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Synthesis of Biaryls via Unusual Deoxygenative Dimerization of 1,4-Epoxy-1,4-dihydroarenes Catalyzed by Palladium Complexes

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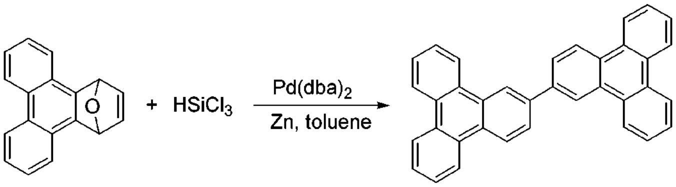
ABSTRACT



Treatment of various 1,4-epoxy-1,4-dihydroarenes with trichlorosilane in toluene in the presence of a palladium complex affords the corresponding biaryls in good to excellent yields. The process appears to occur via a novel palladium-catalyzed hydrosilylative dimerization of 1,4-epoxy-1,4-dihydroarenes and subsequent elimination of $HOSiCl_3$ and H_2O.

Metal-mediated addition of a H−Si bond to an unsaturated carbon−carbon bond is a powerful process for the synthesis of various alkyl and vinyl silanes.[1] The hydrosilylation also applies to dienes,[2,3] diynes,[4,5a] and enynes[5] leading to new carbocycles.[2] Palladium complexes are known to be active catalysts for these reactions. Activated bicyclic olefins, particularly 7-oxa- and 7-azanorbornadienes, show rich addition chemistry in the presence of metal complexes.[6−8] Recently, we observed that these olefins undergo homo [2 + 2],[9] cross [2 + 2],[10] and [2 + 2 + 2][11] cyclization in the presence of nickel complexes. Additions of an electrophile or nucleophile to activated bicyclic olefins catalyzed by palladium or nickel complexes are also known.[6−8] Our

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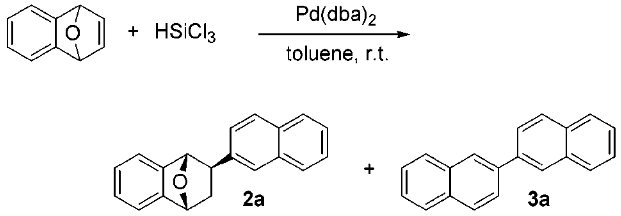
interest in the development of new metal-mediated addition reactions of bicyclic olefins has led us to explore the addition of the H−Si bond to bicyclic olefins. Herein, we report a novel method for the synthesis of various substituted biaryls from hydrosilylative dimerization of 7-oxanorbornadienes catalyzed by palladium complexes. This regioselective catalytic reaction proceeds extremely rapidly via an unusual reductive dimerization of 7-oxanorbornadienes (Scheme 1).

Scheme 1



The reaction of 7-oxabenzonorbornadiene (**1a**) with trichlorosilane was carried out in toluene in the presence of 2.5 mol % of Pd(dba)$_2$ at ambient temperature for ca. 1 min. A black precipitate was observed at the end of the reaction. Analysis of the reacted solution showed that **1a** was completely converted to **2a**^{12} and 2,2′-binaphthyl (**3a**) in 99/1 ratio in 86% combined yield (Table 1. entry 1). The reaction is completely regioselective; no other regioisomers of **3a** and **2a** were observed. Control experiments show that no **3a** and **2a** were formed in the absence of either Pd(dba)$_2$ or trichlorosilane (entries 2 and 3). Products **3a** and **2a** were characterized by NMR and mass data.

Table 1. Effect of Reaction Conditions on the Reaction of 7-Oxabenzonorbornadiene (**1a**) with Trichlorosilane

entry[a]	catalyst	silanes	solvents	time (min)	yield, %[b] (**2a/3a**)
1	Pd(dba)$_2$	$HSiCl_3$	toluene	1	86 (99/1)
2		$HSiCl_3$	toluene	30	0
3	Pd(dba)$_2$		toluene	30	0
4	Pd(dba)$_2$	$HSiCl_{2Me}$	toluene	1	85 (89/11)
5	Pd(dba)$_2$	$HSiClMe_2$	toluene	5	0
6	Pd(dba)$_2$	$HSiEt_3$	toluene	60	0
7	Pd(dba)$_2$	$HSiCl_3$	toluene	3	95 (95/5)
8	Pd(dba)$_2$	$HSiCl_3$	toluene	60	94 (88/12)
9	Pd(dba)$_2$[c]	$HSiCl_3$	toluene	60	96 (11/89)
10	Pd(dba)$_2$[d]	$HSiCl_3$	toluene	60	98 (8/92)
11	Pd(dba)$_2$[c]	$HSiCl_3$	toluene	360	98 (0/100)
12	Pd(dba)$_2$/PPh$_3$	$HSiCl_3$	toluene	5	28 (88/12)[e]
13	Pd(dba)$_2$/2PPh$_3$	$HSiCl_3$	toluene	30	33 (100/0)[f]
14	Pd(dba)$_2$	$HSiCl_3$	THF	1	76 (99/1)
15	Pd(dba)$_2$	$HSiCl_3$	CH_{2Cl2}	1	85 (100/0)
16	Pd(MeCN)$_2$Cl$_2$	$HSiCl_3$	toluene	1	82 (98/2)
17	Pd(OAc)$_2$	$HSiCl_3$	toluene	1	78 (95/5)
18	Pd(PPh$_3$)$_2$Cl$_2$	$HSiCl_3$	toluene	30	0[g]
19	Pd(dppe)Cl$_2$	$HSiCl_3$	toluene	30	0[g]

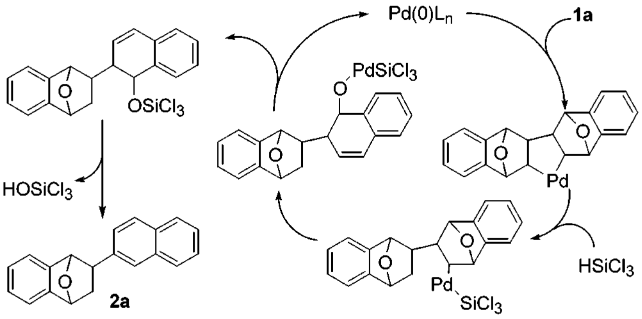
[a] Reaction conditions: **1a** (1.00 mmol), silane (2.5 mmol), Pd(dba)$_2$ (0.025 mmol), solvent (2 mL). Entries 7−11 were carried out at 0 °C for 1 min and then left at ambient temperature; the others were at ambient temperature only. [b] Total yields of **2a** and **3a**. The ratio (**2a**/**3a**) is given in parentheses and was determined by ^{1}H NMR. [c] 2 equiv of Zn powder was added in the reaction. [d] 120 mg of silica gel was added to the reaction. [e] 49% of **1a** was observed from ^{1}H NMR. [f] 1-Naphthol in 67% yield was obtained. [g] 1-Naphthol in quantitatively yield was obtained.

To further understand the nature of the present palladium-catalyzed reaction, the effect of silane, palladium catalyst, ligand, and solvent used on the product yield was examined. The results are listed in Table 1. Similar to tichlorosilane, dichloromethylsilane is active for the conversion of **1a** to **2a** and **3a** (entry 4). However, chlorodimethylsilane and triethylsilane do not give the expected products (entries 5−6). In addition to Pd(dba)$_2$, other palladium complexes, Pd(CH$_3$CN)$_2$Cl$_2$ and Pd(OAc)$_2$, are also very active catalysts, but Pd(PPh$_3$)$_2$Cl$_2$ and Pd(dppe)$_2$Cl$_2$ are completely inactive for the reaction (entries 16−19). Instead, **1a** underwent ring opening to give 1-naphthol, when these phosphine complexes were used. Similarly, addition of PPh$_3$ to the catalytic solution containing Pd(dba)$_2$ greatly inhibits the formation of **3a** and **2a** (entries 12−13). The choice of solvent is crucial to the success of the catalytic reaction. Toluene appears to be the best among the solvents employed. THF and dichloromethane gave **3a** and **2a** in 76 and 85% yields, respectively (entries 1, 14−15). Solvents with a high coordinating ability such as acetonitrile, DMF, and DMSO afford none of the desired products.

The ratio of **3a** and **2a** is also affected by the reaction time and the reagent used. Treating **1a** and trichlorosilane in the presence of Pd(dba)$_2$ at 0 °C (entry 7) for 3 min gave a **2a/3a** ratio of 95/5. Further stirring of the solution led to a slow conversion of **2a** to **3a** (entry 8). Addition of zinc powder or silica gel to the reaction solution enhances the transformation (entries 9−11). Treatment of **2a** with only trichlorosilane and silica gel led to the formation of **3a**, smoothly indicating that the dehydration is not a palladium-catalyzed reaction.

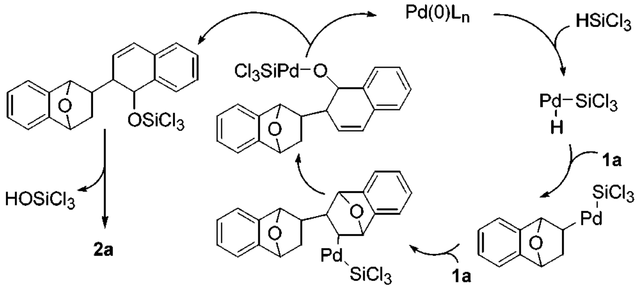
The mechanism for the present binaphthyl formation is still ambiguous, but presumably binaphthyl **3a** is from the dehydration of the corresponding oxabenzonorbornene **2a**. On the basis of the observed products and known palladium chemistry, we propose two plausible pathways for the formation of **2a**. The first one as shown in Scheme 2 involves the coordination of two molecules of **1a** to a palladium(0) species to give a palladium(II) cycle. Reaction of this five-

Scheme 2



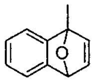
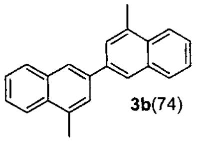
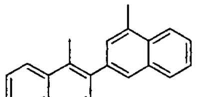
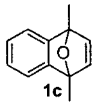
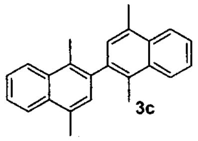
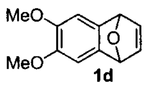
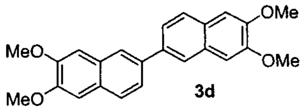
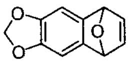
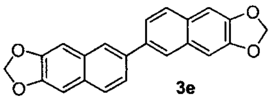
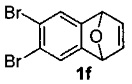
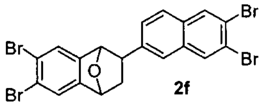
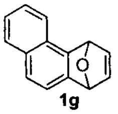
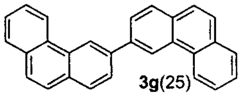
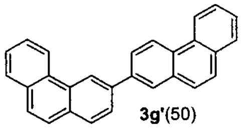
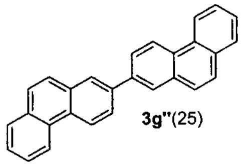
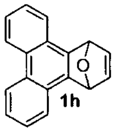
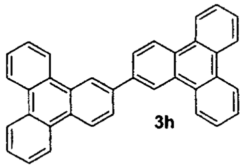
membered palladocycle with $HSiCl_3$ via σ-bond metathesis and subsequent rearrangement gives product **2a**. The formation of metallacycles from two unsaturated carbon−carbon bonds is known[13] and is proposed as a key step in many metal-catalyzed reactions.[9−11,14] In addition, σ-bond metathesis between a palladium(II)−carbon bond and a Si−H bond has been proposed previously.[3a,b] The other possible pathways involve the oxidative addition of $HSiCl_3$ to a Pd(0) species as a key step. Subsequent coordination of 7-oxanorbornadiene molecules, insertion into Pd−H and Pd−carbon bonds, β-oxyelimination, and elimination of $HOSiCl_3$ lead to the formation **2a** (Scheme 3). Both pathways appear to account for the formation of **2a** from **1a** and $HSiCl_3$ satisfactorily. The actual mechanism for the present catalytic reaction requires further studies, but the first mechanism (Scheme 2) seems to explain better the coupling of two molecules of **1** to give **2** or **3**.

Scheme 3



The binaphthyl formation is successfully extended to substituted 7-oxabenzonorbornadienes which were synthesized from the corresponding substituted benzynes and furan.[15] The results are summarized in Table 2. Thus **1b** bearing a methyl group at the bridgehead reacts with trichlorosilane under reaction conditions similar to those for the formation of compound **3a** to give isomers **3b** and **3b′** in a 74/26 ratio. In principle, there are three possible isomers, **3b**, **3b′** and **3b″**, for this reaction. Scheme 3 shows the plausible intermediates that react with trichlorosilane to give these three isomers. Because of the rigid nature of 7-oxabenzonorbornadiene, these palladocycle intermediates are expected to be rigid too. The steric repulsion between the bridgehead groups of the 7-oxabenzonorbornadiene moieties in each intermediate is likely a dominating factor for the

Table 2. Results of the Reaction of 1,4-Epoxy-1,4-Dihydroarenes with Trichlorosilane

entry[a]	substrate	Product(ratio)[b]	Yield(%)[c]
1	**1a**	**3a**	94(95)
2	 **1b**	 **3b**(74)  **3b'**(26)	78(86)
3	 **1c**	 **3c**	30(31)
4	 **1d**	 **3d**	85(87)
5	 **1e**	 **3e**	89(92)
6	 **1f**	 **2f**	81(85)
7	 **1g**	 **3g**(25)  **3g'**(50)  **3g''**(25)	85(88)
8	 **1h**	 **3h**	80(84)

[a] Reaction conditions for entries 1, 4, 5, and 8: **1** (1.00 mmol), $HSiCl_3$ (2.5 mmol), Zn powder (2.00 mmol), $Pd(dba)_2$ (0.025 mmol) and toluene (2 mL); ambient temperature with stirring for 6−8 h. For entries 2, 3, and 6: **1** (1.00 mmol), $HSiCl_3$ (2.5 mmol), $Pd(dba)_2$ (0.025 mmol), toluene (2 mL); ambient temperature with stirring for ca. 1 min. [b] The ratios were determined by ^1H NMR. [c] Isolated yields; yields in parentheses were determined by ^1H NMR using a standard internal method.

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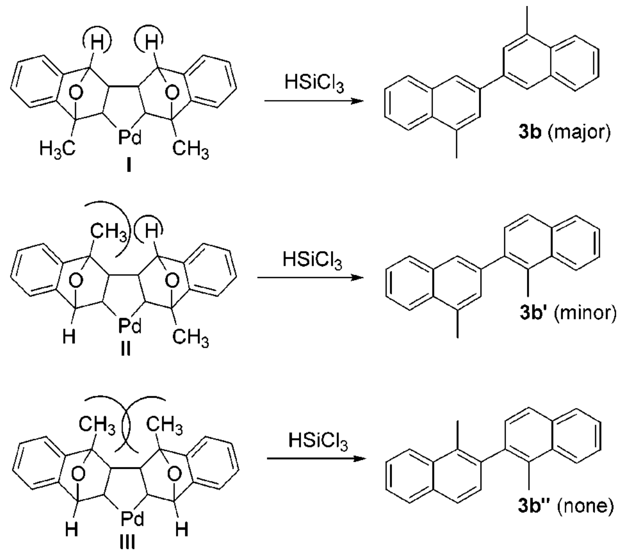
observed selectivity.[16] For example, in intermediate **III** (Scheme 4), the two bridgehead methyl groups trans to the palladium center are expected to exhibit much stronger repulsion than that in the other intermediates. Thus, the formation of **III** is least likely. The formation of **3b** as the major product may be explained on the basis of the fact that intermediate **I** which has two hydrogen atoms at the bridgeheads trans to the palladium center is most favorable.

Scheme 4



Dimethyl-substituted benzonorbornadiene **1c** also undergoes reductive dimerization to afford the expected tetramethylbinaphthyl albeit in lower yield. Substitution on the aromatic ring of 7-oxabenzonorbornadiene does not affect the reductive dimerization but does influence the ratio of **2**/**3**. Substrates **1d** and **1e** both bearing electron-donating alkoxy groups react smoothly with trichlorosilane to afford the corresponding biaryls in 87 and 92% yields. In contrast, dibromo-substituted 7-oxabenzonorbornadiene gave only the reductive coupling product **2f**. Attempts to dehydrate this product by using zinc metal powder or silica gel failed. Two other 1,4-epoxy-1,4-dihydroarenes, **1g** and **1h**, were tested for the present biaryl formation reaction. The reaction of **1g** with trichlorosilane proceeded smoothly to form three isomers, **3g**, **3g′**, and **3g″**,[17] in an ca. 1/2/1 ratio in 88% combined yield. The reaction of **1h** with trichlorosilane gave a single product, **3h**,[18] in excellent yield.

We have observed an unusual palladium-catalyzed biaryl formation from 1,4-epoxy-1,4-dihydroarenes and trichlorosilane via a reductive dimerization intermediate. This method is very effective for the synthesis of various biaryls that generally show high photoluminescence. Studies on the application of these products as materials in an organic light emitting diode (OLED) are underway.

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Supporting Information Available: Experimental procedures and spectral data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] The stereochemistry of intermediates **I**−**III** is also expected to affect the steric energy. In all these possible intermediates, only the stereochemistry with both **1a** moieties cis to each other and the palladium center exo to these two moieties is considered. This stereochemistry facilitates further reaction of the intermediates with trichlorosilane due to less steric hindrance.

[17] These compounds are known, see: Badger, G. M.; Donnelly, J. K.; Spotswood, T. M. *Aust. J. Chem.* **1964**, *17*, 8.

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