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Platinum-Catalyzed Novel Reactions of Nitriles and an Azirine with *o*-Bis(dimethylsilyl)benzene

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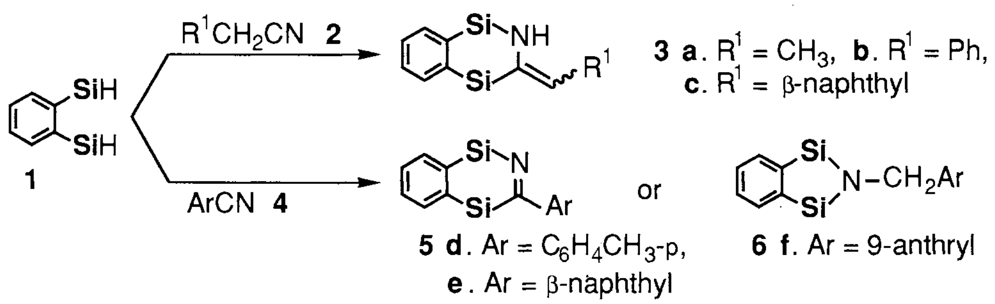
Nitriles and 2-phenylazirine underwent dehydrogenative double silylation with *o*-bis(dimethylsilyl)benzene in the presence of (ethylene)bis(triphenylphosphine)-platinum catalyst to give silyl enamines and imines in excellent yields.

The double silylation of acetylenic and olefinic bonds with disilanes catalyzed by transition metal complexes is one of the most significant developments in the field of synthetic organosilicon chemistry.[1,2] However, double silylation across carbon-nitrogen double and triple bonds has never been reported, although the products coming from the reaction, as demonstrated recently,[3] are expected to be useful in organic syntheses. On the other hand, we previously came across a useful variation in which platinum catalyzed the dehydrogenative double silylation of unsaturated hydrocarbons like acetylenes, dienes and olefins with bis(hydrosilane) species.[4] Further research along this line has revealed that the new variation is applicable to nitriles and an azirine to give a novel class of heterocyclic compounds in high yields. In this communication we disclose preliminary results of the platinum-catalyzed reactions.

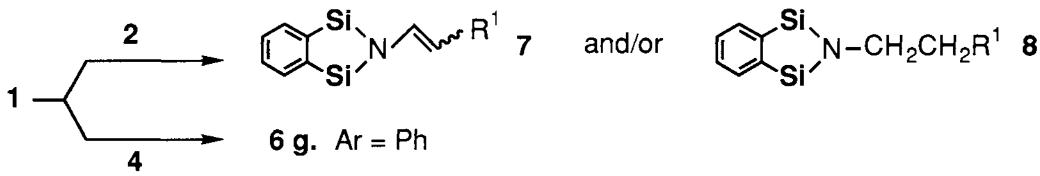
In a typical experiment, a benzene solution of *o*-bis(dimethylsilyl)benzene (**1**, 0.25 mmol), propionitrile (0.25 mmol) and (ethylene)bis(triphenylphosphine)platinum (0.01 mmol) was refluxed under nitrogen atmosphere. Although the reaction, as judged by GLC analysis, had proceeded more than 90% conversion within first 3 h, we kept heating for 20 h to ensure complete consumption of the starting materials. Evaporation of the solvent and distillation (Kugelrohr) gave **3a**[5] in 57% isolated yield (Eq. 1).



(1)

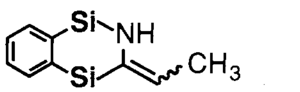
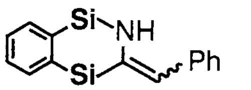
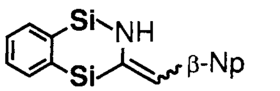
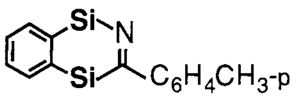
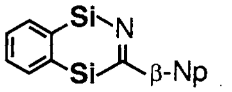
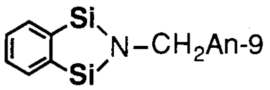
(Catalyst: $Pt(H_2C{=}CH_2)(PPh_3)_2$; **Si** = $SiMe_2$)

The platinum-catalyzed reactions of nitriles, as summarized in Table 1, were very selective and the yields were usually very high.[5] The most interesting feature is that the nitriles having an α-hydrogen gave N-silyl enamines (**3a-c**) while cyanoarenes were converted into the corresponding imines (**5d** and **5e**). Only exceptional case was the reaction of 9-anthronitrile which selectively gave N,N-bis(silyl)amine (**6f**). The formation of **6f** is obviously due to sequential hydrosilylation of the carbon-nitrogen triple bond with the both Si-H moieties in **1**.[6] The rhodium-catalyzed double silylation of nitriles with bis(hydrosilane) species was reported by Corriu and coworkers.[7] However, the reactivities of nitriles in the presence of platinum catalyst are quite different from those of the rhodium-catalyzed reactions. Thus, when $RhCl(PPh_3)_3$ was used as catalyst, nitriles having an α-hydrogen gave N,N-bis(silyl) enamines **7** and/or amines **8** (Eq. 2). On the other hand, cyanoarenes either were unreactive or gave only **6**.



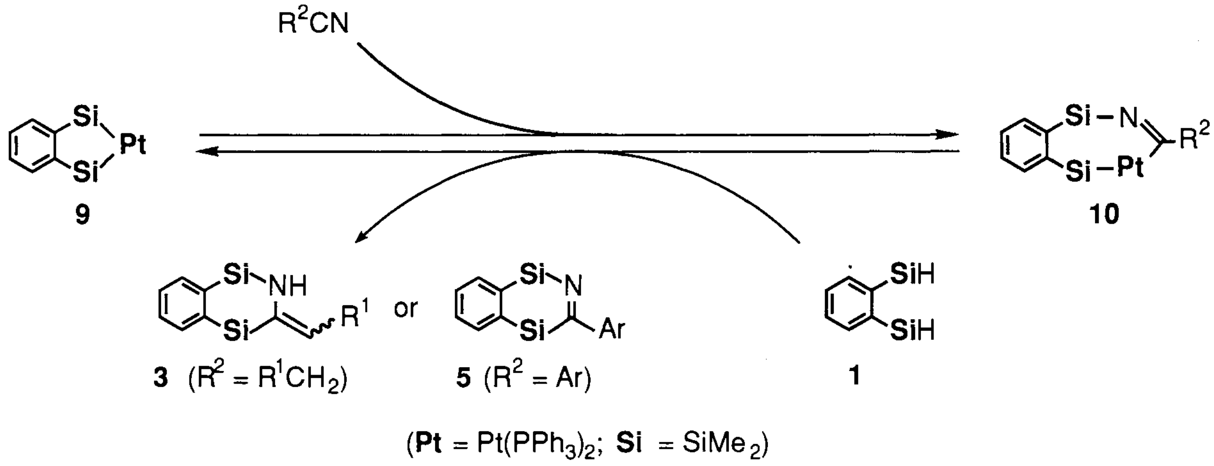
(Catalyst: $RhCl(PPh_3)_3$; **Si** = $SiMe_2$) (2)

Table 1. Platinum-Catalyzed Double Silylation of Nitriles with *o*-Bis(dimethylsilyl)benzene[a)]

Nitrile	Solvent	Time/h	Product	Yield/%	Bp or mp/°C
CH_3CH_2CN	Benzene	20		92[b)]	90(0.2)[d)]
$PhCH_2CN$	Benzene	19		100[b)]	—
β-$NpCH_2CN$	Benzene	11		88[c)]	-80 – -75[e)]
p-$CH_3C_6H_4CN$	Toluene	6		78[c)]	130(0.003)[d)]
β-NpCN	Toluene	15		73[c)]	160(0.001)[d)]
9-AnCN	Toluene	15		64[b)]	162 – 5[e)]

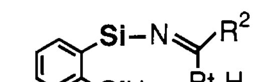
a) All reactions were carried out at reflux temperature; RCN : **1** : $Pt(H_2C{=}CH_2)(PPh_3)_2$ = 1 : 1 : 0.04; Np = naphthyl; An = anthryl; **Si** = $SiMe_2$. b) GLC yields. c) Isolated yields. d) Bp; reduced pressures (mmHg) are in parentheses. e) Mp.

In the previous paper on the dehydrogenative double silylation of acetylenes,[4] we have proposed a mechanism that is initiated by the formation of the cyclic bis(silyl)platinum complex (**9**)[8] (Scheme 1). When propionitrile was treated with *o*-bis(deuteriodimethylsilyl)benzene under the catalytic conditions, **3a** was formed in 88% yield without the incorporation of deuterium. In addition, the stoichiometric reaction (80 °C, 2 h) of **9** with phenylacetonitrile (1 equiv.) in the presence of **1** (2.5 equiv.) quantitatively gave **3b**.



Scheme 1.

Accordingly, the mechanism depicted in Scheme 1 can be visualized for the reaction of a carbon-nitrogen triple bond. However, an alternative pathway that proceeds through the intermediacy of the complex **11** cannot be ruled out in view of the reaction of 9-anthronitrile which gave **6f**.



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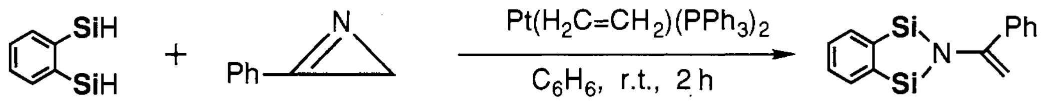
In relation to the nitrile reactions, we also looked at the reactivities of carbon-nitrogen double bonds. N-Benzylidenemethylamine was not reactive under the present catalytic conditions. However, 2-phenylazirine[9] underwent ring opening dehydrogenative double silylation with **1** to give **12**.[5] It is interesting to note that three isomeric bis(silyl) enamines (**3**, **7**, and **12**) can be selectively synthesized by choosing the catalyst (Rh vs.Pt) and the starting material (phenylacetonitrile vs. 2-phenylazirine).



(3)

In summary, nitriles and an azirine undergo dehydrogenative double silylation with the bis(hydrosilane) species to give a new class of heterocyclic compounds. Further studies are aimed at the application of these products to organic synthesis and understanding of the mechanism.

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References

1) T. Hayashi, T.-a. Kobayashi, A. M. Kawamoto, H. Yamashita, and M. Tanaka, *Organometallics,* **9**, 280 (1990) and the references cited therein.

2) Very recently Ishikawa et al. reported the uncatalyzed double silylation of various unsaturated compounds with a benzodisilacyclobutene under thermolytic conditions. See M. Ishikawa, H. Sakamoto, and T. Tabuchi, *Organometallics*, **10**, 3173 (1991).

3) R. J. P. Corriu, J. J. E. Moreau, and M. Pataud-Sat, *J. Org. Chem.*, **55**, 2878 (1990).

4) M. Tanaka, Y. Uchimaru, and H. -J. Lautenschlager, *Organometallics* , **10**, 16 (1991).

5) All new compounds gave satisfactory spectral and/or analytical data as follows. **3a**: IR (cm^{-1}) 3380, 1600, 1270; ^1H NMR ($CDCl_3$) δ 7.5 - 7.3 m (4H, aromatic), 4.7 q (1H, vinylic, J = 6.5 Hz), 3.4 br s (1H, NH), 1.6 d (3H, CH_3, J = 6.5 Hz), 0.35 s (6H, $SiCH_3$), 0.34 s (6H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 144.3, 143.7, 143.0, 132.9, 132.3, 128.4, 128.1, 106.7, 10.0, 1.7 (2C), -0.94 (2C); MS m/z (relative intensity) 247 (M^+, 38), 192 (M^+ - C_3H_5N, 100); HR MS Found: 247.1220. Calcd for $C_{13}H_{21}NSi_2$: 247.1213. **3b**: IR (cm^{-1}) 3350, 1625, 1260; ^1H NMR ($CDCl_3$) δ 7.6 - 7.1 m (9H, aromatic), 5.6 s (1H, vinylic), 4.69 br s (1H, NH), 0.45 s (6H, $SiCH_3$), 0.37 s (6H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 145.2, 143.8, 143.3, 137.7, 133.0, 132.4, 128.7 (2C), 128.6, 128.4, 127.8 (2C), 125.1, 111.0, 1.54 (2C), -0.98 (2C); MS m/z (relative intensity) 309 (M^+, 44), 192 (M^+ - C_8H_7N, 100); HR MS Found: 309.1361. Calcd for $C_{18}H_{23}NSi_2$: 309.1369. **3c**: IR (cm^{-1}) 3350, 1610, 1250; ^1H NMR ($CDCl_3$) δ 7.8 - 7.3 m (11H, aromatic), 5.75 s (1H, vinylic), 4.85 br s (1H, NH), 0.49 s (6H, $SiCH_3$), 0.39 s (6H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 145.9, 143.7, 143.1, 135.2, 133.8, 133.0, 132.3, 131.4, 128.7, 128.4, 128.2, 127.5, 127.4, 127.1, 126.0, 125.4, 125.0, 111.0, 1.56 (2C), -0.96 (2C); MS m/z (relative intensity) 359 (M^+, 100), 192 (M^+ - $C_{12}H_9N$, 55); HR MS Found: 359.1520. Calcd for $C_{22}H_{25}NSi_2$: 359.1525. **5d**: IR (cm^{-1}) 1640, 1610, 1260; ^1H NMR ($CDCl_3$) δ 7.6 - 7.1 m (8H, aromatic), 2.38 s (3H, CH_3), 0.54 s (6H, $SiCH_3$), 0.52 s (6H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 144.9, 143.2, 142.6, 139.9, 133.2, 132.6, 129.0 (2C), 128.9, 128.5, 128.3, 126.3 (2C), 21.4, 0.22 (2C), -0.02 (2C); MS m/z (relative intensity) 309 (M^+, 16), 294 (M^+ - CH_3, 20), 193 (M^+ - C_8H_6N, 100); HR MS Found: 309.1364. Calcd for $C_{18}H_{23}NSi_2$: 309.1369. **5e**: IR (cm^{-1}), 1630, 1600, 1260; ^1H NMR ($CDCl_3$) δ 7.8 - 7.3 m (11H, aromatic), 0.55 s (6H, $SiCH_3$), 0.52 s (6H, $SiCH_3$). **6f**: IR (cm^{-1}) 1620, 1250; ^1H NMR ($CDCl_3$) δ 8.5 - 7.3 m (13H, aromatic), 5.24 s (2H, N-CH_2), 0.08 s (12H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 147.1 (2C), 132.1, 131.4 (2C), 130.9 (2C), 128.9 (2C), 128.4 (2C), 127.6, 127.4, 127.2, 125.5 (2C), 125.1 (2C), 124.9 (2C), 38.4, 0.42 (4C); MS m/z (relative intensity) 397 (M^+, 85), 191(M^+ - $C_{16}H_{14}$, 100); HR MS Found: 397.1664. Calcd for $C_{25}H_{27}NSi2$: 397.1683. **12**: IR (cm^{-1}) 1605, 1250; ^1H NMR ($CDCl_3$) δ 7.5 - 7.2 m (9H, aromatic), 5.0 s (1H, vinylic), 4.8 s (1H, vinylic), 0.21 s (12H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 149.4, 146.5, 141.5, 131.2, 128.6, 127.8, 127.6, 127.3, 104.3; MS m/z (relative intensity) 309 (M^+, 65), 294 (M^+ - CH_3, 100); Anal. Found: C 69.56, H 7.43, N 4.39%. Calcd for $C_{18}H_{23}NSi_2$: C 69.84, H 7.49, N 4.52%.

6) For zinc chloride-catalyzed hydrosilylation of nitriles, see E. Frainnet, J. P. Llonch, F. Dubourdin, and M. R. Calas, *Bull. Soc. Chim. Fr.*, **1966**, 1171 and for cobalt-catalyzed sequential hydrosilylation of nitriles, see T. Murai, T. Sakane, and S. Kato, *J. Org. Chem.*, **55**, 449 (1990).

7) R. J. P. Corriu, J. J. E. Moreau, and M. Pataud-Sat, *J. Organomet. Chem.*, **228**, 301 (1982).

8) C. Eaborn, T. N. Metham, and A. Pidcock, *J. Organomet. Chem.*, **63**, 107 (1973).

9) For transition metal catalyzed ring opening transformations of azirines, see H. Alper and C. P. Mahatantila, *Organometallics*, **1**, 70 (1982) and the references cited therein.

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