Rhodium-catalysed anomalous dimerization of styrenes involving the cleavage of the *ortho* C–H bond†

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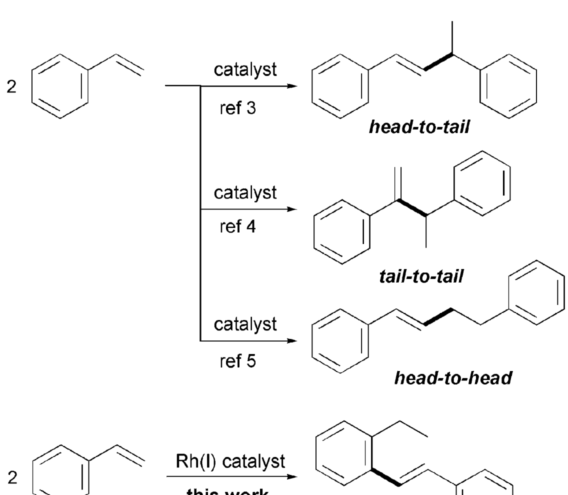
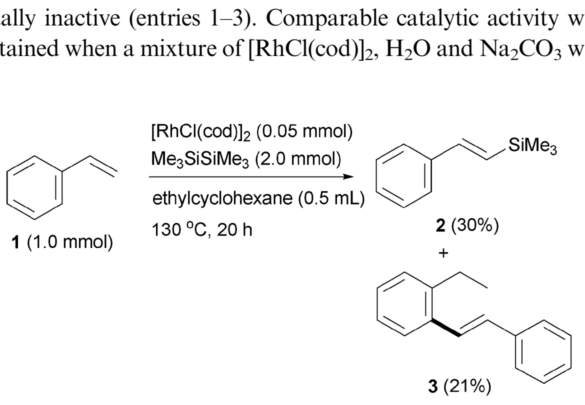
The dimerization of styrene derivatives in the presence of a rhodium catalyst proceeds to give stilbene derivatives, in which the *ortho* C–H bond of styrenes is cleaved and functionalized.

Transition metal-catalysed dimerization of alkenes represents an industrially important process for preparing higher alkenes from simple and small alkenes.[1] In addition to the practical importance, the mechanistic aspects of these dimerization processes have received much attention as a model system for the polymerization and oligomerization of alkenes.[2] Among the alkenes for use in catalytic dimerization, styrene derivatives have been extensively studied. Catalytic dimerization of styrenes generally produces a head-to-tail isomer,[3] while there are a few reports on catalyst systems that can afford tail-to-tail[4] or head-to-head[5] isomers in a regioselective manner (Scheme 1). Although the regiochemical outcome depends on the catalyst system employed, a new carbon–carbon bond is formed between the vinylic carbons in all reported systems. Herein, we report a new mode for the catalytic dimerization of styrenes, in which the new carbon–carbon bond is formed between the benzene ring at the 2-position and the vinylic carbon.



Scheme 1 Catalytic dimerization of styrenes.

In the course of our studies on the development of new catalytic reactions mediated by a rhodium–silyl species generated *in situ*,[6] we examined the reaction of styrene (**1**) with hexamethyldisilane in the presence of a rhodium catalyst (Scheme 2). As a result, vinylsilane **2**, which was presumably produced *via* a silyl-metallation/β-hydride elimination sequence,[7] was obtained in 30% yield, along with byproduct **3**, the molecular weight of which, by GC-MS analysis, turned out to be twice that of **1**. However, the ^{1}H NMR spectrum of the dimer **3** was, to our surprise, absolutely different from those of either the expected head-to-tail, tail-to-tail, or head-to-head dimers. Intensive assignment of the ^{1}H NMR spectra led us to establish the structure of **3**, in which the new carbon–carbon bond is formed between the benzene ring at the 2-position and the vinylic carbon (Scheme 2). X-ray crystallographic analysis of the anthracene derivative **4**, which was obtained through the dimerization of 9-(4-vinylphenyl)anthracene, provided unambiguous confirmation of our structure assignment (Fig. 1).‡



Scheme 2 Unexpected formation of **3**.

Intrigued by the unusual mode of dimerization, we systematically examined a variety of transition metals for their ability to catalyse the dimerization of styrene. Clearly, the stoichiometric amount of hexamethyldisilane is not required for the dimerization process, and that, instead, would induce an undesired dehydrogenative silylation. Thus, we investigated a catalytic reaction in the absence of hexamethyldisilane (Table 1). In contrast to the result shown in Scheme 2, the use of [RhCl(cod)]$_2$ did not afford any dimerization products (entry 4). On the other hand, [Rh(OH)(cod)]$_2$ and [Rh(OMe)(cod)]$_2$ exhibited promising catalytic activity (entries 5 and 6), while other metal based catalysts, including Ru$_3$(CO)$_{12}$, Ni(cod)$_2$ and Pd(PPh$_3$)$_4$, were totally inactive (entries 1–3). Comparable catalytic activity was obtained when a mixture of [RhCl(cod)]$_2$, H$_2$O and Na$_2$CO$_3$ was

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† Electronic supplementary information (ESI) available: Experimental details and spectral data of new compounds. CCDC reference number 684849. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b806285d

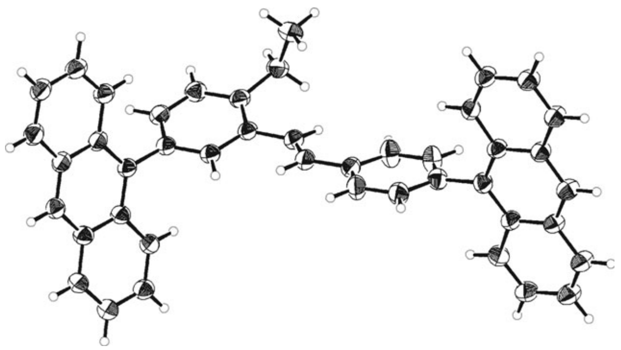
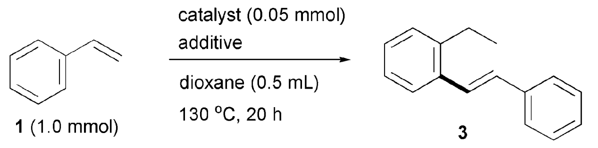


Fig. 1 ORTEP view of anthracene derivative **4**.

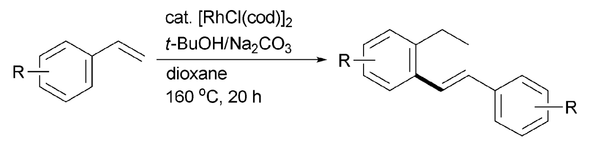
Table 1 Catalyst screening for the dimerization of styrenes[a]

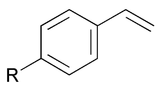
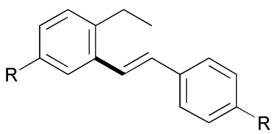
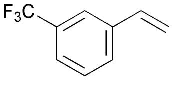
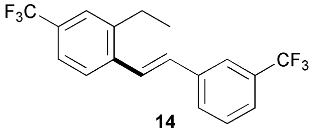
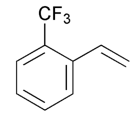
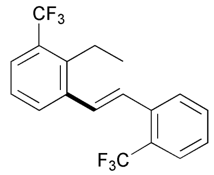


Entry	Catalyst	Additive	GC yield of **3** (%)
1[b]	$Ru_3(CO)_{12}$	None	0
2[b]	$Ni(cod)_2$	None	0
3[b]	$Pd(PPh_3)_4$	None	0
4	$[RhCl(cod)]_2$	None	0
5	$[Rh(OH)(cod)]_2$	None	13
6	$[Rh(OMe)(cod)]_2$	None	15
7	$[RhCl(cod)]_2$	H_2O (0.10 mmol) + Na_2CO_3 (0.20 mmol)	12
8	$[RhCl(cod)]_2$	*t*-BuOH (0.10 mmol) + Na_2CO_3 (0.20 mmol)	22
9[c]	$[RhCl(cod)]_2$	*t*-BuOH (0.20 mmol) + Na_2CO_3 (0.40 mmol)	24[d]

[a] Reaction conditions: **1** (1.0 mmol), catalyst (0.05 mmol), additive, and dioxane (0.5 mL) at 130 °C for 20 h in a sealed tube. [b] 0.10 mmol of the catalyst was used. [c] At 160 °C with 0.10 mmol of the catalyst. [d] Isolated yield.

Table 2 Rh-catalysed dimerization of styrenes[a]



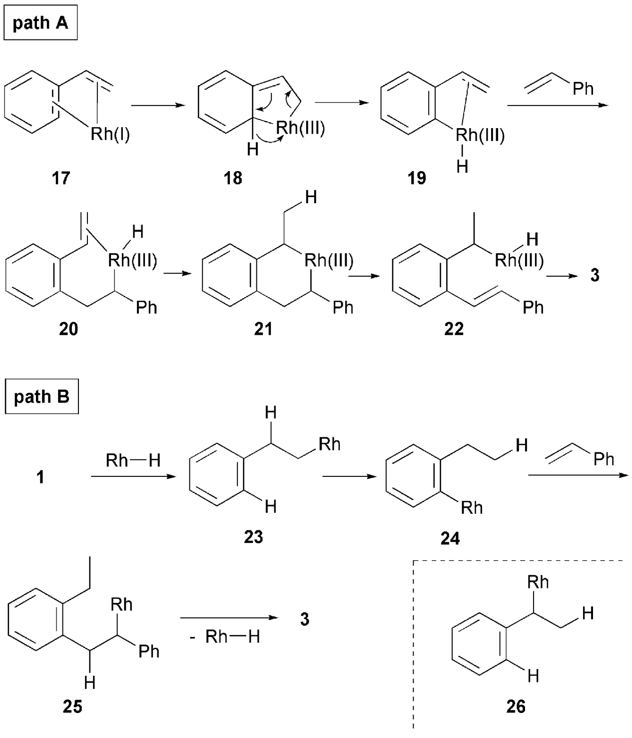
Entry	Styrene	Product	Yield (%)
			
1	R = H (**1**)	**3**	24
2	R = CF_3 (**5**)	**6**	63
3	R = F (**7**)	**8**	50
4	R = Me (**9**)	**10**	44
5	R = OMe (**11**)	**12**	24
6	 **13**	 **14**	42
7	 **15**	 **16**	57

[a] Reaction conditions: **1** (1.0 mmol), $[RhCl(cod)]_2$ (0.10 mmol), *t*-BuOH (0.20 mmol), Na_2CO_3 (0.40 mmol), and dioxane (0.5 mL) at 160 °C for 20 h in a sealed tube.

used as the catalyst (entry 7). Thus, we subsequently examined a variety of alcohol additives in place of H_2O. Among the alcohols examined, *t*-BuOH proved to be the optimal choice (entry 8).[8,9] Under the conditions using *t*-BuOH, we also examined the effect of solvents (mesitylene, ethylcyclohexane, DMF, and *t*-BuOH) and bases (Cs_2CO_3, CsF, CsOPiv, Et_3N, and DBU), although the yield of **3** did not improve. However, conducting the reaction at higher temperature (160 °C) led to a slight increase in yield (entry 9). It should be noted that other types of dimerization products (head-to-tail, head-to-head and tail-to-tail) were not observed in this rhodium catalyst system.

Although the catalytic activity was not satisfactory at this point, we decided to examine the effect of substituents using these catalytic conditions (Table 2). Gratifyingly, introduction of a trifluoromethyl group at the *para* position of styrene dramatically increased the yield of the dimer (entry 2). Similarly, the use of 4-fluorostyrene furnished the product in an improved yield (entry 3). In contrast, the reactions of styrenes bearing other electron-withdrawing substituents, such as ester (18%), nitro (0%) and cyano (0%) groups, were disappointing (data not shown in Table 2). Electron-rich styrenes, as in **9** and **11**, were also dimerized under these conditions (entries 4 and 5). We next examined the effect of the position of the trifluoromethyl group on the efficiency of catalytic dimerization. When the *meta*-substituted isomer **13** was used, the corresponding dimer **14** was obtained in a modest yield (entry 6). The new carbon–carbon bond was formed at the less-hindered site in a regioselective manner. The *ortho*-substituted isomer **15**, wherein the steric demand is posed, can also be successfully applied to catalytic dimerization (entry 7). It should be noted that styrenes containing a substituent on the vinyl moiety, such as propenyl- and isopropenylbenzene, did not afford any dimerized products.[10]

Although the mechanism of dimerization involving the cleavage of the *ortho* C–H bond remains elusive, two possible pathways that account for the observed product are illustrated in Scheme 3. The first possible path begins with the oxidative cyclization of the π-complex **17**, affording a metallacycle **18** containing a Rh(III) center (path A). A 1,2-hydride shift subsequently gives a hydride–Rh(III) complex **19**. The overall process from **17** to **19** can be viewed as a formal oxidative addition of the *ortho* C–H bond of styrenes.[11] Insertion of another styrene into the aryl–Rh bond in **19**, followed by an intramolecular hydrometallation, forms a metallacycle **21**. The



Scheme 3 Mechanistic possibilities.

elimination of the benzylic β-hydrogen in **21** then affords a hydride–Rh(III) complex **22**, which finally leads to a dimer **3** by reductive elimination. An alternative mechanism is mediated by a hydride–Rh complex (formal valence of Rh could be I or III), which could be generated *in situ* by the reaction of the rhodium precursor with added alcohol or residual water (path B). Hydrometallation of **1** provides an alkyl–rhodium species **23**, which then leads to an aryl–Rh complex **24** *via* a 1,4-transposition of the rhodium center.[12,13] The reaction of **24** with another styrene *via* a Mizoroki–Heck-like mechanism (hydrometallation/β-hydride elimination) furnishes the final product **3** while regenerating the hydride–rhodium species. The required regiochemistry for the initial hydrometallation (**1** → **23**) is unfavorable compared with the formation of **26**. Thus, path B would be viable only when the reaction of benzyl–rhodium complex **26** with another styrene is relatively slow.[14]

In summary, we have described an unusual rhodium-catalysed dimerization of styrenes, which involves the cleavage of an *ortho* C–H bond. Although a substantial number of reports have appeared involving the catalytic *ortho* C–H bond functionalization of benzenes bearing polar coordinating groups (*i.e.*, pyridine, ketone, *etc.*),[15] the reaction described herein represents the first catalytic *ortho* C–H functionalization of styrenes.[16]

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Notes and references

‡ Compound **4**. $C_{44}H_{32}$, M = 560.70, triclinic, a = 11.4861(2), b = 12.8423(2), c = 21.3357(4) Å, α = 96.9557(7), β = 96.5045(7), γ = 100.6850(7)°, U = 3039.99(9) Å^3, T = 113(2) K, space group $P\bar{1}$, Z = 4, μ(Cu Kα) = 0.523 mm^{-1}, 57689 reflections measured, 4723 unique (R_{int} = 0.0956) which were used in all calculations. The final $R1$ and $wR2$ were 0.0898 and 0.2162 ($I > 2\sigma(I)$).

1 C. Janiak, *Coord. Chem. Rev.*, 2006, **250**, 66, and references therein.
2 J. Skupinska, *Chem. Rev.*, 1991, **91**, 613, and references therein.
3 For selected examples, see: (*a*) M. G. Barlow, M. J. Bryant, R. N. Haszeldine and A. G. Mackie, *J. Organomet. Chem.*, 1970, **21**, 215; (*b*) K. Kawamoto, A. Tatani, T. Imanaka and S. Teranishi, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 1239; (*c*) F. Dawans, *Tetrahedron Lett.*, 1971, **12**, 1943; (*d*) T. Tsuchimoto, S. Kamiyama, R. Negoro, E. Shirakawa and Y. Kawakami, *Chem. Commun.*, 2003, 852; (*e*) C. Sui-Seng, L. F. Groux and D. Zargarian, *Organometallics*, 2006, **25**, 571; (*f*) N. Galdi, C. D. Monica, A. Spinella and L. Oliva, *J. Mol. Catal. A: Chem.*, 2006, **243**, 106.
4 (*a*) G. Wu, A. L. Rheingold and R. F. Heck, *Organometallics*, 1987, **6**, 2386; (*b*) G. Wu, S. J. Geib, A. L. Rheingold and R. F. Heck, *J. Org. Chem.*, 1988, **53**, 3238.
5 (*a*) W. P. Kretschmer, S. I. Troyanov, A. Meetsma, B. Hessen and J. H. Teuben, *Organometallics*, 1998, **17**, 284; (*b*) T. Kondo, D. Takagi, H. Tsujita, Y. Ura, K. Wada and T.-a. Mitsudo, *Angew. Chem., Int. Ed.*, 2007, **46**, 5958.
6 (*a*) Y. Ishii, N. Chatani, S. Yorimitsu and S. Murai, *Chem. Lett.*, 1998, **27**, 157; (*b*) M. Tobisu, Y. Kita and N. Chatani, *J. Am. Chem. Soc.*, 2006, **128**, 8152; (*c*) M. Tobisu, Y. Ano and N. Chatani, *Chem.–Asian J.*, 2008, **8**, 201.
7 For a recent review on catalytic dehydrogenative silylation of alkenes, see: B. Marciniec, *Coord. Chem. Rev.*, 2005, **249**, 2374.
8 Yields with other additives are as follows: phenol (0%), 1-methylcyclohexanol (16%), 2-adamantanol (15%), *t*-amyl alcohol (18%), and AcOH (0%).
9 The exact role of these additives is currently unclear. One possibility is the formation of [Rh(OBu-*t*)(cod)] species. See: S. K. Agarawal and R. C. Mehrotra, *J. Indian Chem.*, 1985, **62**, 805.
10 Notes: (*a*) In all cases shown in Table 2, the starting styrenes were completely consumed after 20 h. Relatively poor material balance is due to the oligomerization of styrenes, since no other significant products were observed by GC analysis of the crude reaction mixture; (*b*) Vinyl heteroaromatics did not give the corresponding dimers; (*c*) Attempts at cross-coupling with other alkenes, such as trimethylvinylsilanes and norbornene, have been unsuccessful thus far.
11 A similar mechanism is proposed in the oxidative addition of the *ortho* C–H bond of acetophenones. See: (*a*) F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani and S. Murai, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 62; (*b*) T. Matsubara, N. Koga, D. G. Musaev and K. Morokuma, *J. Am. Chem. Soc.*, 1998, **120**, 12692; (*c*) T. Matsubara, N. Koga, D. G. Musaev and K. Morokuma, *Organometallics*, 2000, **19**, 2318.
12 For a review, see: S. Ma and Z. Gu, *Angew. Chem., Int. Ed.*, 2005, **44**, 7512.
13 For examples of a 1,4 shift of an alkyl–metal species, see: (*a*) J. C. Calabrese, M. C. Colton, T. Herskovitz, U. Klabunde, G. W. Parshall, D. L. Thorn and T. H. Tulip, *Ann. N. Y. Acad. Sci.*, 1983, **415**, 302; (*b*) K. Oguma, M. Miura, T. Satoh and M. Nomura, *J. Am. Chem. Soc.*, 2000, **122**, 10464; (*c*) L. Wang, Y. Pan, X. Jiang and H. Hu, *Tetrahedron Lett.*, 2000, **41**, 725; (*d*) T. Matsuda, M. Shigeno and M. Murakami, *J. Am. Chem. Soc.*, 2007, **129**, 12086.
14 Preliminary labeling studies indicated that the majority of the cleaved *ortho* hydrogen atom was incorporated into the methyl group of the product (see supporting information for details). These results agree with both of our proposed mechanisms.
15 For recent reviews, see: (*a*) F. Kakiuchi and N. Chatani, *Adv. Synth. Catal.*, 2003, **345**, 1077; (*b*) A. R. Dick and M. S. Sanford, *Tetrahedron*, 2006, **62**, 2439; (*c*) K. Godula and D. Sames, *Science*, 2006, **312**, 67; (*d*) *Topics in Organometallic Chemistry*, ed. N. Chatani, Springer-Verlag, Berlin, 2007, vol. 24.
16 Carbon–carbon triple bond directed *ortho* C–H bond functionalization has been reported recently: N. Chernyak and V. Gevorgyan, *J. Am. Chem. Soc.*, 2008, **130**, 5636.