The Ruthenium-Catalyzed Addition of C-H Bonds in Aromatic Nitriles to Olefins

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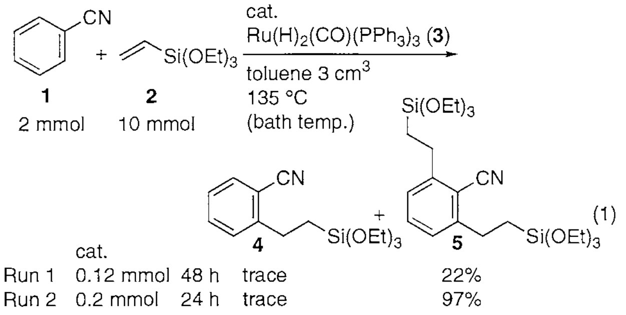
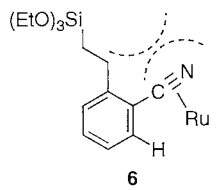
The reaction of aromatic nitriles with triethoxyvinylsilane proceeded in the presence of a $Ru(H)_2(CO)(PPh_3)_3$-catalyst to give the corresponding C-H/olefin coupling products in high yields. The nitrile group is capable of directing the ruthenium to the *ortho* C-H bond *via* π-bonded mode.

Two types of coordination modes are possible during the interaction of organonitriles with transition metals, namely the formation of σ-bonded nitriles[1-3] and π-bonded nitriles.[4] The former type of nitrile complexes has been well documented in the literature,[1-3] while, in the case of the latter, considerably less is known.[4] It is interesting to note that, in spite of a limited number of studies on π-bonded nitrile complexes, the participation of π-bonded nitriles in a C-H bond cleavage step during the transition metal-catalyzed dimerization of acrylonitrile has been proposed by several groups,[5,6] even though the question remains as to whether the dimerization reaction proceeds through the π-bonded nitrile or not. Relative to the above issues, it would be of interest to examine the reactivity of benzonitriles in the ruthenium-catalyzed addition of aromatic compounds to olefins.[7] If the nitrile group participates as the catalyst directing group, it would be expected to do so in a π-bonded manner. In this communication, we wish to report the ruthenium-catalyzed addition of *ortho* C-H bonds in aromatic nitriles to olefins.

We examined the reaction of benzonitrile (**1**) with triethoxyvinylsilane (**2**) using $Ru(H)_2(CO)(PPh_3)_3$ (**3**) as the catalyst (Eq. 1). The addition of a C-H bond at the position *ortho* to the nitrile group took place to give the corresponding 1:2 coupling product **5** in 22% yield as the predominant product (Eq. 1, Run 1). This exclusive *ortho* selectivity implies that a nitrile group is able to direct the ruthenium to the *ortho* C-H bond, very likely in a π-bonded manner. Higher catalyst loading (10 mol% relative to **1**) increased the yield of the coupling product to 97% (Eq. 1, Run 2). In both runs, a 1:2 addition product was formed predominantly throughout the reaction. When the reaction was conducted using an equivalent amount of olefin **2** in the presence of 10 mol% catalyst, the 1:1 addition product **4** and 1:2 addition product **5** were obtained in 18% and 19% yields based on **1**, respectively, after 24 h. This result suggests that even when a large amount of the starting nitrile remains, the 1:2 addition product **5** is favorable to form. From these observations, we proposed that **5** seem to be formed without dissociation of the 1:1 adduct **4** from the ruthenium center during the catalytic reaction to a great extent. The favorable formation of the 1:2 adduct may be attributed to the stability of the 1:1 adduct complex, such as **6**, as the result of a larger binding constant or a decrease in steric congestion (while a ketonic carbon has two substituents, a nitrile carbon has only one) compared with the cases of aromatic ketone coupling.[8]





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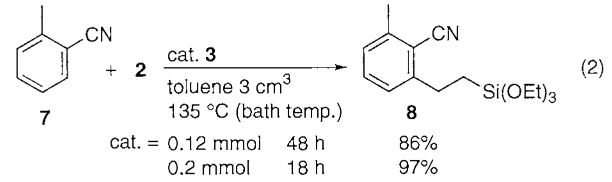
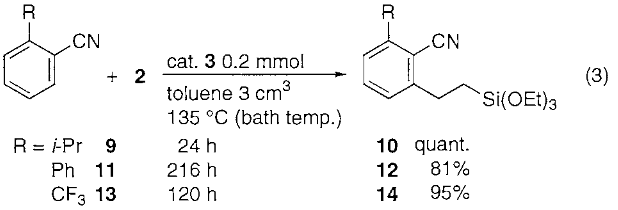
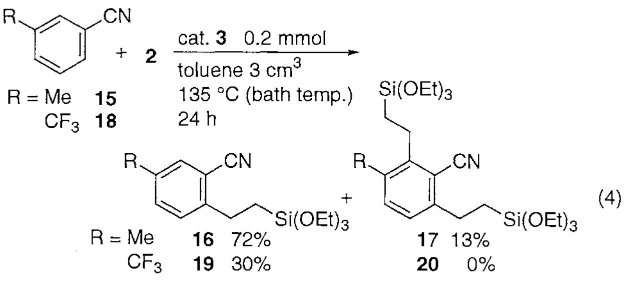
This C-H/olefin coupling can be applied to a variety of aromatic nitriles. In the case of the reaction of *o*-tolunitrile **7** with **2**, even when the reaction was carried out under lower catalyst loading conditions (6 mol%), the coupling product was obtained in 86% yield (Eq. 2).[9] The aromatic nitrile **9**, which contains a sterically bulky isopropyl group at the *ortho* position showed good reactivity. The reaction of *o*-phenylbenzonitrile **11** also gave the corresponding coupling product in 81% yield while the reaction was sluggish (216 h). Even in the case of the reaction of a nitrile **13** having an electron-withdrawing group, the desired coupling reaction proceeded. Unfortunately, however, the reactions of *o*-fluoro-, *o*-methoxy-, and *o*-cyanobenzonitriles with **2** gave no coupling product.

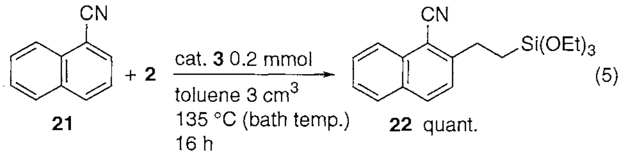


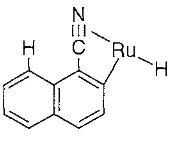


In the cases of the reaction of *m*-substituted benzonitriles, two different reaction sites are available at the *ortho* position. When *m*-methylbenzonitrile **15** was tested, C-C bond formation occurred at less the congested *ortho* position (Eq. 4). This siteselectivity is similar to that for the reaction of *m*-methyl acetophenone with **2**.[7d] The reaction of *m*-trifluoromethylbenzonitrile **18** gave the coupling product **19** in 30% yield after 24 h. Prolonged reaction time (72 h) failed to improve the yield. In the cases of the reactions of Eq. 4, 1:1 adducts were obtained as the major product. This product selectivity is different from that of reaction 1, probably because of steric considerations not electronic ones. In fact, in the reactions of *p*-methyl- and *p*-trifluoromethylbenzonitrile, the corresponding 1:2 adducts were obtained in quantitative and 20% yields, respectively, after 24 h as the predominant product.



We examined the reactivity of some phenyl acetonitriles (e.g., Ph_2CHCN, *o*-$CH_3C_6H_4CH_2CN$, and $PhCH(CN)CH_3$) in which the π-electrons of the nitrile group are not conjugated with the aromatic electrons. None of these reacted with olefin **2**, even after 24 h, suggesting that the π-conjugation between the directing group and the aromatic ring is essential for the desired C-H/olefin coupling. In this context, we examined the reaction of 1-cyanonaphthalene (**21**), which has two different C-H bonds, i.e., one, a C-H bond adjacent to the nitrile group and the other, a C-H bond at the peri position. The C-H bond at the peri position appears to be much suitable for the nitrile group directed C-H bond cleavage because of less strain in the cyclometallated intermediate **24** than in the *ortho* intermediate **23**. Interestingly, however, C-C bond formation occurred exclusively at the β position (Eq. 5). This observation also suggests the importance of π-conjugation.





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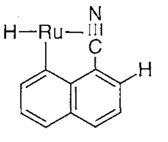

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The reaction of *o*-methylbenzonitrile **7** with several olefins (e.g., styrene, ethylene, *tert*-butylethylene, 1-hexene, methyl methacrylate, and acrylonitrile) was also examined using 10 mol% of the ruthenium catalyst. Unfortunately, however, no coupling product was obtained in all runs.

In summary, we have demonstrated that a ruthenium-complex is capable of catalyzing the addition of the C-H bond in an aromatic nitrile to an olefin. Since this coupling reaction occurred predominantly at the position *ortho* to the nitrile group, the π-coordination of the nitrile to the ruthenium appears to be important in the progress of this catalytic reaction.

Supporting Information Available (4 pages) including spectral data of new compounds are available on request to the author by telefax (+81-6-6879-7396).

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References

1 J. A. Davies and F. R. Hartley, *Chem. Rev.*, **81**, 79 (1981); R. A. Michelin, M. Mozzon, and R. Bertani, *Coord. Chem. Rev.*, **147**, 299 (1996).

2 R. A. Walton, *Q. Rev., Chem. Soc.*, **9**, 126 (1965).

3 B. N. Storhoff, *Coord. Chem. Rev.*, **23**, 1 (1977).

4 For examples of π-bonded nitrile complexes, see: M. F. Farona and N. J. Bremer, *J. Am. Chem. Soc.*, **88**, 3735 (1966); S. C. Jain and R. Rivest, *Inorg. Chim. Acta.*, **3**, 249 (1969); W. J. Bland, R. D. W. Kemmitt, and R. D. Moore, *J. Chem. Soc., Dalton Trans*, **1973**, 1292; J. L. Thomas, **97**, 5943 (1975); E. O. Sherman, Jr. and P. R. Schreiner, *J. Chem. Soc., Chem. Commun.*, **1976**, 3; R. M. Bullock, C. E. L. Headford, S. E. Kegley, and J. R. Norton, *J. Am. Chem. Soc.*, **107**, 727 (1985); T. C. Wright, G. Wilkinson, M. Motevalli, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, **1986**, 2017; P. A. Chetcuti, C. B. Knobler, and M. F. Hawthorne, *Organometallics*, **7**, 650 (1988); J. Barrera, M. Sabat, and W. D. Harman, *J. Am. Chem. Soc.*, **113**, 8178 (1991); J. Barrera, M. Sabat, and W. D. Harman, *Organometallics*, **12**, 4381 (1993); J. L. Kiplinger, A. M. Arif, and T.G. Richmond, *Organometallics*, **16**, 246 (1997).

5 Neth. Appl. 6603115 (1966) (to Rhone-Poulenc); *Chem. Abstr.*, **66**, 85483 (1967); A. Misono, Y. Uchida, M. Hidai, and H. Kanai, *J. Chem. Soc., Chem. Comm.* **1967**, 357. A. Misono, Y. Uchida, M. Hidai, H. Shinohara, and Y. Watanabe, *Bull. Chem. Soc. Jpn.*, **41**, 396 (1968); E. Billig, C. B. Strow, and R. L. Pruett, *J. Chem. Soc., Chem. Commun.* **1968**, 1307; D. T. Tsou, J. D. Burrington, E. A. Maher, and R. K. Grasselli, *J. Mol. Catal.*, **22**, 29 (1983).

6 K. Kashiwagi, R. Sugise, T. Shimakawa, T. Natuura, M. Shirai, F. Kakiuchi, and S. Murai, *Organometallics*, **16**, 2233 (1997).

7 a) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, and N. Chatani, *Nature*, **366**, 529 (1993). b) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, and N. Chatani, *Pure Appl. Chem.*, **66**, 1527 (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) M. Sonoda, F. Kakiuchi, N. Chatani, and S. Murai, *Bull. Chem. Soc. Jpn.*, **70**, 3117 (1997). e) N. Fujii, F. Kakiuchi, A. Yamada, N. Chatani, and S. Murai, *Bull. Chem. Soc. Jpn.*, **71**, 285 (1998). f) T. Sato, F. Kakiuchi, N. Chatani, and S. Murai, *Chem. Lett.*, **1998**, 893. g) F. Kakiuchi, T. Sato, T. Tsujimoto, M. Yamauchi, N. Chatani, and S. Murai, *Chem. Lett.* **1998**, 1053. h) F. Kakiuchi, T. Sato, M. Yamauchi, N. Chatani, and S. Murai, *Chem. Lett.*, **1999**, 19.

8 The similar catalytic coupling of acetophenone with the same olefin **2** gave a mixture of 1:1 and 1:2 adducts. As an exception, the catalytic reaction of acetophenone with trimethylvinylsilane gave 1:2 adduct predominately (Ref. 7b).

9 In a representative procedure, a 10-cm^3, two necked, round-bottomed flask equipped with a reflux condenser, a nitrogen inlet with a gas bubbler, a magnetic stirring bar, and an inlet tube sealed with a rubber septum, was flushed with dry nitrogen, and then the apparatus was flame dried under a flow of dry nitrogen. In the flask was placed $Ru(H)_2(CO)(PPh_3)_3$ (0.12 mmol) under a flow of nitrogen. To the flask were added 3 cm^3 of toluene, *o*-tolunitrile (2 mmol), and triethoxyvinylsilane (1900 mg, 10 mmol). The mixture was heated under vigorous refluxing conditions (135 °C, oil bath temperature) with stirring. After heating for 48 h, the mixture was allowed to cool to room temperature, and toluene and unreacted triethoxyvinylsilane were removed by rotary evaporation (40 °C/5 mmHg, 1 mmHg = 133.322 Pa). The product was isolated by bulb-to-bulb distillation (120 °C/2 mmHg) in 78% yield. The GC yield of the product (86% yield) was determined in a separate run under the same reaction conditions described above except for the use of hexadecane as an internal standard for GC.