ORGANOMETALLICS

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Switch of Addition and Ring-Opening Reactions of Oxabicyclic Alkenes with Terminal Alkynes by sp^2-C,P- and sp^3-C,P-Palladacycle Catalysis

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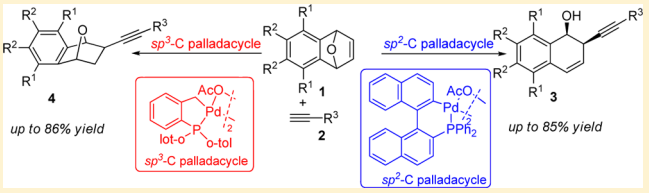
S *Supporting Information*

ABSTRACT: Palladacycles were found to be efficient catalysts for the reaction of oxabicyclic alkenes with terminal alkynes. A switch of reaction selectivity was realized using a palladacycle with an sp^2 or sp^3 C−Pd bond. Addition products were afforded predominantly using a palladacycle with an sp^3 C−Pd bond, while ring-opening compounds were the major products when palladacycles having an sp^2 C−Pd bond were used. DFT calculations revealed that the different *trans* effects of the sp^2-C and sp^3-C donors in palladacycles are responsible for the switch in selectivity.



Palladacycles constitute one of the most important classes of organopalladium catalysts, due to their versatile frameworks, remarkable catalytic activity, synthetically easy accessibility, extra stability toward air and moisture, and relatively low toxicity. They have successfully been used not only in carbon−carbon and carbon−heteroatom bond forming processes[1] but also in asymmetric catalysis,[2] in addition to their wide applications in a variety of fields such as biological chemistry, material science, organic synthesis, and ligand resolution.[3,4] Many advantages as catalysts have been revealed, and high turnover numbers have been achieved. Recent advances have demonstrated that the palladacycles are real transition-metal catalysts,[5,6] where the C−Pd bond of the palladacycle is kept intact, despite the fact that they serve as catalyst precursors in some reactions.[1b] The most notable structural characteristic of palladacycles is the presence of a C−Pd bond in addition to the bond of a coordination atom with Pd.[3a] The effect of different coordination atoms of palladacycles on the catalytic activity has been reported in the past few decades.[1a,7] In contrast, the influence of the nature of the C−Pd bond has rarely been studied, though both sp^2 and sp^3 carbons serve as coordination atoms. Thus, this represents a blind spot regarding whether the C−Pd bond of the palladacycle plays an important role in the catalytic reaction and what is the effect of sp^2 and sp^3 carbons connected to Pd. Obviously, the lack of such knowledge will hamper the development of palladacycle catalysts as well as new reactions catalyzed by them. In a program aimed at the development of palladacycles as real transition-metal catalysts,[6] we observed that phosphapalladacycles with an sp^2 or sp^3 C−Pd bond showed totally different selectivities in the reaction of oxabicyclic alkenes with terminal alkynes.[8] The former afforded mainly ring-opening products, while the latter gave addition products dominantly. Further investigations revealed that the different nature of the C−Pd bond contributes to the switch in selectivity. Herein, we disclose our preliminary results as well as a computational study for rationalization of the selectivity switch.

On the basis of our previous results,[6] the reaction of 7-oxabenzonorbornadiene (**1a**) with phenylacetylene (**2a**) was tested in the presence of palladacycle **5** with an sp^2 C−Pd bond in 1,2-dichloroethane (DCE) at 50 °C (Figure 1, Table 1). The ring-opening product **3a** was afforded in 84% yield accompanied by an 11% yield of addition product **4a** (entry 1).[9] Controlled experiments revealed that other palladium species, including $Pd(CH_3CN)_2Cl_2$, $Pd(OAc)_2$, $Pd(dba)_2$, $Pd(OAc)_2$/PPh_3, and $Pd(OAc)_2$/dppp, failed to effect the reaction. It

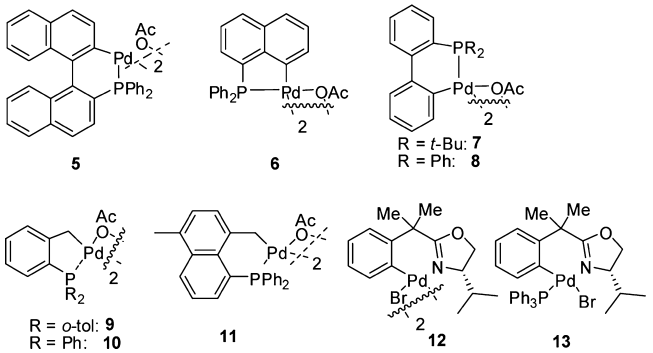
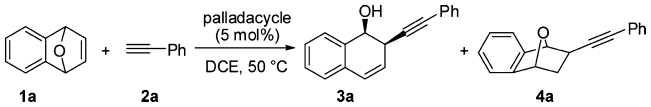


Figure 1. Palladacycles with different scaffolds and donor atoms.

Received: July 3, 2013
Published: August 8, 2013

dx.doi.org/10.1021/om400653x | *Organometallics* 2013, 32, 4465−4468

Table 1. Reaction of 1a with Phenylacetylene (2a) with Different Palladacycle Catalysts[a]



entry	palladacycle	yield of **3a**, %[b]	yield of **4a**, %[b]
1	**5**	84	11
2	**6**	61	20
3	**7**	18	
4	**8**	70	16
5	**9**	9	83
6	**10**	13	75
7	**11**	5	75
8[c]	**12**		
9[c]	**13**		

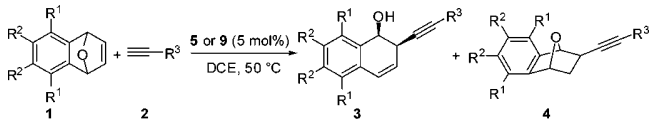
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), palladacycle (5 mol %). [b]Isolated yields. [c]Only starting material was recovered.

comes as a surprise to find that addition product **4a** was provided in 83% yield when palladacycle **9** was the catalyst (entry 5), while neither **3a** nor **4a** was obtained when palladacycle **12** with nitrogen as the coordination atom was used (entry 8). In order to determine the influence of the palladacycle structure on the reaction, some other palladacycles were tested. It is clearly showed that the palladacycles **5**−**8** with an sp^2 C−Pd bond provided the ring-opening product **3a** as major isomer (entries 1−4), while the palladacycles **9**-**11** with an sp^3 C−Pd bond mainly furnished the addition product **4a** (entries 5−7). It is also noted that only palladacycles with P as the coordination atom are suitable catalysts in the reaction, while those with N as the coordination atom could not catalyze the reaction (entries 8 and 9). The best yield for ring-opening product **3a** was 84%, with palladacycle **5** having an sp^2 C−Pd bond (entry 1). Palladacycle **9** with an sp^3 C−Pd bond is so far the optimal catalyst for the formation of addition product **4a** with 83% yield (entry 5). These results demonstrate that the nature of the C−Pd bond in the palladacycle plays a key role in determining the selectivity in the reaction of **1a** with **2a**. The influence of solvents, base, temperature, and additives on the selectivity of the reaction was investigated; it was found that the addition of base (such as Et_3N, bipyridine, *i*-Pr_2NEt, and Cs_2CO_3) and $ZnCl_2$ suppressed the reaction, while the temperature influenced the catalytic activity of palladacycle **5** but had a little effect on the reaction using palladacycle **9**. A screening of the common solvents revealed that the non-coordinating solvent DCE was the best (see the Supporting Information).[10]

The substrate scope was investigated under the optimized conditions, and the results are shown in Table 2. As expected, the use of palladacycle **5** as catalyst led to the ring-opening products **3** as the major products, while with palladacycle **9**, reactions mainly provided the addition products **4**. A range of monosubstituted acetylenes **2** were viable substrates (entries 3−16, Table 2). The reactions also work well for oxabicyclic alkene **1** bearing different substituents on the phenyl ring (entries 17−22, Table 2). As expected, no reaction took place when 1-phenylpropyne was used.

On the basis of the observations of us and others,[5d,6] a plausible mechanism of the reaction can be proposed (Scheme 1). Palladacycle **5** or **9** reacts with the alkyne **2a** to give alkynylpalladium intermediate **A**. The carbopalladation of

Table 2. Substrate Scope for Reaction of Alkynes 2 with 1 Catalyzed by Palladacycles 5 and 9[a]

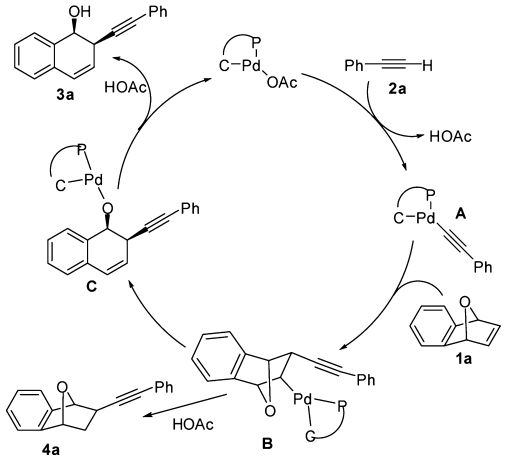


1a: R^1 = H, R^2 = H,
1b: R^1 = OMe, R^2 = H
1c: R^1 = H, R^2 = OMe
1d: R^1 = H, R^2 = Br

entry	**1**	**2** (R^3)	cat.	**3** (yield, %[b])	**4** (yield, %[b])
1	**1a**	**2a** (Ph)	**5**	**3a** (84)	**4a** (11)
2			**9**	**3a** (9)	**4a** (83)
3	**1a**	**2b** (4-MeC_6H_4)	**5**	**3b** (72)	**4b** (27)
4			**9**	**3b** (10)	**4b** (79)
5	**1a**	**2c** (4-$CF_3C_6H_4$)	**5**	**3c** (55)	**4c** (36)
6			**9**	**3c** (11)	**4c** (74)
7	**1a**	**2d** (2-MeC_6H_4)	**5**	**3d** (64)	**4d** (21)
8			**9**	**3d** (18)	**4d** (67)
9	**1a**	**2e** (2-$CF_3C_6H_4$)	**5**	**3e** (51)	**4e** (32)
10			**9**	**3e** (19)	**4e** (77)
11	**1a**	**2f** (6-MeO-naphthyl)	**5**	**3f** (64)	**4f** (16)
12			**9**	**3f** (27)	**4f** (66)
13	**1a**	**2g** ($SiMe_3$)	**5**	**3g** (75)	**4g** (8)
14			**9**	**3g** (13)	**4g** (86)
15	**1a**	**2h** (*n*-Bu)	**5**	**3h** (550	**4h** (5)
16			**9**	**3h** (19)	**4h** (47)
17	**1b**	**2a** (Ph)	**5**	**3i** (85)	**4i** (10)
18			**9**	**3i** (16)	**4i** (78)
19	**1c**	**2a** (Ph)	**5**	**3j** (77)	**4j** (13)
20			**9**	**3j** (21)	**4j** (78)
21	**1d**	**2a** (Ph)	**5**	**3k** (63)	**4k** (25)
22			**9**	**3k** (30)	**4k** (60)

[a]Reaction Conditions: **1** (0.2 mmol), **2** (0.4 mmol), palladacycle: (5 mol %). [b]Isolated yields.

Scheme 1. Plausible Mechanism of the Reaction of 1a with 2a Catalyzed by Palladacycle



oxabicyclic alkene **1a** with intermediate **A** affords intermediate **B**, which could undergo two diverging pathways, giving different products and regenerating the palladacycle catalyst. Protonolysis of **B** releases the adduct **4a**, while the *β*-O elimination of **B** provides the ring-opening product **3a**. In order to rationalize the reversal of the selectivity of the reaction with sp^2-C,P- and sp^3-C,P-palladacycles, density functional theory

dx.doi.org/10.1021/om400653x | *Organometallics* 2013, 32, 4465−4468

(DFT) calculations[11] were used to model the protonolysis and β-O elimination of intermediate **B** (Figure 2).[12]

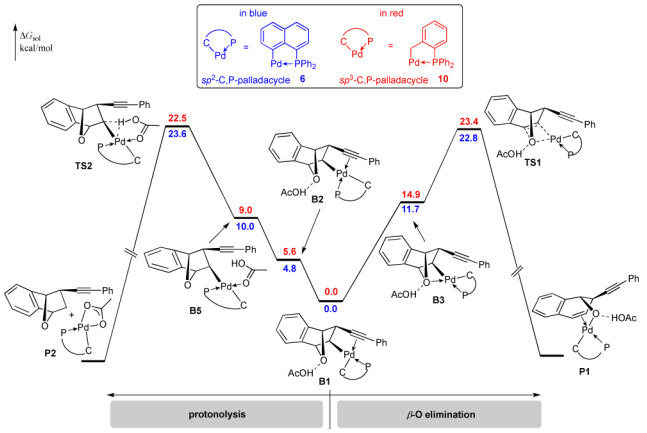


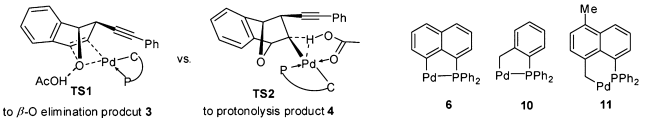
Figure 2. Free energy surface of the favored β-O elimination and protonolysis pathways diverging after intermediate **B1**, in the sp^2-C,P-palladacycle **6** (blue numbers) and sp^3-C,P-palladacycle **10** (red numbers) catalyzed reactions.

The intermediate **B** in Scheme 1 has four major configurations, due to the fact that the alkyne or the oxa moiety can serve as the fourth ligand to coordinate to Pd and the two C−Pd bonds can be either *trans* or *cis* to each other. Calculations found that the most stable conformation is **B1** for both the sp^2-C,P- and sp^3-C,P-palladacycles, in which the alkyne coordinates to Pd and the two C−Pd bonds are in a *cis* conformation. Keeping the coordination of the alkyne moiety to Pd and changing the configuration of the two C−Pd bonds from *cis* in **B1** to *trans* in **B2** raises the energy by 4.8 and 5.6 kcal/mol, respectively for the sp^2-C,P- and sp^3-C,P-palladacycles. The liability of the two C−Pd bonds being *trans* can be explained by the concept of "transphobia",[13] the basic idea of which is that the destabilization of the complex increases with an increase in the structural *trans* effects (STEs)[14] of the pair of ligands that are mutually *trans*. Since generally sp^2 C and sp^3 C have greater structural *trans* effects than a P ligand in palladacycles,[15] the two C−Pd bonds in intermediate **B** tend to be mutually *cis* to avoid unfavorable destabilization.

In the most favored β-O elimination pathway,[12] **B1** undergoes a ligand exchange to afford **B3**. The ligand exchange step is energetically unfavorable. Then, β-O elimination takes place via transition state **TS1**, with respective barriers of 22.8 and 23.4 kcal/mol for sp^2-C,P- and sp^3-C,P-palladacycles. In the most favored protonolysis pathway,[12] **B1** undergoes configurational isomerization to **B2**, followed by a ligand exchange of AcOH to replace the alkyne, affording **B5**. Then protonolysis of the C−Pd bond takes place via transition state **TS2**, with respective barriers of 23.6 and 22.5 kcal/mol for sp^2-C,P- and sp^3-C,P-palladacycles.

On comparison of the barriers of the competitive β-O elimination and protonolysis steps, it is found that, with an sp^2-C,P-palladacycle, β-O elimination is favored over protonolysis by 0.8 kcal/mol, while with the sp^3-C,P-palladacycle, protonolysis is favored over β-O elimination by 0.9 kcal/mol. As shown in Table 3, the product ratios (elimination:protonolysis **3**:**4**) predicted by calculations are 3.7 for sp^2-C,P-palladacycle **6** and 0.22 for sp^3-C,P-palladacycle **10**, in good agreement with the experiments. The product ratio of the reaction catalyzed by palladacycle **11** was also calculated; both

Table 3. Computed Barriers (in kcal/mol) of β-O Elimination (TS1) and Protonolysis (TS2) Pathways of Reaction Catalyzed by Different Palladacycles and the Comparison of the Computed and Experimental Product Ratio



				product ratio **3**:**4**	
entry	palladacycle	TS1	TS2	calcd	exptl
1	**6**	22.8	23.6	3.7	3.1
2	**10**	23.4	22.5	0.22	0.17
3	**11**	21.4	18.8	0.012	0.067

calculation and experiment results show a higher selectivity for the protonolysis product. Thus, our calculations reproduced the experimental results fairly well, at least qualitatively.[16]

The effect of the hybridization natures of C−Pd bonds in palladacycles on the selectivity of the reaction can be understood by comparing the structures of transition states **TS1** and **TS2**. In **TS1**, the forming O−Pd bond is *trans* to the sp^2 or sp^3 C−Pd bond of the palladacycle, while in **TS2**, the breaking C−Pd bond is *trans* to the sp^2 or sp C−Pd bond of the palladacycle. Since sp^3 C is a stronger donor and has a greater *trans* effect than sp^2 C, forming an O−Pd bond *trans* to the sp^2 C−Pd bond in β-O elimination and breaking a C−Pd bond *trans* to the sp^3 C−Pd bond in protonolysis would be favored, respectively.

In conclusion, tuning of selectivity in the reaction of oxabicyclic alkenes with terminal alkynes was realized using sp^2-C,P- and sp^3-C,P-palladacycles as the catalysts, affording ring-opening and addition products, respectively. DFT calculations suggest that the different *trans* effects of the sp^2 C and sp^3 C donors in palladacycles are responsible for the switch in selectivity. This study not only represents the first application of palladacycles in the turning of reaction selectivity but also affords an insight into the understanding of impact of palladacycle structures on the reaction, which will help us greatly in the design and application of palladacycles in catalysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, and figures givng full experimental procedures, additional characterization data, and detailed DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

■ ACKNOWLEDGMENTS

This work was financially supported by the Major Basic Research Development Program (2011CB808700), the National Natural Science Foundation of China (21272251,

21121062, 20932008), the External Cooperation Program of the Chinese Academy of Sciences, the Technology Commission of Shanghai Municipality, and the Croucher Foundation of Hong Kong. The calculations at UNT were supported by Grant CHE-0910527 from the National Science Foundation.

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(9) When chiral palladacycle **5** was used in the reaction, the ee values for the products were as follows: **3a**, ee = 16%, $[\alpha]^{20}_{D} = -44°$ (c = 1.0, $CHCl_3$); **4a**, ee = 21%.

(10) For more optimized conditions, please see the Supporting Information.

(11) DFT calculations were carried out with the Gaussian 09 program. The energies used in this communication are the relative free energies in solvent ΔG_{sol}, which consists of SMD single-point energies in solvent computed at the M06/6-311++G(3df,3pd)/LanL2DZ level of theory plus gas phase free energy correction at M06/6-31G(d)/LanL2DZ level of theory. See the Supporting Information for the detailed computational methodology.

(12) Shown in Figure 2 are the favored pathways of β-O elimination and protonolysis. See Supporting Information for other unfavorable pathways.

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(16) We also investigated the electronic and steric effects of the palladacycles by DFT calculations, which support our rationale for the switch of selectivity in the reactions catalyzed by sp^2-C,P- and sp^3-C,P-palladacycles. Please see the Supporting Information for details.