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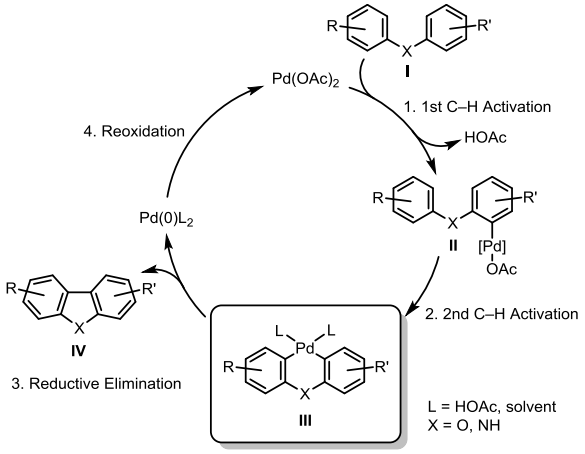
Synthesis of Stable Diarylpalladium(II) Complexes — Detailed Study of the Aryl–Aryl Bond Forming Reductive Elimination**

Tobias Gensch[+],[a] Nils Richter[+],[a] Gabriele Theumer,[a] Olga Kataeva,[a,b] and Hans-Joachim Knölker*[a]

Abstract: We have developed the synthesis of diarylpalladium(II) complexes by twofold aryl C–H bond activation. These intermediates of oxidative cyclization reactions are stabilized by chelation with acetyl groups while still maintaining sufficient reactivity to study their reductive elimination. We found four distinct triggers for the reductive elimination of these complexes to dibenzofurans and carbazoles. Thermal elimination occurs at very high temperatures, whereas ligand-promoted and oxidatively induced reductive eliminations proceed readily at room temperature. Under these conditions, no isomerization occurs. In contrast, weak Brønsted acids, such as acetic acid, lead to a sequence of proto-demetalation, isomerization to a κ^3-diarylpalladium(II) complex and reductive elimination to non-symmetrical cyclization products.

Palladium-catalyzed arene cross coupling is one of the most important reactions for the construction of complex molecules in organic chemistry, owing to its broad scope, reliable applicability, and choice of protocols.[1] Fundamental mechanistic understanding has helped developing this class of reactions even further.[2] In traditional cross coupling reactions, oxidative addition of an aryl halide to a palladium(0) species leads to an arylpalladium(II) complex, which then undergoes ligand exchange via transmetalation to diarylpalladium(II) intermediates. These readily undergo reductive elimination, releasing the biaryl product. Recently, many methods have been developed in which either one or both aryl ligands are introduced to palladium via C–H bond activation.[3,4] This approach can shorten syntheses and reduce waste generation, as well as open up new possible retrosynthetic disconnections.[5] Despite the importance of diarylpalladium(II) complexes as intermediates in traditional and direct cross coupling catalysis, their study and characterization has been limited by their inherent instability and propensity to undergo reductive elimination.[6]

We have developed a general strategy of consecutive palladium-catalyzed coupling reactions for the synthesis of biologically active carbazole derivatives.[7] Thus, diarylamines are obtained by Buchwald–Hartwig amination and subsequently converted to carbazoles in a palladium(II)-catalyzed oxidative cyclization, an intramolecular variant of cross-dehydrogenative coupling.[8] As part of this ongoing program, we have recently achieved the isolation of a diarylpalladium(II) complex, the key intermediate of this oxidative cyclization.[9] Chelation by appended weakly coordinating ligands stabilized this intermediate sufficiently for isolation (2% yield), thus confirming the mechanistic hypothesis for the oxidative cyclization. However, detailed investigations were not possible due to the only low amounts of diarylpalladium(II) complex obtained at that time.[9] Herein, we describe the design and synthesis of more stable diarylpalladium(II) complexes still having sufficient reactivity to allow the study of the reductive elimination. With these compounds in hand, we have discovered four mechanistically distinct triggers for reductive elimination from diarylpalladium(II) complexes, resulting in selective formation of different isomers of the cyclized products.



Scheme 1. General mechanism of the oxidative cyclization of diaryl compounds by palladium(II).

In the palladium(II)-catalyzed oxidative cyclization of diaryl compounds **I** the biaryl bond formation proceeds via two consecutive C–H bond activations (Scheme 1). Reductive elimination from the resulting diarylpalladium(II) complex **III** generates the product **IV** and a palladium(0) species which can be re-oxidized to palladium(II). A stabilization of the intermediate diarylpalladium(II) complexes **III** can be achieved by rigid ligands attached to the aryl substituents, thus suppressing the reductive elimination. In order to study the reductive elimination as the central step of the catalytic cycle, the stabilization of the diarylpalladium(II) complex should not be too high. In the present work, we show that acetyl-containing diaryl compounds, due to their rigidity and weak coordination, enable the synthesis of stable diarylpalladium(II) complexes which can be investigated for their behavior towards reductive elimination.

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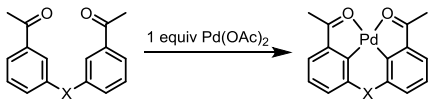
We obtained the tetracoordinate complex **2a** in 17% yield by reaction of palladium(II) acetate with bis(3-acetylphenyl) ether (**1a**) after 4 days at 70 °C in glacial acetic acid (Table 1). Higher temperatures and longer reaction times led via reductive elimination to a dibenzofuran with the acetyl substituents in position 1 and 7 (for systematic numbering of dibenzofuran and carbazole, see the supporting information). Various solvent systems, concentrations, and additives (such as acetates) resulted in decreased yields or gave no product at all. Using the bis(3-acetylphenyl)amine (**1b**), the corresponding complex **2b** was obtained in 30% yield after 2 h at 90 °C in a 1:1 mixture of acetic acid and 1,2-dichloroethane (DCE). Similarly, reductive elimination of complex **2b** to the 2,5-disubstituted carbazole is the major follow-up reaction, thus limiting the yield of the palladacycle.

Table 1: Synthesis of the diarylpalladium(II) complexes **2**.



1a: X = O
1b: X = NH

2a: X = O
2b: X = NH

Entry	X	Reaction conditions[a]	Yield
1	O	1.0 equiv $Cu(OAc)_2$, HOAc, 70 °C, 4 d	7%
2	O	HOAc, 70 °C, 4 d	17%
3	NH	HOAc, 80 °C, 3 h	12%
4	NH	HOAc/DCE (1:1), 90 °C, 2 h	30%

[a] 40–70% of starting material (**1**) and 10–20% of non-symmetrical cyclization product (**6**) but no other side-product were isolated along with complex **2**.

The structures of the complexes **2a** and **2b** could be confirmed by crystal structure analysis (Figures 1 and 2).[10,11] The molecular structures are highly planar and very similar to each other. In comparison with the previously reported pivaloyloxy-chelated analog featuring a six-membered palladacycle,[9] slightly shorter Pd–C (1.94 vs. 1.95 Å) and longer Pd–O bonds (2.18 vs. 2.14 and 2.10 Å) are present in the symmetrical complexes **2a** and **2b**.

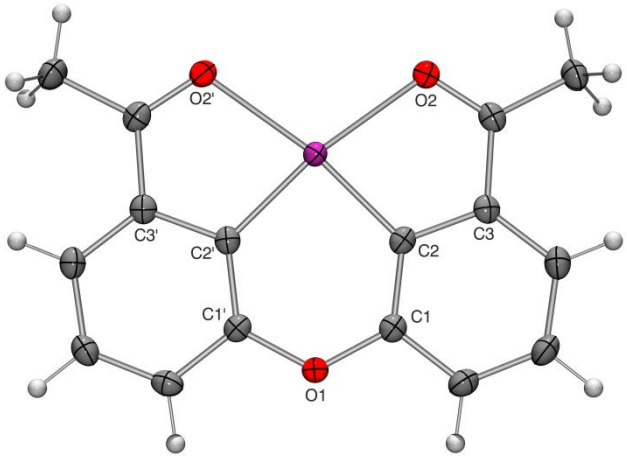


Figure 1. Molecular structure of complex **2a** in the crystal. Thermal ellipsoids are shown at 50% probability level. Selected bond distances in Å and angles in °: Pd–C2 1.9321(19), Pd–C2' 1.9341(19), Pd–O2 2.1778(14), Pd–O2' 2.1871(14), C2-Pd-C2' 90.44(8), C2-Pd-O2 80.71(7).

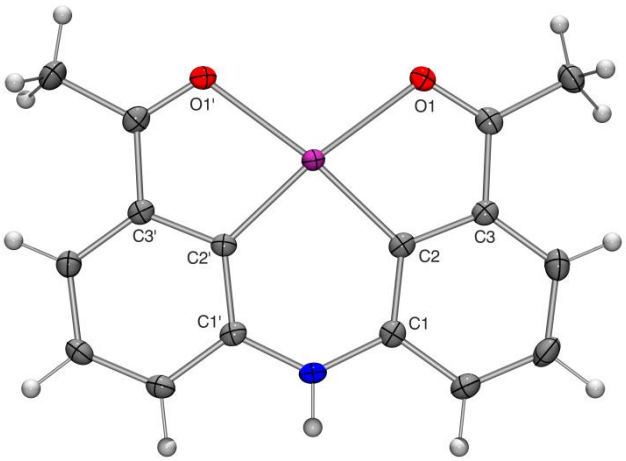
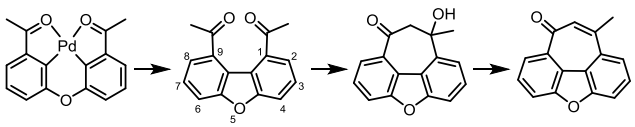


Figure 2. Molecular structure of complex **2b** in the crystal. Thermal ellipsoids are shown at 50% probability level. Selected bond distances in Å and angles in °: Pd–C2 1.935(2), Pd–C2' 1.942(2), Pd–O1 2.1798(18), Pd–O1' 2.1803(18), C2-Pd-C2' 92.27(10), C2-Pd-O1 81.02(9).

The successful isolation of the diarylpalladium(II) complexes **2** in significant amounts enabled us to study their reductive elimination behavior (Table 2). First, we tested the thermal stability of these compounds in indifferent aromatic solvents. Surprisingly, after 7 days of heating in toluene at reflux, complex **2a** could be re-isolated almost quantitatively. An increase of the temperature to 170 °C (using *p*-xylene as solvent in a sealed tube) was necessary in order to achieve a thermal induction of the reductive elimination of complex **2a**. Along with the cyclized 1,9-diacetyldibenzofuran (**3a**), two products resulting from aldol addition and condensation could be isolated, which originate from the immediate elimination product **3a**. In contrast, addition of triphenylphosphane to a solution of complex **2a** triggers the reductive elimination to **3a** even at room temperature.[12] We propose that coordination of the phosphane at the palladium atom weakens the complex and enables a rapid reductive elimination. Likewise, treatment of complex **2a** with an excess of hydrogen peroxide (30% aq. soln.) leads to the formation of **3a** at room temperature. This reaction most likely involves the oxidation of **2a** to a Pd(IV) species prior to reductive elimination.[13]

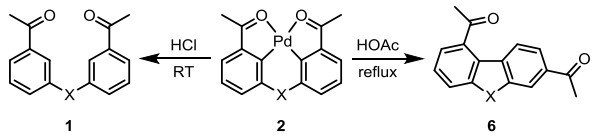
Table 2: Reaction conditions for the reductive elimination of complex **2a**.



2a **3a** **4** **5**

Entry	Reaction conditions	**2a**	**3a**	**4**	**5**
1	toluene, 110 °C, 7 d	98%			
2	*p*-xylene, 170 °C, 3 d	27%	29%	4%	38%
3	PPh_3 (4 equiv), RT, 8 h	21%	75%	trace	
4	H_2O_2 (excess), CH_2Cl_2, RT, 5 h	29%	41%		

Table 3: Reactions of the diarylpalladium(II) complexes **2** with Brønsted acids.



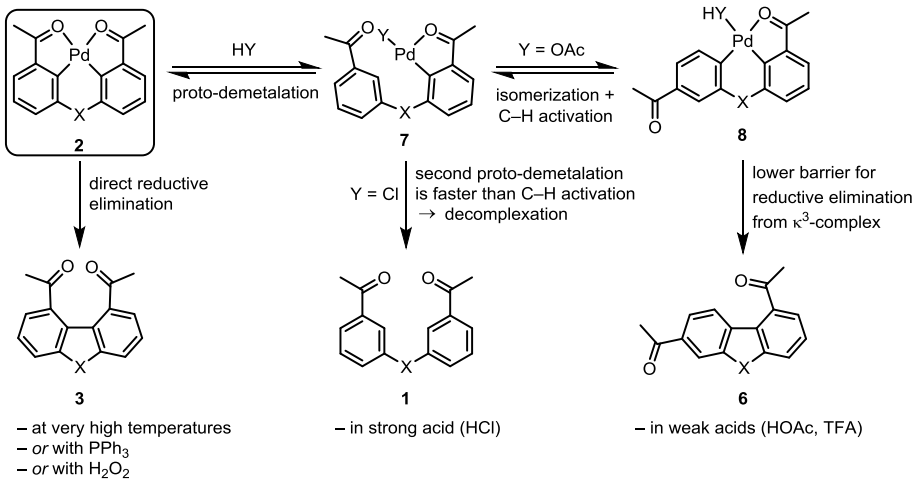
a: X = O
b: X = NH

	X	Reaction conditions	Product, yield
a	O	HOAc, reflux, 3 d	**6a**, 46%[a]
a	O	HCl/CH_2Cl_2 (1:4), RT, 1.5 h	**1a**, 85%
b	NH	HOAc, reflux, 3 d	**6b**, 85%
b	NH	HCl/CH_2Cl_2 (1:20), RT, 30 min	**1b**, 100%

[a] By-product: 3-acetyldibenzofuran (8% yield); 24% of complex **2a** recovered.

In order to explain the formation of the isomeric non-symmetrical cyclization products obtained on synthesis of the diarylpalladium(II) complexes **2**, the complexes **2** were subjected to acidic reaction conditions (Table 3). We observed an unexpected reactivity of the complexes **2** in glacial acetic acid. After 3 days of heating in HOAc at reflux, 76% of complex **2a** were consumed and the non-symmetrical 1,7-diacetyldibenzofuran (**6a**) was formed along with 3-acetyldibenzofuran. The latter product probably results from **6a** by a proton-initiated retro-Friedel–Crafts acylation. Under the same reaction conditions, complex **2b** was consumed completely to afford the non-symmetrical 2,5-diacetylcarbazole (**6b**) in 85% yield. Refluxing complex **2a** in trifluoroacetic acid leads to an accelerated formation of **6a** within a few hours, along with major decomposition of material, despite the lower reaction temperature. In neither of these experiments, we could observe any of the symmetrical 1,9-diacetyldibenzofuran (**3a**). When the diarylpalladium(II) complexes **2** were subjected to even stronger acids like HCl (mixture of conc. HCl and CH_2Cl_2), demetalation to the diaryl compounds **1** occurred rapidly at room temperature (**1a**: 85% yield; **1b**: 100% yield). The reversibility of C–H palladation under acidic conditions is well-documented.[14] Thus, the formation of the non-symmetrical cyclization products **6** can be rationalized by a sequence of proto-demetalation, isomerization to the κ^3-diarylpalladium(II) complex **8**, and reductive elimination (Scheme 3). Two factors may dictate the selectivity of this elimination pathway. Firstly, reductive elimination from **2** forms a highly strained product and requires high activation energies, as shown in the thermally induced reductive elimination (Table 2, entries 1 and 2). Secondly, the κ^3-diarylpalladium(II) complex **8** is less stabilized due to less chelation, thus enabling elimination at lower temperatures. Based on our present observations, formation of the isomeric cyclization products during the synthesis of the complexes **2** most likely occurs directly from the κ^3-intermediates, rather than via intermediate formation of **2** and subsequent isomerization–elimination. The related pivaloyloxy-substituted diarylpalladium(II) complex previously reported mainly undergoes reductive elimination without isomerization in HOAc at 80 °C.[9] We attribute this behaviour to the reduced stability as a consequence of the less favorable coordination geometry in the six-membered palladacycle. As a consequence, pathways leading to reductive elimination prior to isomerization may become favored. Thus, the preferential formation of the undesired non-linear isomer in the course of our total synthesis of antipathine A can be rationalized by the present findings.[15]

In conclusion, we have developed the synthesis of stable diarylpalladium(II) complexes by twofold aryl C–H bond activation of tethered diaryl compounds. These complexes are model compounds for the palladium-catalyzed biaryl bond formation and can be used for studying the reductive elimination leading to C–C bond formation. We have discovered four distinct triggers for the reductive elimination from these complexes. The thermal elimination occurs at very high temperatures (170 °C), whereas the ligand-promoted reductive elimination using triphenylphosphane and the oxidatively induced elimination proceed at room temperature. Each of these variants gives rise to the cyclization products without isomerization. Weak Brønsted acids, as a fourth potential trigger, lead to an isomerization–reductive elimination sequence and thus to the formation of non-symmetrical cyclization products. The selectivity offered by the different mechanistic alternatives for the reductive elimination of diarylpalladium(II) complexes will have an impact on future total syntheses of biologically active carbazole alkaloids. Moreover, the present findings are highly useful for interpretation, design, and application of C–C bond forming reactions using palladium in a more general context.



Scheme 2. Reactivity pathways for the demetalation of diarylpalladium(II) complexes **2**.

Keywords: C–H bond activation • metallacycles • palladium • reaction mechanisms • reductive elimination

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[10] Crystallographic data for **2a** (red crystals): $C_{16}H_{12}O_3Pd$, M = 358.66 g mol^{-1}, crystal size: 0.31 × 0.25 × 0.26 mm^3, monoclinic, space group $P2_1/n$, a = 8.3419(6), b = 9.4988(7), c = 15.8730(12) Å, β = 91.130(2)°, V = 1257.50(16) Å^3, Z = 4, ρ_{calcd} = 1.894 Mg/m^3, μ = 1.479 mm^{-1}, λ = 0.71073 Å, T = 150(2) K, θ range: 2.50–29.99°, reflections collected: 19752, independent: 3637 (R_{int} = 0.0411), 183 parameters. The structure was solved by direct methods and refined by full-matrix least-squares on F^2; final R indices [$I > 2\sigma(I)$]: R_1 = 0.0255, wR_2 = 0.0553; maximal residual electron density: 0.443 e Å^{-3}. CCDC-1480675 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] Crystallographic data for **2b**: $C_{16}H_{13}NO_2Pd$, M = 357.67 g mol^{-1}, crystal size: 0.20 × 0.12 × 0.03 mm^3, monoclinic, space group $P2_1/n$, a = 8.2620(5), b = 9.4443(5), c = 16.0679(9) Å, β = 91.9950(10)°, V = 1253.00(12) Å^3, Z = 4, ρ_{calcd} = 1.896 Mg/m^3, μ = 1.480 mm^{-1}, λ = 0.71073 Å, T = 150(2) K, θ range: 2.50–28.00°, reflections collected: 19982, independent: 3023 (R_{int} = 0.0156), 187 parameters. The structure was solved by direct methods and refined by full-matrix least-squares on F^2; final R indices [$I > 2\sigma(I)$]: R_1 = 0.0245, wR_2 = 0.0548; maximal residual electron density: 0.490 e Å^{-3}. CCDC-1480676 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] Phosphanes have been shown to influence the direct coupling to biaryl compounds; see for example: M. Lafrance, D. Lapointe, K. Fagnou, *Tetrahedron* **2008**, *64*, 6015–6020; b) M. Wakioka, Y. Nakamura, Y. Hihara, F. Ozawa, S. Sakaki, *Organometallics* **2014**, *33*, 6247–6252.

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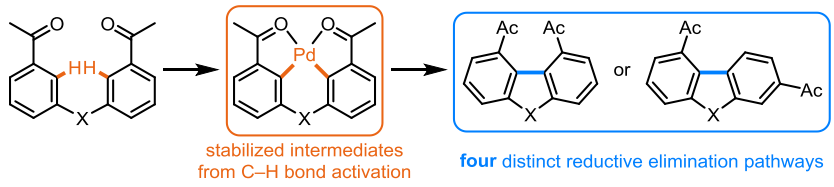

COMMUNICATION

Diarylpalladium(II) intermediates of oxidative cyclization reactions can be synthesized as stabilized chelates by twofold aryl C–H bond activation. The study of the reductive elimination of these complexes to dibenzofurans and carbazoles unveiled four distinct triggers: a) thermal elimination at high temperature, b) ligand-promoted, and c) oxidatively induced reductive elimination at room temperature, which all proceed without isomerization. Whereas weak Brønsted acids, such as acetic acid, induce a sequence of proto-demetalation, isomerization to a κ^3-diarylpalladium(II) complex and reductive elimination to non-symmetrical isomers.

*Tobias Gensch, Nils Richter, Gabriele Theumer, Olga Kataeva, and Hans-Joachim Knölker**

Synthesis of Stable Diarylpalladium(II) Complexes — Detailed Study of the Aryl–Aryl Bond Forming Reductive Elimination