{-1}), wherein the halide and the amino group are inverted. The octahedral Pd^{IV} complexes obtained so far by oxidative addition of methyl, allyl, or benzyl halide from the metallacycle **7** in Scheme 2,[8a,15] have the halide *trans* to the norbornyl ring as in **8a**.

Both the calculated structures **8** and **8a** display chelation by the aromatic amino group.[16] We calculated the energy barriers for the four possible C–C bond-forming reductive eliminations from these two complexes since **8a** might be present in solution in thermodynamic equilibrium with **8**. The distortion of the octahedral structure, caused by the strained chelating ring, favors reductive elimination from **8** to **13**, which eventually leads to **3** (Figure 1 and see Figure S3 in the Supporting Information).

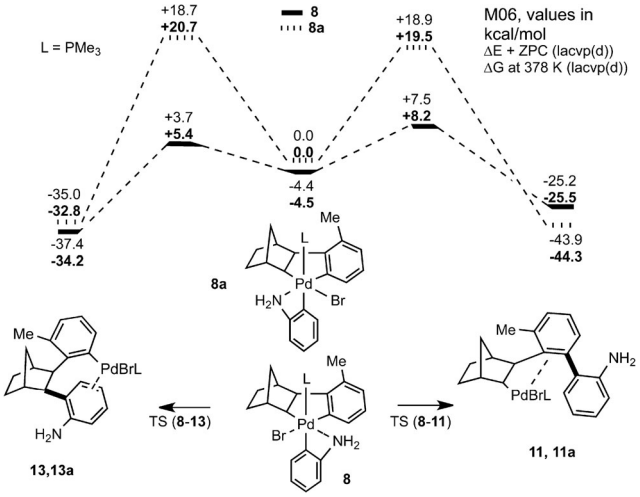


Figure 1. Modeled pathways for *ortho*-bromoaniline.

A possible explanation of amine chelation and of the unusual reactivity which arises from it can be found upon considering the relative electronic densities of the three palladium-bonded carbon atoms involved. In **8**, the palladium-bonded C_{sp^2} of the aniline ring is the more electron rich and the norbornyl C_{sp^3} is the electrophile (summary of calculated charges in Table S1 in the Supporting Information). Frontier molecular orbital analysis of these complexes strongly supports this conclusion. The HOMO around the palladium bonded C_{sp^2} of the aniline ring nicely matches the LUMO around the C_{sp^3} belonging to the metallacycle of complex **8** (Figure 2).

It should be observed that potential chelating groups are not always able to shift the reaction towards C_{sp^2}–C_{sp^3} bond

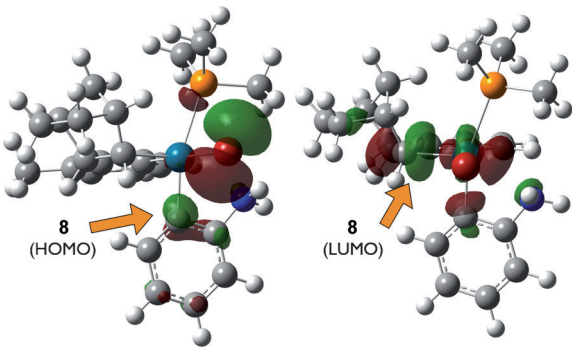


Figure 2. Frontier orbitals for the calculated complex **8**. Orange arrows indicate the carbon atoms involved in the cross-coupling.

formation. For example, the acetylated *ortho*-bromoaniline leads to C_{sp^2}–C_{sp^2} bond formation and the reaction product is a carbazole, which results from elimination of norbornene—in this case acting catalytically—and subsequent ring closure with C–N bond formation.[4]

We calculated reductive eliminations from a Pd^{IV} complex with an acetyl-protected amino group (see Figure S4 in the Supporting Information). In this case, Pd^{IV} structures converged to a minima in which chelation occurs to neither the nitrogen nor the oxygen atom, and the lowest barrier is that for the C_{sp^2}–C_{sp^2} formation (by 1.6 kcal mol^{-1} in ΔG). This effect should be attributed to the steric hindrance of the acetyl group and to the reduced electron density on the nitrogen atom. As a result the structure of the palladium intermediate approaches that of a trigonal bipyramid, which is more reactive than the octahedral intermediate and leads to the C_{sp^2}–C_{sp^2} bond formation as previously shown by us.[3a] On the contrary, analogous to the unsubstituted NH_2, the CH_2CONH_2 favors C_{sp^2}–C_{sp^3} bond formation through a distorted octahedral complex, as reported in the accompanying paper,[1] while $CONH_2$[17] as well as CH_2NH_2,[18] which do not cause octahedral distortion, favor C_{sp^2}–C_{sp^2} bond formation (see the Supporting Information).

Since alkali carbonates are needed to perform the palladium-catalyzed process, calculations were also carried out to ascertain whether carbonate coordination could offer more favorable energetic pathways. In particular we used DFT to test a different route to product **3** from the Pd^{IV} complex **8**; that is, through C_{sp^2}–N reductive elimination followed by C–C ring closure (Scheme 2). To this end, we replaced the bromide with a bicarbonate anion. The energy barrier to C_{sp^2}–N formation is, however, higher than that the corresponding to C_{sp^2}–C_{sp^3} formation ($\Delta G = +36.9$ versus $+6.0$ kcal mol^{-1}, respectively; see Figure S5 in the Supporting Information). Upon deprotonation of the amino group by a stronger carbonate base, the N-arylation transition state is expectedly less demanding in terms of energy ($\Delta G = +32.8$ kcal mol^{-1}), but still outmatched by the Pd^{IV} C_{sp^2}–C_{sp^3} reductive elimination. Final ring closure to **3** displays a barrier of $+21$ kcal mol^{-1}, thus indicating that a Buchwald–Hartwig amination takes place at the Pd^{II} stage rather than at the Pd^{IV} stage (see Figure S6 in the Supporting Information).

The result of our theoretical study thus shows that the chelating amino group determines C_{sp^2}–C_{sp^3} coupling in arylnorbornyl-derived palladacycles containing *ortho*-substituents; such palladacycles would typically be expected to favor C_{sp^2}–C_{sp^2} coupling.

As shown in Table 1 (entries 16–19) and in Table 2 (entries 15, 17) haloarenes without *ortho* substituents also react with *ortho*-bromoanilines in most cases with modest yields; the yields are lower because of the easy formation of type **10** compounds arising from the starting aryl iodide only.[7] According to our previous studies[3a] these reactions should involve transmetalation and not oxidative addition of *ortho*-bromoaniline to the palladacycle. We cannot exclude, however, that chelation of the amino group favors oxidative addition also in this case.

In conclusion we have worked out a simple procedure which allows the synthesis of compounds belonging to the important class of dihydrodibenzoazepine and dibenzoazepine derivatives starting from simple and commercially available compounds. The process is based on the sequential reaction of three components, an aryl iodide, a bromoaniline, and either norbornene or norbornadiene in the presence of palladium as a catalyst. Whereas the use of norbornene leads to dihydrodibenzoazepine derivatives, norbornadiene allows an additional step consisting of a retro-Diels–Alder reaction, thus leading to the parent dibenzoazepines. Chelation of the amino group to palladium plays a key role for the selective formation of the dibenzoazepine product causing a deviation from the usual C_{sp^2}–C_{sp^2} bond formation to a C_{sp^2}–C_{sp^3} bond formation. Theoretical calculations support the experimental findings, thus giving a rationale for the interpretation of the preferred reaction course.

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