Palladium Catalysis

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Palladium-Catalyzed Intramolecular Carbene Insertion into C(sp^3)–H Bonds

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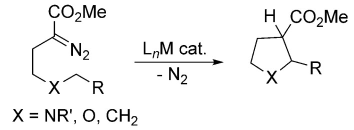
Abstract: *A palladium-catalyzed carbene insertion into C(sp^3)–H bonds leading to pyrrolidines was developed. The coupling reaction can be catalyzed by both Pd^0 and Pd^{II}, is regioselective, and shows a broad functional group tolerance. This reaction is the first example of palladium-catalyzed C(sp^3)–C(sp^3) bond assembly starting from diazocarbonyl compounds. DFT calculations revealed that this direct C(sp^3)–H bond functionalization reaction involves an unprecedented concerted metalation–deprotonation step.*

The development of practical and green methods for C–C bond formation by the selective functionalization of unactivated C–H bonds is an area of great interest that has been extensively studied over the last years.[1] Among the vast array of such transformations, the C–H insertion of metal carbenoids derived from diazocarbonyl substrates constitutes a particularly attractive method (Scheme 1).[2] In this approach, the electron-rich C–H bonds generally exhibit higher reactivity toward the carbene center and show an activation order of tertiary > secondary ⩾ primary C(sp^3)–H. Thus, although the insertion into tertiary and secondary C(sp^3)–H bonds has been thoroughly studied, the analogous process involving primary C(sp^3)–H and C_{Ar}(sp^2)–H bonds remains comparatively underdeveloped.



Scheme 1. Metal-catalyzed C–H insertion of diazoesters.

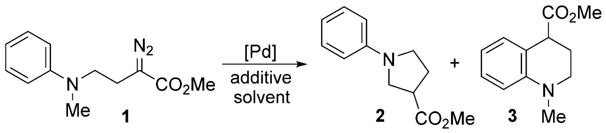
The C–H insertion reactions of diazocarbonyl substrates have been traditionally carried out in the presence of Rh^{II}[3] or Cu catalysts.[4] Although other metals have emerged as potentially useful catalysts for this type of transformation,[5–10] the use of palladium has been restricted to a couple of examples of α-diazo β-ketoester insertion into C(sp^2)–H bonds.[11,12] This fact is highly surprising if we take into account the great success of Pd catalysis in cross-coupling reactions of diazo compounds with either organic halides or arylboronic acids.[13]

As part of our research program on the synthesis of azaheterocycles, we have been exploring different ways to increase the versatility of Pd catalysis in C–C bond-forming reactions.[14,15] In this regard, we decided to investigate the feasibility of Pd as a catalyst for the carbenoid C–H insertion from diazocarbonyl substrates.

Herein we report an operationally simple procedure for the Pd-catalyzed intramolecular assembly of C(sp^3)–C(sp^3) bonds starting from α-diazoesters, in which both Pd^0 and Pd^{II} catalysts are effective. Mechanistically, this direct C(sp^3)–H bond functionalization process is different from those reported in the literature based on Rh^{II} or Cu catalysts.[3,4]

Our investigation began by testing the Pd-catalyzed cyclization of α-diazoester **1** in order to assess the regioselectivity of the C–H bond activation process (Scheme 2).

A variety of Pd sources, ligands, additives, and solvents were investigated (see the Supporting Information for details). Based on these studies, we established three experimental procedures for the cyclization reaction. Thus, treatment of **1** with $Pd(OAc)_2$ (10 mol %) and Cs_2CO_3 (2 equiv) in $CHCl_3$ at reflux afforded a 2:1 mixture of pyrrolidine **2** and tetrahydroquinoline **3**, which resulted from the activation of the C(sp^3)–H and the aryl C_{Ar}(sp^2)–H bonds, respectively. The use of $Pd_2(dba)_3$ (2.5 mol %) as the catalyst in the presence of Cs_2CO_3 (2 equiv) in 1,2-dichloroethane (DCE) at 80 °C led to a 2.2:1 mixture of **2** and **3**. Finally, among the different ligands explored to modify the selectivity of the C–H insertion from **1**, when using $Pd_2(dba)_3$ (2.5 mol %) as the precatalyst, we found that the bidentate phosphines 1,3-bis(diphenylphosphino)propane (dppp), 1,1′-bis(diphenylphosphino)ferrocene (dppf), and 4,5-bis(diphenylphosphino)-9,9-dimethyl-xanthene (xantphos; 5 mol %) gave slightly better C(sp^3)–H to C_{Ar}(sp^2)–H activation ratios (2.6–2.8:1).



Scheme 2. Pd-catalyzed cyclization of diazoester **1**.

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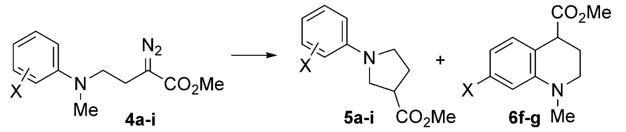
These results showed that a) the C–H carbenoid cyclization can be catalyzed by both Pd^0 and Pd^{II}, and b) the C(sp^3)–H insertion is in all cases favored over the C$_{Ar}$(sp^2)–H insertion. With this information in hand, we decided to explore the influence of the introduction of substituents at the aromatic ring on the selectivity of the C–H activation process (see the Supporting Information and Table 1).

Table 1: Selected Pd-catalyzed C–H insertion reactions of α-diazoesters **4a–i**.[a]



No.	**4** (X)	[Pd](mol%)/ L(mol%)	Solv.	Temp.	Product (yield [%])[b]
1	**4a** (2-I)	Pd(OAc)$_2$ (10)/–	CHCl$_3$	reflux[c]	**5a** (55)
2	**4a** (2-I)	Pd$_2$(dba)$_3$ (2.5)/–	CHCl$_3$	reflux	**5a** (89)
3	**4b** (2-Br)	Pd(OAc)$_2$ (10)/–	CHCl$_3$	reflux	**5b** (51)
4	**4b** (2-Br)	Pd$_2$(dba)$_3$ (2.5)/–	CHCl$_3$	reflux	**5b** (66)
5	**4c** (2-Cl)	Pd(OAc)$_2$ (10)/–	CHCl$_3$	reflux	**5c** (56)
6	**4c** (2-Cl)	Pd$_2$(dba)$_3$ (2.5)/ dppf (5)	DCE	80 °C	**5c** (69)
7	**4d** (2-F)	Pd$_2$(dba)$_3$ (2.5)/–	DCE	80 °C	**5d** (62)
8	**4e** (2-Me)	Pd(OAc)$_2$ (10)/–	CHCl$_3$	reflux	**5e** (49)
9	**4e** (2-Me)	Pd$_2$(dba)$_3$ (2.5)/ dppf (5)	DCE	80 °C	**5e** (57)
10	**4f** (3-Cl)	Pd(OAc)$_2$ (10)/–	DCE	80 °C[d]	**5f/6f** (2:1; 39)
11	**4f** (3-Cl)	Pd$_2$(dba)$_3$ (2.5)/–	DCE	80 °C	**5f/6f** (2.7:1; 45)
12	**4g** (3-MeO)	Pd(OAc)$_2$ (10)/–	DCE	80 °C[d]	**5g/6g** (1.3:1; 42)
13	**4g** (3-MeO)	Pd$_2$(dba)$_3$ (2.5)/–	DCE	80 °C	**5g/6g** (1.5:1; 47)
14	**4h** (4-Cl)	Pd$_2$(dba)$_3$ (2.5)/ dppf (5)	DCE	80 °C	**5h** (35)[e]
15	**4i** (4-MeO)	Pd(OAc)$_2$ (10)/–	DCE	80 °C[d]	**5i** (25)[f]
16	**4i** (4-MeO)	Pd$_2$(dba)$_3$ (2.5)/–	CHCl$_3$	reflux	**5i** (38)[f]

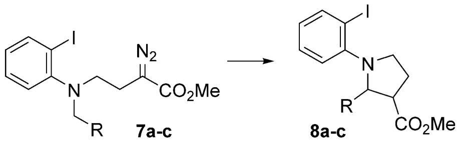
[a] Reaction conditions: [Pd]/L (L = ligand; see table) and Cs$_2$CO$_3$ (2 equiv) in CHCl$_3$ or DCE at the indicated temperature for 24 h. [b] Yields refer to products isolated by chromatography and for entries in which a product mixture was obtained, the yield refers to the combined yield. [c] 16 h. [d] 48 h. [e] ^{1}H NMR analysis of the reaction mixture showed a ≈4:1 C(sp^3)–H:C(sp^2)–H activation ratio. [f] ^{1}H NMR analysis of the reaction mixture showed a ≈5:1 C(sp^3)–H:C(sp^2)–H activation ratio.

To our delight, the C(sp^3)–H insertion was the only reaction observed when 2-idoaniline **4a** was subjected to the optimized reaction conditions (entries 1 and 2). It should be noted that no product resulting from the competitive Pd-catalyzed reaction of the aryl iodide with the α-diazoester moiety[13,16] was detected in these reaction mixtures. The best result was obtained with Pd$_2$(dba)$_3$ in the absence of phosphine ligands, which afforded pyrrolidine **5a** in 89% yield (entry 2).

2-Haloanilines **4b**, **4c**, and **4d**, and 2-methylaniline **4e** also selectively underwent C(sp^3)–H insertion (entries 3–9). In contrast, competition between the C(sp^3)–H and C$_{Ar}$(sp^2)–H insertions was observed in the reactions involving *meta*- and *para*-substituted anilines. While 3-chloroaniline **4f** gave a C–H activation selectivity (entries 10 and 11) similar to the unsubstituted aniline **1**, the cyclization reactions of 3-methoxyaniline **4g** proceeded with lower regioselectivity (entries 12 and 13). Interestingly, higher selectivity was obtained with both electron-poor 4-chloroaniline **4h** (entry 14) and electron-rich 4-methoxyaniline **4i** (entries 15 and 16).

The C-H insertion reaction was not limited to *N*-methylanilines but also proved suitable for substituted C(sp^3)–H bonds (Table 2).

Table 2: Pd-catalyzed C–H insertion of α-diazoesters **7a–c**[a]



No.	**7** (R)	[Pd](mol%)/ L(mol%)	Solv.	Temp.	Product (yield [%])[b]
1	**7a** (C$_6$H$_5$)	Pd$_2$(dba)$_3$ (2.5)/–	CHCl$_3$	reflux	**8a** (66) *cis/trans* 5.5:1
2	**7a** (C$_6$H$_5$)	Pd(OAc)$_2$ (10)/–	CHCl$_3$	reflux	**8a** (46) *cis/trans* 4:1
3	**7a** (C$_6$H$_5$)	Pd$_2$(dba)$_3$ (2.5)/ dppf (5)	DCE	80 °C	**8a** (54) *cis/trans* 4:1
4	**7b** (CH=CH$_2$)	Pd$_2$(dba)$_3$ (2.5)/–	CHCl$_3$	reflux	**8b** (58) *cis/trans* 1.7:1
5	**7b** (CH=CH$_2$)	Pd(OAc)$_2$ (10)/–	CHCl$_3$	reflux	**8b** (43) *cis/trans* 1.7:1
6	**7c** (C$_2$H$_5$)	Pd$_2$(dba)$_3$ (2.5)/–	DCE	80 °C[c]	**8c** (70) *cis/trans* 1.5:1
7	**7c** (C$_2$H$_5$)	Pd(OAc)$_2$ (10)/–	DCE	80 °C[c]	**8c** (45) *cis/trans* 1.1:1

[a] Reaction conditions: See Table 1. [b] Yields are for those of products isolated by chromatography. [c] 39 h.

N-Benzylaniline **7a** regioselectively afforded pyrrolidine **8a** (5.5:1 *cis/trans* mixture) in 66% yield when the reaction was performed in the presence of Pd$_2$(dba)$_3$ (entry 1).[17] The use of either Pd(OAc)$_2$ (entry 2) or Pd$_2$(dba)$_3$/dppf (entry 3) as the catalyst afforded slightly lower yields. More importantly, no competition between allylic insertion and cyclopropanation[18–19] was observed in the Pd-catalyzed reactions of *N*-allylaniline **7b**. Thus, treatment of **7b** with either Pd$_2$(dba)$_3$ (entry 4) or Pd(OAc)$_2$ (entry 5) in CHCl$_3$ at reflux afforded pyrrolidine **8b** (1.7:1 *cis/trans* mixture). Finally, *N*-propylaniline **7c** also underwent a similar regioselective insertion at the C(sp^3)–H bond to give pyrrolidine **8c** (entries 6 and 7). Similar to the reactions involving 2-iodoaniline **4a**, no product resulting from the Pd-catalyzed reaction of the aryl iodide with the α-diazoester moiety was detected in any of the Pd-catalyzed reactions of 2-iodoanilines **7a–c**.

According to previous mechanistic studies, it can be suggested that the Pd-catalyzed transformations described above likely involve the insertion of the in situ generated Pd–

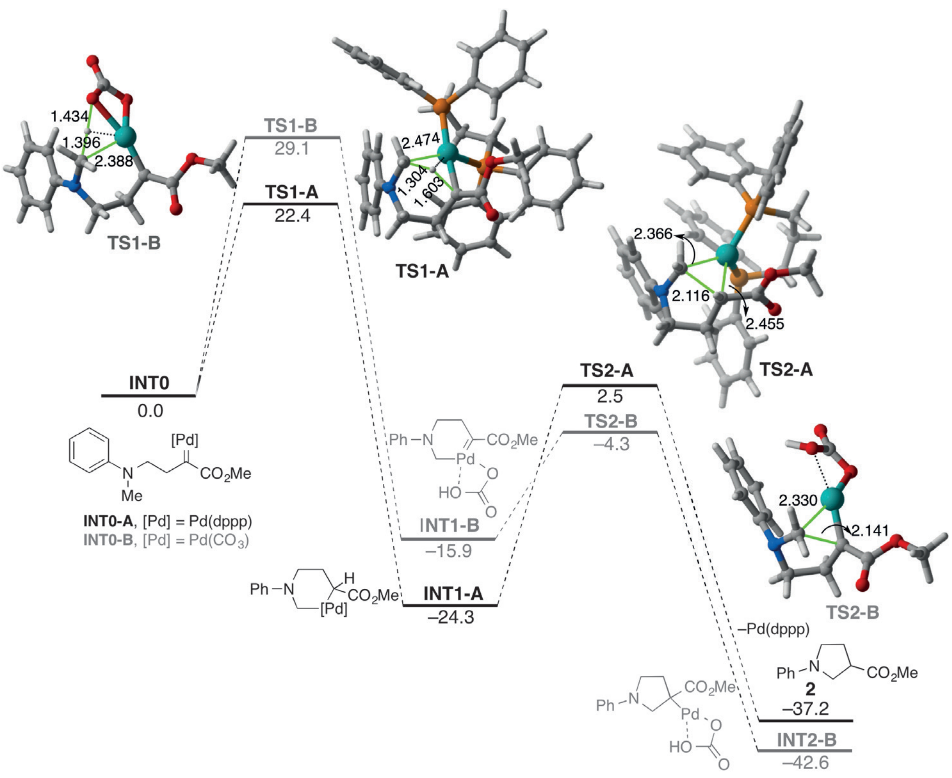


Figure 1. Computed reaction profiles for the formation of pyrrolidine **2**. Relative free energies (ΔG_{298}, at 298 K) and bond distances are given in kcal mol^{-1} and angstroms (Å), respectively. All data were computed at the PCM(CHCl$_3$)-M06L/def2-TZVP//RI-BP86-D3/def2-SVP level. Atom colors: N = blue; O = red; C = gray; P = orange; Pd = turquoise.

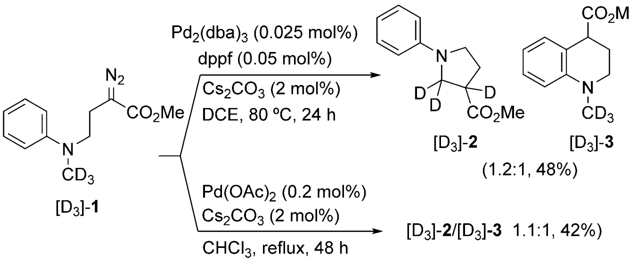
carbenoid intermediate into the C−H bond. For related Rh^{II}- and Cu-catalyzed transformations, this process has been proposed to occur in a concerted but asynchronous manner that directly releases the reaction product and the metal catalyst in one single step.[20]

Density functional theory (DFT) calculations[21] were carried out to gain more insight into the mechanism of the above Pd-catalyzed C(sp^3)−H insertions. Thus, Figure 1 shows the corresponding computed reaction profiles of the processes involving **INT0-A** and **INT0-B**, the initial Pd^0 and Pd^{II}–carbene complexes formed upon reaction of the active catalytic species Pd(dppp) or Pd(CO$_3$) with **1**, respectively.

In the Pd^{II} pathway, the initial complex **INT0-B** evolves to carbene complex **INT1-B** via transition state **TS1-B** with an activation barrier of 29.1 kcal mol^{-1} in a highly exergonic transformation ($\Delta G_R = -15.9$ kcal mol^{-1}). This saddle point is associated with the concerted hydrogen migration from the N−CH$_3$ moiety to the carbonate ligand and Pd−C bond formation (Figure 1). Therefore, this transformation is analogous to related concerted metalation–deprotonation (CMD) C−H activations which are assisted by acetate[22] or carbonate.[14b,15d] Subsequent exergonic ($\Delta G_R = -18.3$ kcal mol^{-1}) insertion of the carbene carbon atom into the Pd−C bond via **TS2-B** ($\Delta G^{\neq} = 11.6$ kcal mol^{-1}) leads to the formation of the Pd^{II} complex **INT2-B**. Final protonolysis of the Pd−C bond would afford pyrrolidine **2** and release the Pd^{II} catalyst.[23] This protonolysis may occur either by intramolecular proton transfer from the HCO$_3^-$ ligand or, more likely, by transmetalation into a cesium enolate, followed by intermolecular protonation with the HCO$_3^-$ released in the reaction medium.[24]

The initial C(sp^3)−H activation in the Pd^0 pathway, which proceeds through the transition state **TS1-A**, resembles the above-discussed CMD process in the sense that this transformation also involves a concerted metalation–deprotonation step. However, in this case the process also forms the new C−H bond. Therefore, this single step can be viewed as a Pd-mediated 1,5-H migration from the N−CH$_3$ moiety to the carbenoid which results in the formal oxidation of the transition metal.[25] This reaction is more exergonic ($\Delta G_R = -24.3$ kcal mol^{-1}) and occurs with a lower activation barrier ($\Delta G^{\neq} = 22.4$ kcal mol^{-1}) than the CMD process involving **TS1-B**. The readily formed Pd^{II} complex **INT1-A** is finally converted into pyrrolidine **2** in a highly exergonic ($\Delta G_R = -12.9$ kcal mol^{-1}) reductive elimination through transition state **TS2-A** ($\Delta G^{\neq} = 26.8$ kcal mol^{-1}) which releases the catalytic species Pd(dppp).

Additional experiments were performed to support the transition-metal-mediated 1,5-H migration. Thus, when trideuterated aniline [D$_3$]-**1** was subjected to the conditions optimized for the Pd-catalyzed reaction of aniline **1**, using Pd$_2$(dba)$_3$/dppf as the catalyst, a 1.2:1 mixture of pyrrolidine [D$_3$]-**2** and tetrahydroquinoline [D$_3$]-**3** was obtained (Scheme 3). This result confirms that the deuterium atom was fully transferred to the carbenoid atom, which nicely agrees with the DFT-proposed mechanism. The use of Pd(OAc)$_2$ as the catalyst afforded a similar C(sp^3)−H/C$_{Ar}$-(sp^2)−H ratio with complete preservation of the deuterium label at the specific position as well. The reaction also proceeded at room temperature, but required longer times and higher catalyst loading. Interestingly, the regioselectivity



Scheme 3. Pd-catalyzed reactions of [D$_3$]-**1**.

of these reactions was very different from that involving aniline **1** under the same conditions, which suggests a primary isotope effect.

In summary, we have developed a regioselective Pd-catalyzed C(sp^3)−H insertion reaction of α-diazoesters to provide pyrrolidines. Both Pd^0 and Pd^{II} are effective in this reaction, which represents the first example of Pd-catalyzed carbenoid insertion into C(sp^3)−H bonds. A salient aspect of this transformation is its broad tolerance to reactive functional groups in the starting material. DFT calculations suggest that this transformation does not involve a concerted asynchronous process, but a metalation–deprotonation reaction.

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