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Reactivity of cis-Bis(dimethylphenylsilyl)bis(phosphine)platinum Complexes toward Unsaturated Compounds Relevant to Double Silylation

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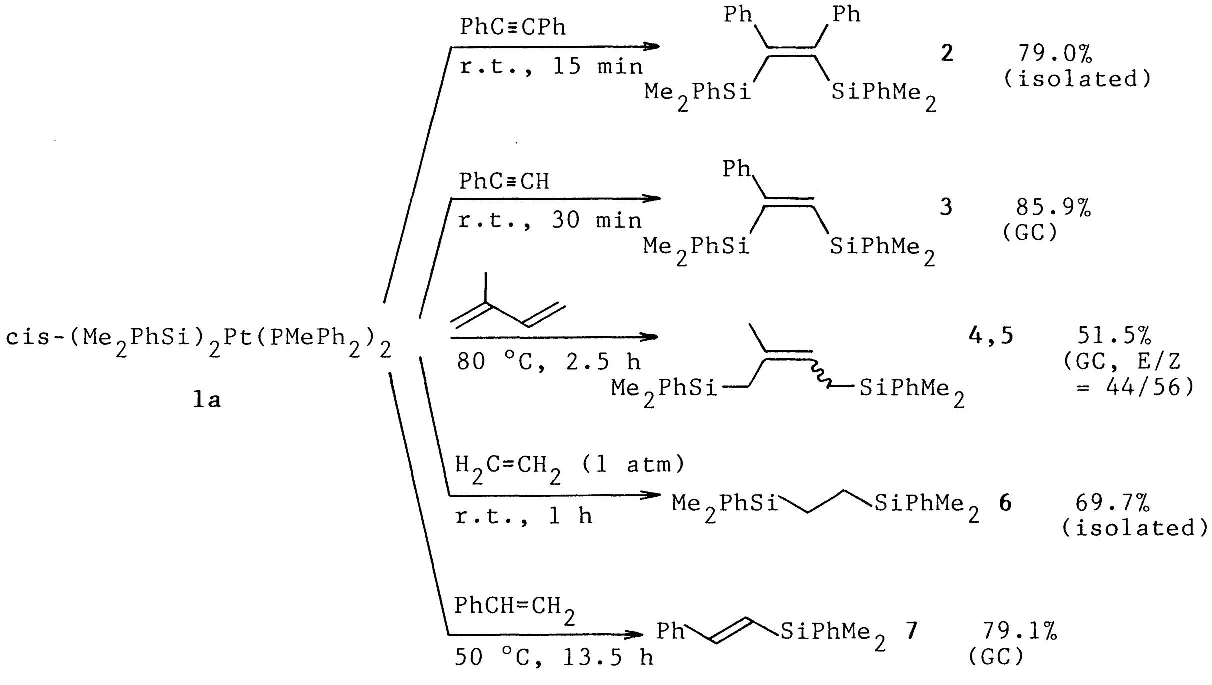
The reaction of phenylacetylene, tolane, or isoprene with cis-bis(dimethylphenylsilyl)bis(methyldiphenylphosphine)platinum readily took place to result in 1,2- or 1,4- double silylation, respectively. Ethylene also underwent double silylation with the platinum complex, but styrene selectively gave E-2-(dimethylphenylsilyl)styrene.

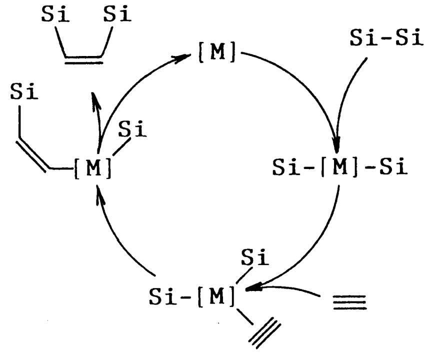
Organosilicon chemicals and materials are attracting increasing attention owing to their versatile chemical and physical properties.1) However, the synthetic methods, in particular, catalytic methods available for silicon compounds are still limited as compared with the maturity in organic synthesis. To develop catalytic reactions for the synthesis of silicon chemicals, the investigation of the reactivities of silyl-transition metal complexes is prerequisite. In the previous paper, we have reported the reductive elimination2) of disilanes from bis(silyl)platinum complexes which might be a key elemental step involved in the catalytic formation of a Si-Si bond from hydrosilanes.3) We now report that bis(silyl)platinum complexes readily react with alkynes, alkadienes, and alkenes.

When cis-bis(dimethylphenylsilyl)bis(methyldiphenylphosphine)platinum (**1a**, 0.023 mmol) was treated with a benzene-d_6 (0.2 ml) solution of tolane (0.046 mmol) in an NMR tube at room temperature, a rapid reaction took place and finished within 15 min. Preparative silica-gel TLC (twice, first with hexane-ether (4:1), then with carbon tetrachloride) followed by Kugelrohr distillation gave analytically pure sample of Z-1,2-bis(dimethylphenylsilyl)-1,2-diphenylethene (**2**)4) in 79.0% yield (Scheme 1). Phenylacetylene also rapidly reacted with the complex **1a** at room temperature to give Z-1,2-bis(dimethylphenylsilyl)-1-phenylethene (**3**)4) in 85.9% GC yield in 30 min. A similar reaction of phenylacetylene with cis-bis(dimethylphenylsilyl)bis(dimethylphenylphosphine)platinum (**1b**) did not proceed at room temperature, but afforded **3** in 81.4% GC yield when heated at 65 °C for 17 h. The Z configuration of **2** and **3** was confirmed by comparison of GC retention times and spectral data with the authentic samples prepared through the reaction of phenyllithium with fluorodimethylsilyl and methoxydimethylsilyl analogues5) of **2** and **3**, respectively. Isoprene also reacted with the complex **1a** though it required higher temperature (80 °C). NMR revealed that the reaction was nearly completed in 1 h. GC analysis of the reaction



Scheme 1.

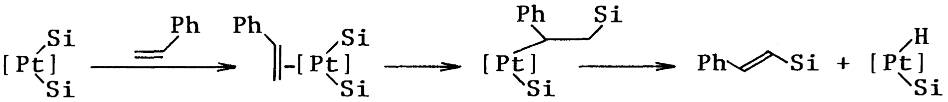
mixture after heating for 2.5 h showed the formation of Z- and E-1,4-bis(dimethylphenylsilyl)-2-methyl-2-butene (**4** and **5**)$^{6)}$ in 28.8 and 22.7% yield, respectively.



Scheme 2.

As is widely known, alkynes and alkadienes undergo double silylation with disilanes in the presence of nickel triad metal complexes.$^{5,7)}$ The reaction is considered to proceed through the mechanism shown in Scheme 2 for acetylene, though not well substantiated. As judged from the present results, the mechanism involving the elemental step of the reaction of a bis(silyl)metal intermediate with unsaturated compounds seems to be valid. There have been several papers which describe the reaction of 1,3-disila-2-metallacycles with alkynes.$^{8)}$ To our best knowledge, however, the only paper dealing with the reaction of non-cyclic bis(silyl)metal complexes is the one by Kumada et al.$^{9)}$ According to this, bis(trichlorosilyl)bipyridylnickel selectively gave the E-adduct when treated with tolane. On the other hand, our reaction gives the Z-adducts, the formation of which is in good agreement with the results reported for catalytic reactions with tolane. The lower reactivity of **1b** as compared with **1a**, which was also the case in the reductive elimination leading to the disilane formation, may be associated with the strength of the silicon-platinum bonds.

There has been reported no successful example of catalytic double silylation of simple olefinic compounds.$^{10)}$ In view of the above mentioned results, however, olefins are also expected to be reactive toward bis(silyl)metal complexes. As a matter of fact, when the complex **1a** dissoved in benzene-d_6 was treated with atmospheric pressure of ethylene at room temperature for 1 h, 1,2-bis(dimethylphenylsilyl)ethane (**6**)[4] was readily formed. In striking contrast with this, the reaction of **1a** with styrene gave E-2-(dimethylphenylsilyl)styrene (**7**), a dehydrogenative silylation product. Based on these reactivities, following reaction sequence is envisaged which also provides a support for the double silylation mechanism depicted in Scheme 2. Similar mechanisms have been postulated for dehydrogenative hydrosilylation of alkenes.[11]



Recently, Ito et al. have reported that palladium complexes catalyze 1,1-double silylation of isocyanides with disilanes to give bis(silyl)imines.[12] In addition, a platinum complex catalyst has also been found to promote the reaction.[13] In connection with theses, it appeared interesting to see the reactivity of the bis(silyl)platinum complexes toward isocyanides. However, when **1a** was treated with N-cyclohexylisocyanide at 100 °C for 15 h, corresponding imine was not formed at all. The only product detected was dimethyldiphenylsilane (**8**, 17.5%), a redistribution product. Likewise, treatment of **1a** with acetone (80 °C, 31 h) caused only the redistribution (**8**, 27.0%; trimethylphenylsilane, 13.3%) and the reductive elimination (1,1,2,2-tetramethyl-1,2-diphenyldisilane, 34.1%), and the treatment with carbon monoxide (1 atm) at 80 °C selectively gave the disilane (84.3%) through reductive elimination.

In summary, the reactivities of bis(silyl)platinum complexes herein described provide not only a mechanistic rationale of the known double silylation of alkynes and alkadienes, but also a clue to develop unkown catalytic reactions starting from olefins and disilanes.

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4) Physical, spectral, and analytical data of new compounds are as follows.
2: bp 142 °C/0.1 Torr; ^{1}H NMR ($CDCl_3$, TMS) δ 0.08 (s, 12H, $SiCH_3$) and 6.6-7.6 ppm (m, 20H, C_6H_5); MS (70 eV) m/z (rel intensity) 448 (M^+, 7.5), 433 (6.4), 313 (10.4), and 135 (100). Anal. Found: C, 80.47; H, 7.22%. Calcd for $C_{30}H_{32}Si_2$: C, 80.30; H, 7.19%.
3: bp 122 °C/0.1 Torr; ^{1}H NMR ($CDCl_3$, TMS) δ 0.21 (s, 6H, $SiCH_3$), 0.22 (s, 6H, $SiCH_3$), 6.80 (s, 1H, =CH-), and 7.0-7.6 ppm (m, 15H, C_6H_5); MS (70 eV) m/z

(rel intensity) 372 (M^+, 0.7), 357 (5.2), 237 (32.6), 236 (38.8), and 135 (100). Anal. Found: C, 77.57; H, 7.64%. Calcd for $C_{24}H_{28}Si_2$: C, 77.35; H, 7.57%.

6: bp 90 °C/0.1 Torr; ^1H NMR ($CDCl_3$, TMS) δ 0.23 (s, 12H, $SiCH_3$), 0.65 (s, 4H, CH_2), 7.2-7.6 ppm (m, 10H, C_6H_5); MS (70 eV) m/z (rel intensity) 298 (M^+, 7.2), 283 (17.6), 197 (10.8), and 135 (100). Anal. Found: C, 72.53; H, 8.82%. Calcd for $C_{18}H_{26}Si_2$: C, 72.41; H, 8.78%.

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