A New Chelation-Assistance Mode for a Ruthenium-Catalyzed Silylation at the C-H Bond in Aromatic Ring with Hydrosilanes

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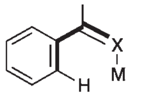
(Received November 21, 2001; CL-011179)

Ruthenium-catalyzed reactions of aromatic compounds having an amino group or a heteroaromatic ring as a directing group with triethylsilane gave the corresponding *ortho* silylated products in good to excellent yields. In contrast to our previous results, in which the reactive substrates with π-conjugation between the hetero atom in the directing group and the carbon atom possessing the C-H bond to be cleaved were used, the present reaction proceeds in cases of substrates having no such π-conjugation.

During this decade transition metal-catalyzed reactions involving C-H bond cleavage have become powerful synthetic tools.[1–6] Among these, the use of chelation-assistance represents the most promising approach to date for attaining high selectivity and efficiency, especially for the derivatization of aromatic C-H bonds.[1–6] For example, when reactions of substituted benzenes with an olefin are carried out without chelation-assistance, usually all possible isomers are obtained in low yields.[7] On the other hand, if the reactions are controlled by means of chelation-assistance, the reactions proceed with perfect site-selectivity in nearly all cases.[1–6] In cases involving the catalytic use of C-H bonds, heteroatoms instead in one termini of a conjugated enone moiety serve as excellent ability directing groups (hereafter referred to as π-conjugated chelation-assistance) and a large number of examples that belong to this category have been reported.[1–4] The mechanistic importance of π-conjugated chelation-assistance has been previously pointed out by us[1b] and is supported by the *ab* initio theoretical calculations reported by Koga and Morokuma.[8] In contrast, it has been reported, in some cases, that hetero atoms which are not a component of the π-conjugation are also able to function as a directing group (hereafter referred to as non-π-conjugated chelation-assistance)[5,6] although catalytic reactions belonging to the latter category are very rare. The development of catalytic reactions in this category would be expected to open a new area for the catalytic use of C-H bonds.



an example of
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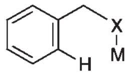

an example of
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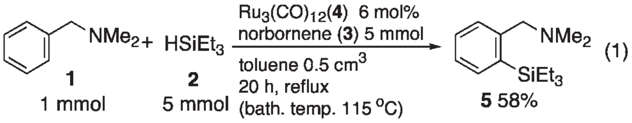
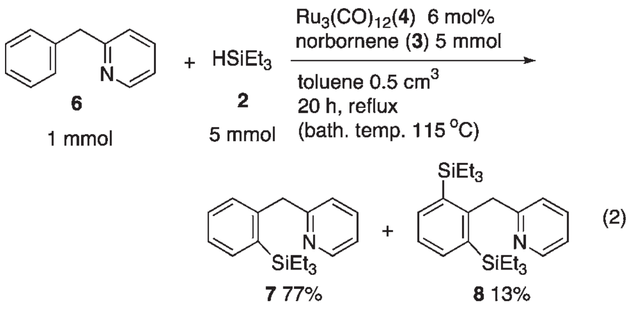
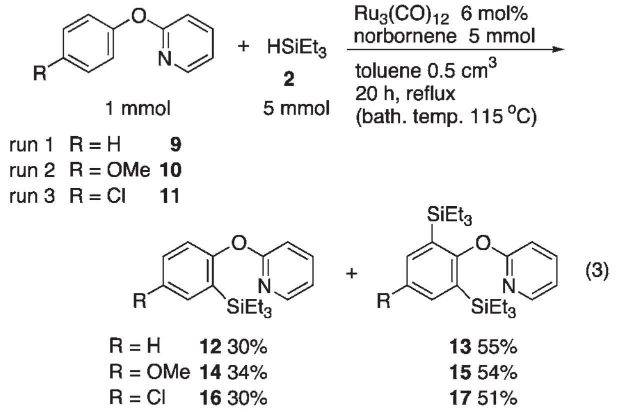
After various attempts, we were able to define conditions for the silylation of arenes. In this communication, we describe a silylation reaction of the C-H bonds of several arenes with triethylsilane using a $Ru_3(CO)_{12}$-catalyst *via* non-π-conjugated chelation-assistance. Very recently, we reported on a π-conjugated chelation-assistance version of the ruthenium-catalyzed silylation reaction of arenes with hydrosilanes.[2b]

When the reaction of *N*,*N*-dimethylbenzylamine (**1**) with triethylsilane (**2**) was carried out in the presence of norbornene (**3**) which functioned as a hydrogen scavenger in refluxing toluene using $Ru_3(CO)_{12}$ (**4**) as a catalyst, the *ortho* silylation product **5** was obtained in 58% yield (eq 1).[9] This result demonstrates, for the first time, for this type of reaction that a catalytic reaction involving aromatic C-H bond cleavage can proceed in the non-π-conjugated chelation-assisted fashion.



When benzylpyridine (**6**) was used, silylation took place at the position ortho to the substituent. The corresponding 1 : 1 and 1 : 2 coupling products were obtained in 77% and 13% yields, respectively. In place of the methylene tether, an ether oxygen tether is also applicable. The reactions of aryl 2-pyridyl ethers **9**–**11** with silane **2** were examined (eq 3). Phenyl pyridyl ether **9** gave the corresponding products **12** and **13** in 30% and 55% yields, respectively (run 1). The presence of a methoxy group did not affect the reactivity (run 2). It is interesting to note that the C-Cl bond, which is generally more reactive than the C-H bond, remained intact in the coupling products **16** and **17** (run 3). In each case, the selectivity for the 1 : 2 coupling product was increased (60–65% selectivity) compared with that for reaction 2 (14% selectivity). These results indicate that the oxygen atom increases the contribution of resonance form **B** (Figure 1) which enhances the ability of the nitrogen atom in the pyridine ring to coordinate. Thus, the increase in the contribution of resonance form **B** facilitates the second C-H bond cleavage without the dissociation of the ruthenium complex. The electronic effect of the substituents on the phenyl ring had no significant effect on product selectivity.





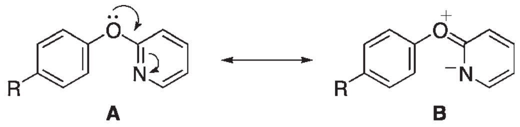
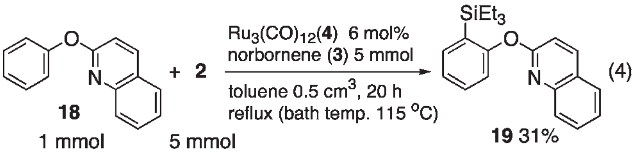
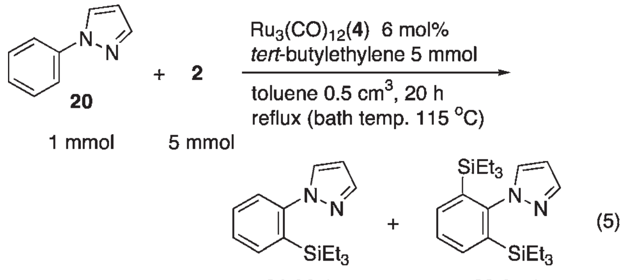


Figure 1.

The quinoline nitrogen can also be used as a directing group. The silylation of 2-phenoxyquinoline took place, but the reactivity was somewhat low (31% yield) and the starting material was recovered in 60% yield even after 48 h (eq 4). Steric repulsion between the ruthenium center and the peri hydrogen at the C8 position of the quinoline ring appears to be important.



A five-membered azole derivative can also be used as a directing group. When the reaction of *N*-phenylpyrazole (**20**) with silane **2** was carried out in refluxing toluene in the presence of norbornene as a hydrogen acceptor, several products, including the silylation products and unidentified products were formed. *Tert*-butylethylene, instead of norbornene, was employed as a hydrogen scavenger suppressing the formation of unidentified products (eq 5). The ortho silylated products **21** and **22** were obtained in 36% and 25% yields, respectively. In the case of **20**, it is difficult to envisage conjugation between the *ortho* position and the coordinating nitrogen atom.



The present results suggest that non-π-conjugated chelation-assistance in C-H bond cleavage, in fact, takes place in catalytic conversion of C-H bonds to C-Si bonds. These results provide new opportunities for transition metal-catalyzed reactions involving C-H bond cleavage. We are currently broadening the scope of this silylation reaction and attempting to elucidate the reaction pathway of this process.

This work was supported, in part, by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan. F. K. thanks the Mitsubishi Chemical Corporation Fund for financial support.

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

1 Our representative results: a) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, and N. Chatani, *Nature*, **366**, 529 (1993). b) F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, and S. Murai, *Bull. Chem. Soc. Jpn.*, **68**, 62 (1995). c) F. Kakiuchi, T. Sato, K. Igi, N. Chatani, and S. Murai, *Chem. Lett.*, **2001**, 386. The latest paper in this series: d) F. Kakiuchi, H. Ohtaki, M. Sonoda, N. Chatani, and S. Murai, *Chem. Lett.*, **2001**, 918.

2 Our results with respect to the ruthenium-catalyzed silylation of aromatic and heteroaromatic compounds: a) F. Kakiuchi, M. Matsumoto, M. Sonoda, T. Fukuyama, N. Chatani, S. Murai, N. Furukawa, and Y. Seki, *Chem. Lett.*, **2000**, 750. b) F. Kakiuchi, K. Igi, M. Matsumoto, N. Chatani, and S. Murai, *Chem. Lett.*, **2001**, 422.

3 Representative reviews, see: F. Kakiuchi and S. Murai, in "Topics in Organometallic Chemistry," ed. by S. Murai, Springer-Verlag, Berlin (1999), pp 47–79; Y. Guari, S. Sabo-Etienne, and B. Chaudret, *Eur. J. Inorg. Chem.*, **1999**, 1047; B. M. Trost, F. D. Toste, and A. B. Pinkerton, *Chem. Rev.*, **101**, 2067 (2001).

4 R. Grigg and V. Savic, *Tetrahedron Lett.*, **38**, 5737 (1997); U. Dürr and H. Kisch, *Synlett*, **1997**, 1335; Y. Guari, S. Sabo-Etienne, and B. Chaudret, *J. Am. Chem. Soc.*, **120**, 4228 (1998); S. Busch and W. Leitner, *Chem. Commun.*, **1999**, 2305; C. P. Lenges and M. Brookhart, *J. Am. Chem. Soc.*, **121**, 6616 (1999); S. K. Gupta and W. P. Weber, *Macromolecules*, **33**, 108 (2000); P. W. R. Harris, C. E. F. Rickard, and P. D. Woodgate, *J. Organomet. Chem.*, **601**, 172 (2000); C.-H. Jun, K.-Y. Chung, and J.-B. Hong, *Org. Lett.*, **3**, 785 (2001).

5 S. E. Diamond, A. Szalkiewicz, and F. Mares, *J. Am. Chem. Soc.*, **101**, 490 (1979); L. N. Lewis and J. F. Smith, *J. Am. Chem. Soc.*, **108**, 2728 (1986). See, also: G. Dyker, *Angew. Chem., Int. Ed.*, **38**, 1699 (1999) and references cited therein.

6 N. Chatani, T. Fukuyama, F. Kakiuchi, and S. Murai, *J. Am. Chem. Soc.*, **118**, 493 (1996); T. Fukuyama, N. Chatani, F. Kakiuchi, and S. Murai, *J. Org. Chem.*, **62**, 5647 (1997); N. Chatani, T. Fukuyama, H. Tatamidani, F. Kakiuchi, and S. Murai, *J. Org. Chem.*, **65**, 4039 (2000).

7 For example, see: P. Hong, B.-R. Cho, and H. Yamazaki, *Chem. Lett.*, **1979**, 339.

8 For a theoretical calculation of the $Ru(H)_2(CO)(PPh_3)_3$-catalyzed C-H/olefin coupling, see: T. Matsubara, N. Koga, D. G. Musaev, and K. Morokuma, *J. Am. Chem. Soc.*, **120**, 12692 (1998); T. Matsubara, N. Koga, D. G. Musaev, and K. Morokuma, *Organometallics*, **19**, 2318 (2000).

9 Supporting Information (4 pages) including typical experimental procedures and spectral data for the new compounds are available on request to the author by telefax (+81-6-6879-7396).