Ruthenium-Catalyzed Addition of Aromatic Imines at the *ortho* C-H Bonds to Olefins

Fumitoshi Kakiuchi, Masakazu Yamauchi, Naoto Chatani, and Shinji Murai*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

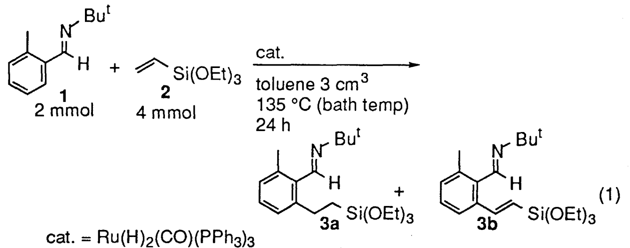
(Received October 18, 1995)

Additions of aromatic imines at the ortho carbon-hydrogen bonds to olefins were catalyzed by ruthenium complexes affording 1:1 addition products in good to excellent yields. In some cases, a by-product arising from dehydrogenative coupling was also obtained. Both aldimines and ketimines reacted well. Olefins such as styrene, 3,3-dimethyl-1-butene, and ethylene yielded corresponding products in good yields.

The possibility of direct use of a carbon-hydrogen bond for practical organic synthesis has attracted both organic and organometallic chemists for many decades. Recently, we have demonstrated the catalytic addition of aromatic and vinylic carbon-hydrogen bonds to carbon-carbon multiple bonds with the aid of ruthenium complexes.[1-3] These reactions are important since examples of practically useful reactions are still rare.[4,5] In these new catalytic reactions, coordination of the sp^2 oxygen atom in aromatic ketones to the ruthenium center seems essential for the success of the reaction, thus bringing the ruthenium closer to an ortho carbon-hydrogen bond.

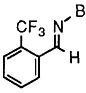
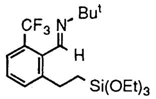
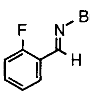
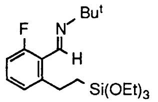
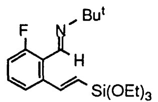
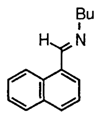
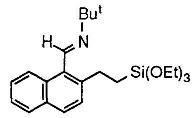
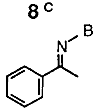
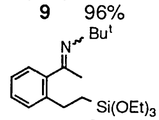
Coordination of sp^2 nitrogen atoms to transition-metals leading to cleavage of C-H bonds by the metals is a well documented phenomenon in stoichiometric reactions.[6,7] We thought that imines should be good candidates for the chelation-assisted C-H/olefin coupling reaction. In this communication, we report a ruthenium-catalyzed C-H/olefin coupling reaction between aromatic imines and olefins. A portion of this work have been presented briefly in our account.[2]

Reaction of *N*-(2-methylbenzylidene)-*tert*-butylamine (**1**) with triethoxyvinylsilane (**2**) in the presence of $Ru(H)_2(CO)(PPh_3)_3$ as the catalyst gave the corresponding 1:1 coupling product **3a** and the dehydrogenated coupling product **3b** in 26% and 8% yields, respectively (Eq. 1).[8,9] This result showed that aromatic aldimines are also applicable to the ruthenium catalyzed C-H/olefin coupling. To improve the efficiency of this new catalytic reaction, the reaction parameters were examined. Complexes $Ru(CO)_2(PPh_3)_3$, $Ru(CO)_3(PPh_3)_2$ and $Ru(OAc)(H)(CO)(PPh_3)_2$ showed similar catalytic activities to that of $Ru(H)_2(CO)(PPh_3)_3$. It is noteworthy that $Ru(OAc)(H)(CO)(PPh_3)_2$ was totally ineffective in the case of aromatic ketones.[1c] The use of $Ru_3(CO)_{12}$ greatly increased the yields of the coupling products **3a** and **3b** (81% and 10% yields, respectively; Eq. 1).[10] Other ruthenium complexes, e.g., $RuCl_2(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) $Ru(OAc)(Cl)(CO)(PPh_3)_2$, and $Ru(H)(Cl)(CO)(PPh_3)_3$ were not effective. $Fe_3(CO)_{12}$, $Os_3(CO)_{12}$, and $RhCl(PPh_3)_3$ showed no catalytic activity.



	3a	3b
cat. = $Ru(H)_2(CO)(PPh_3)_3$		
0.04 mmol	26%	8%
0.12 mmol	50%	22%
cat. = $Ru_3(CO)_{12}$		
0.04 mmol	81%	10%

Table 1. Ruthenium-catalyzed addition of carbon-hydrogen bond in aromatic imines to triethoxyvinylsilane (**2**)[a]

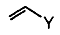
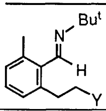
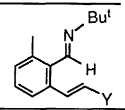
Imine	Product and Yield[b]	
 **4**	 **5** 75%	
 **6**	 **7a** 79%	 **7b** 8%
 **8**[c]	 **9** 96%	
 **10**	 **11** 78% (*anti*:*syn* = 62:38)	

[a]Reaction conditions: imine (2 mmol), **2** (4 mmol), $Ru_3(CO)_{12}$ (0.04 mmol), toluene (3 cm^3), 135 °C (oil bath temperature), 24 h. [b]GC yields. [c]The reaction was complete within 1 h.

Selected results obtained for various types of aromatic imines with **2** are listed in Table 1. Reaction of imine **4** having a trifluoromethyl group at the ortho position afforded exclusively the corresponding coupling product **5** in 75% yield. Fluorine-substituted imine **6** also reacted with **2** to give **7a** and **7b** in 79% and 8% yields, respectively. It is noteworthy that even though a carbon-fluorine bond is prone to react with transition-metals,[11] the fluorine substituent in **6** remained. As shown, both electron-releasing (Me) (Eq. 1) and electron-withdrawing (CF_3 and F) (Table 1) groups are applicable in this coupling reaction. Naphthalene derivative **8** gave **9** in 96% yield. The reaction of a ketimine **10** derived from acetophenone also proceeded smoothly to afford **11** in 78% yield as a mixture of *syn* and *anti* isomers.[12] Interestingly, no 1:2 coupling product was formed even in the presence of an excess amount of **2**, which is in contrast to the $Ru(H)_2(CO)(PPh_3)_3$-catalyzed coupling reaction of acetophenone with **2** which yields a mixture of the corresponding 1:1 and 1:2 coupling products.[1a,c,2] Steric congestion around the imino group in **10** and **11** probably strongly suppresses the second C-H/olefin coupling step.

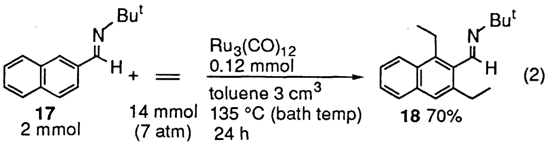
Reactions of aldimine **1** with various olefins gave the results shown in Table 2. The imine **1** smoothly reacted with vinylsilanes to give the coupling products in high yields (Runs 1 and 2). Ethylene underwent the coupling reaction quantitatively (Run 3). Styrene and *tert*-butylethylene also gave coupling products albeit in low yields (Runs 4 and 5).

Table 2. Ruthenium-catalyzed reaction of **1** with various olefins[a]

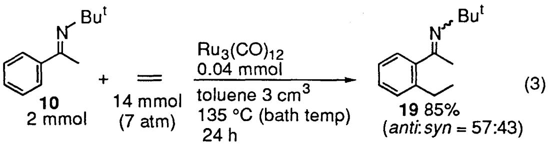
Run	Olefin		Product and Yield[b]	
				
1	SiMe$_3$[c]	4 mmol	**12a** 72%	**12b** 7%
2	SiMe$_2$(OEt)[d]	4 mmol	**13a** 83%	**13b** 4%
3	= [d,e]	14 mmol (7 atm)	**14** 97%	
4	Bu^t	10 mmol	**15** 16%	
5	Ph	10 mmol	**16a** 19%	**16b** 4%

[a]Reaction conditions: imine **1** (2 mmol), olefin (4-14 mmol), $Ru_3(CO)_{12}$ (0.12 mmol), toluene (3 cm^3), 135 °C (oil bath temperature), 24 h. [b]GC yields. [c]In addition to **12a** and **12b**, desilylated product, **14**, was also obtained in 12% yield. [d]Catalyst: 0.04 mmol. [e]The reaction was carried out in an autoclave.

The reaction of aldimine **17** with ethylene gave 1:2 coupling product **18** in 70% isolated yield (Eq. 2). In contrast, the reaction of a ketimine **10** afforded 1:1 coupling product **19** predominantly (Eq. 3). This selectivity can be attributed to the steric congestion in the case of the ketimine as described above.

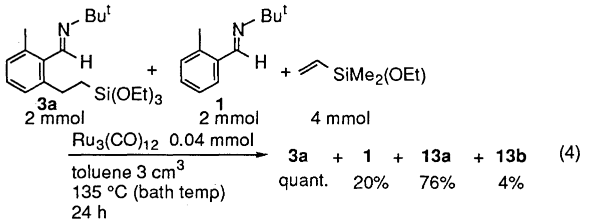


17 2 mmol **18** 70% (2)



10 2 mmol **19** 85% (*anti*:*syn* = 57:43) (3)

In many cases, the dehydrogenated coupling products were obtained in addition to the 1:1 coupling products. A control experiment, as shown in Eq. 4, indicated that **3b** was not formed from **3a** even though **13b** was formed in 4% yield. The mechanism leading to the formation of the dehydrogenated coupling products is not clear at present time.



3a 2 mmol **1** 2 mmol 4 mmol

3a + **1** + **13a** + **13b** (4)
quant. 20% 76% 4%

In summary, it has been demonstrated that aldimines and ketimines undergo the ruthenium-catalyzed C-H/olefin coupling reaction. We believe that our methodology and related catalytic systems will prove to have many applications and that further improvements are likely to emerge.

Supporting Information Available (8 pages) including spectral data of new compounds are available on request to the author by telefax (+81-6-879-7396).

References and Notes

1 a) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, and N. Chatani, *Nature(London)*, **366**, 529 (1993); b) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, and N. Chatani, *Pure Appl. Chem.*, **66**, 1257 (1994); c) F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, and S. Murai, *Bull. Chem. Soc. Jpn.*, **68**, 62 (1995); d) F. Kakiuchi, Y. Tanaka, T. Sato, N. Chatani, and S. Murai, *Chem. Lett.*, **1995**, 679; e) F. Kakiuchi, Y. Yamamoto, N. Chatani, and S. Murai, *Chem. Lett.*, **1995**, 681; f) M. Sonoda, F. Kakiuchi, N. Chatani, and S. Murai, *J. Organomet. Chem.*, in press.

2 S. Murai, *J. Synth. Org. Chem. Jpn.*, **54**, 992 (1994) (in English).

3 M. Sonoda, F. Kakiuchi, A. Kamatani, N. Chatani, and S. Murai, *Chem. Lett.*, in press (accompanying paper).

4 Extensive reviews of this field have been given in References 1c and 2.

5 Very recently, similar $Ru(H)_2(CO)(PPh_3)_3$-catalyzed C-H/olefin coupling reactions under the same reaction conditions have been reported. See, H. Guo and W. P. Weber, *Polymer Bull.*, **32**, 525 (1994). H. Guo, M. A. Tapsak, and W. P. Weber, *Polymer Bull.*, **33**, 417 (1994). B. M. Trost, K. Imi, and I. W. Davies, *J. Am. Chem. Soc.*, **117**, 5371 (1995).

6 M. Crespo, X. Solans, and M. Font-Bardía, *Organometallics*, **14**, 355 (1995); C. J. Elsevier, W. P. Mul, and K. Vrieze, *Inorg. Chim. Acta.*, **198-200**, 689 (1992).

7 Very recently, Rh-catalyzed coupling of 2-phenylpyridines with olefins was reported, see: Y.-G. Lim, Y. H. Kim, and J.-B. Kang, *J. Chem. Soc., Chem. Commun.*, **1994**, 2267. For dehydrogenative coupling of aromatic aldimines with triorganosilanes using platinum complexes, see: N. A. Williams, Y. Uchimaru, and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, **1995**, 1129.

8 The yields of the products were determined by GC unless otherwise noted.

9 When the reaction of **1** with **2** was carried out using a 3-fold amount (0.12 mmol) of $Ru(H)_2(CO)PPh_3)_3$, the coupling products **3a** and **3b** were obtained in 50% and 22% GC yields, respectively.

10 A typical procedure is as follows. A toluene (3 cm^3) solution of $Ru_3(CO)_{12}$ (26 mg, 0.04 mmol), imine (2 mmol), **2** (760 mg, 4 mmol), and hexadecane (an internal standard for GC) was heated under vigorous reflux (at 135 °C, oil bath temperature) with stirring. After heating for several hours, a mixture of the 1:1 addition product and the dehydrogenated coupling product was isolated by bulb-to-bulb distillation.

11 J. L. Kiplinger, T. G. Richmond, and C. E. Osterberg, *Chem. Rev.*, **94**, 373 (1994).

12 The possibility of the existence of thermal *syn-anti* isomerism in imines is well documented. For example, see: C. G. McCarty in "The Chemistry of the Carbon-nitrogen Double Bond," ed by S. Patai, John Wiley & Sons, London (1970), Chap. 9.