Synthesis and Properties of an Overcrowded Silabenzene Stable at Ambient Temperature**

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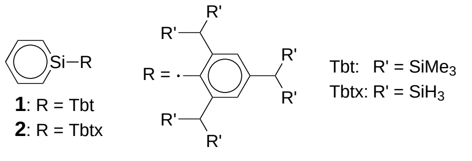
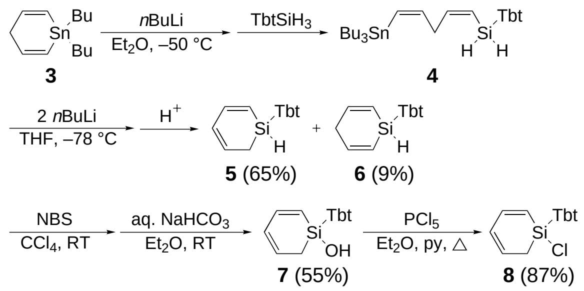
Benzene, a 6π-electron ring system, is the simplest and most fundamental example of an aromatic compound.[1] Because of similarities and differences between carbon and silicon, the chemistry of the silicon-substituted analogues of benzene, the silabenzenes, have been explored extensively.[2] Although aromatic character of silabenzene has been theoretically predicted and some silabenzenes were observed spectroscopically in the gas phase and in low-temperature matrices,[3] their high reactivity prevented the syntheses of silabenzenes as stable molecules. Märkl et al.[4] previously reported the synthesis of 2,6-bis(trimethylsilyl)-1,4-di-*tert*-butylsilabenzene, but it was reported as stable only below $-100\,^\circ$C in solution (THF/Et$_2$O/petroleum ether, 4/1/1) and, judging from its relatively high field ^{29}Si NMR chemical shift ($\delta = 26.8$), stabilized by the coordination of a Lewis-base solvent (see below). In contrast, we have recently succeeded in the synthesis of the first stable silabenzenoid compound, 2-silanaphthalene,[5] by protecting its reactive silicon center with an extremely bulky substituent group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl ("Tbt"). We report here the synthesis and characterization of the stable silabenzene bearing the Tbt group **1**.

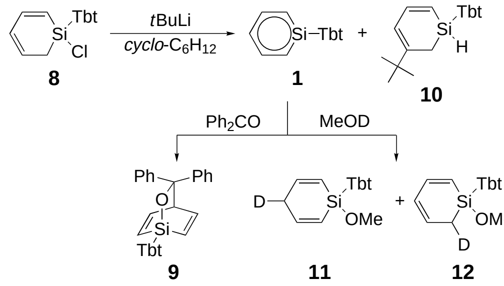


We first tried to synthesize a precursor of **1** by introducing the Tbt group to some silacyclohexadienes, but the substitutions were not favorable.[6] After examining several routes, we finally succeeded in the synthesis of **8**, which is a suitable precursor of **1**, starting from stannacyclohexadiene **3**[7] and Tbt-substituted trihydrosilane[8] (Scheme 1).



Scheme 1. Synthesis of **8**, a precursor of silabenzene **1**.

Treatment of **8** with one equivalent of *t*BuLi afforded two products. One of them was identified as **1** by its downfield shifted ^{29}Si NMR signal ($\delta = 92.5$, [D$_{12}$]cyclohexane) and by comparison of the ^{13}C and ^{1}H NMR chemical shifts with calculated values (see below). Silabenzene **1** was trapped with Ph$_2$CO to afford the [4+2] cycloadduct **9** (Scheme 2), the structure of which was determined by X-ray crystallographic analysis (Figure 1).[9] The other product in the reaction with *t*BuLi was **10** which bears a *tert*-butyl group on the ring. The



Scheme 2. Synthesis of silabenzene **1** from precursor compound **8**, and the treatment of **1** with diphenyl ketone (trapping reaction) and with methan[^{2}H]ol.

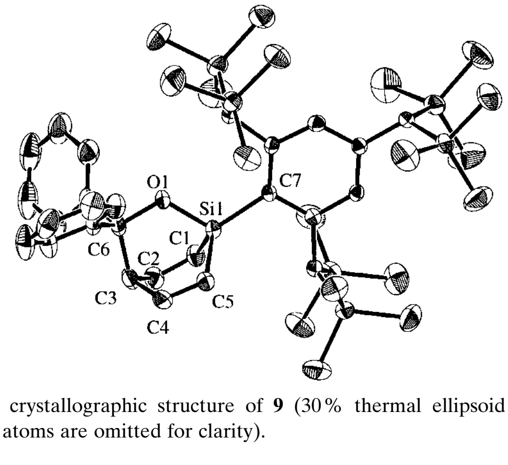


Figure 1. X-ray crystallographic structure of **9** (30% thermal ellipsoid plots, hydrogen atoms are omitted for clarity).

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formation of **10** is most likely interpreted in terms of some radical pathways, although the accurate mechanism is unclear at present. In a separate reaction, **1** treated with MeOD formed adducts **11** and **12** in a 3:2 ratio. These reactions of **1** as a 1,3-diene are clearly different from those of 2(Tbt)-2-silanaphthalene, which reacted only as unconjugated Si–C double bond with several reagents.[5]

The NMR signals due to the silabenzene ring of **1** were assigned by 2D NMR techniques and the results are shown in Table 1 along with chemical shifts calculated for the model compound **2**. The observed values are in excellent agreement with calculated ones. The ^{29}Si chemical shift of the central silicon atom of **1** ($\delta = 92.5$) is close to that previously reported for 2(Tbt)-2-silnaphthalene ($\delta = 87.3$).[5]

Table 1. Selected chemical shifts (δ) as observed by ^{29}Si, ^{13}C, and ^{1}H NMR spectroscopy and as calculated[10, 11] for **1** and **2**.

	Observed[a] **1** (R = Tbt)	Calculated[b] **2** (R = Tbtx)
Si	92.51	89.88
C2	122.18	126.67
C3	143.38	148.52
C4	116.13	121.50
H2	6.80	6.99
H3	7.80	8.08
H4	6.51	6.78

[a] [D$_{12}$]Cyclohexane, TMS, room temperature. [b] Carried out at the GIAO-B3LYP/6-311G(d)(6-311G(3d) on Si)//B3LYP/6-31G(d) level.

The $^{1}J_{\text{Si–C}}$ value for **1** (83 Hz) observed for a Si–C bond in the ring is larger than that of a single bond (for example 50 Hz for Me$_4$Si)[12] and lies between the two $^{1}J_{\text{Si–C}}$ values obtained for 2(Tbt)-silanaphthalene (92 and 76 Hz).[5] The $^{1}J_{\text{Si–C}}$ value of **1** is also almost the same as the 84 Hz reported for (Me$_3$Si)$_2$Si=C(Ad)OSiMe$_3$ (Ad = 1-adamantyl),[13] with a Si–C bond length of 1.764 Å.[14] These results indicate the delocalized character of **1**, which is supported by the calculated structure of a model compound **2**. The Si–C2 bond length in **2** is 1.777 Å, which is a middle value between Si–C single and double bonds, and is similar to the average value of two Si–C bond lengths of 2-silanaphthalene (calculated to be 1.750 and 1.791 Å).[5] Other C–C bond lengths in **2** (C2–C3 = 1.401 Å; C3–C4 = 1.402 Å) are found to be almost the same as those of benzene (1.39 – 1.40 Å).[1]

No change was observed in its NMR spectrum even after the [D$_{12}$]cyclohexane solution of **1** was stored for many weeks at room temperature under an inert atmosphere. Removal of the solvent and redissolution in the same solvent did not change the NMR signals either, indicating that **1** is stable in the solid state at ambient temperature. Furthermore, measurement of ^{29}Si NMR in THF/C$_6$D$_6$ (6/1) induced no significant change of the chemical shift ($\delta = 93.4$), suggesting that **1** is not coordinated by THF. These stabilities of **1** are clearly different from those Märkl[4] previously reported for 2,6-bis(trimethylsilyl)-1,4-di-*tert*-butylsilabenzene, demonstrating the excellent steric protection afforded by the Tbt group. Unfortunately, isolation of **1** has not been achieved yet since separation of the mixture of **1** and **10** requires exposure to air.

Experimental Section

A solution of **8** (33.2 mg, 0.0487 mmol) in dry cyclohexane (2 mL) was placed in a glovebox filled with argon and *t*BuLi (0.59 M hexane solution, 0.08 mL, 0.05 mmol) was added. After the solution was transferred into an NMR tube and then degassed, the tube was sealed. After measurement of NMR spectra, the tube was opened in a glovebox and benzophenone (18 mg, 0.010 mmol) was added. Purification by GPLC and FCC afforded **9** (9.1 mg, 27%) and **10** (7.9 mg, 20%). Compounds **9**–**12**, and **4**–**7** in the synthesis of **8** showed satisfactory spectroscopic and analytical data, which will be reported elsewhere.

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[9] Crystal structure data of **9**: Rigaku R-AXIS IV imaging plate detector, Mo$_{K\alpha}$ radiation, graphite monochromator. The reflections were recorded at 293 K from a colorless prismatic crystal with dimensions $0.4 \times 0.3 \times 0.1$ mm^3 to $2\theta_{\max} = 55°$. The structure was solved by direct methods (SHELXS86) and refined by full-matrix least-squares optimization. C$_{45}$H$_{74}$OSi$_7$, $M_r = 827.68$, monoclinic, space group $P2_1/a$, $Z = 4$, $a = 18.521(4)$, $b = 11.189(3)$, $c = 26.28(3)$ Å, $\beta = 107.133(5)°$, $V = 5204(3)$ Å^3, $\rho_{\text{calcd}} = 1.056$ g cm^{-3}, $\mu = 2.12$ cm^{-1}; of 8596 measured reflections, 6779 observed for $I > 3\sigma(I)$. Hydrogen atoms were placed in calculated positions and not refined, all other atoms were refined anisotropically. $R = 0.054$, $R_W = 0.049$ for 478 parameters; max./min. residual electron density $0.22/-0.35$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-127402. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Catalytic Intermolecular Pauson – Khand Reactions in Supercritical Ethylene**

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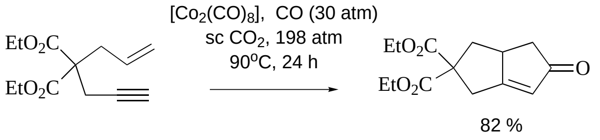
Supercritical fluids are rapidly becoming alternative reaction media for conventional organic reactions.[1] The advantages of reactions in supercritical fluids include the high solubility of gaseous reactants, rapid diffusion of solutes, and weakening of the solvation around the reacting species. In addition, these fluids are easily recycled and allow the separation of the dissolved compounds by selective precipitation, which implicates possibilities in the development of environmentally benign processes. Sequential precipitation of the product and catalyst is possible by a gradual release of pressure.[2]

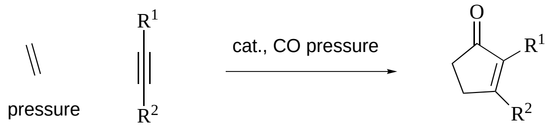
Recent progress has shown that supercritical fluids can substitute conventional organic solvents in various transition metal catalyzed transformations.[3] We demonstrated that catalytic intra- and intermolecular Pauson – Khand reactions could be carried out in supercritical CO_2 with high efficiency (Scheme 1).[4] We report here a new dimension of this application, that is, an intermolecular Pauson – Khand reaction in supercritical ethylene. Ethylene is one of the most abundant raw materials in the petrochemical industry. Direct coupling of ethylene with the proper acetylenes under Pauson – Khand conditions provides an efficient and economical method for preparing synthetically useful cyclopentenones.[5]



Scheme 1. Example for a Pauson – Khand reaction in supercritical (sc) CO_2.

Pauson – Khand reactions of ethylene with stoichiometric amounts of hexacarbonyldicobalt – alkyne complexes have been reported.[6, 7] Rautenstrauch et al. described the first catalytic Pauson – Khand reaction between heptyne and ethylene in toluene in 1990.[8] This catalytic reaction showed a high turnover number (220), but it suffered from the harsh reaction conditions and had a low chemical yield (< 50 %). This might be attributed to the low effective concentration of ethylene in the solvent and the ill-defined, catalytic cobalt – carbonyl species formed under the reaction conditions employed.

Encouraged by our success with CO_2 as a supercritical fluid, we first tried to apply the previously employed conditions for the reaction with ethylene. We ran a series of reactions (48 h at 80 °C) in supercritical CO_2 ($p_{\text{final}} = 200$ atm) with phenylacetylene (**1a**) and ethylene (10 – 45 atm at 34 °C) with various pressures of CO (1 – 30 atm) and in the presence of a catalytic amount of $[Co_2(CO)_8]$ (**I**). The result was disappointing and the chemical yield of 2-phenylcyclopentenone (**1b**) never exceeded 10 %. Therefore, we decided to seek the possibility of a direct coupling reaction in supercritical ethylene (Scheme 2).



Scheme 2. Intermolecular Pauson – Khand reactions between ethylene and alkynes (see Table 1).

Supercritical ethylene can be obtained easily ($T_c = 9\,°C$, $p_c = 34$ atm) and has been used for the preparation of the complex $[Cr(CO)_5(CH_2CH_2)]$ and its polymer.[9, 10] We envisioned that it can also be used for the Pauson – Khand reaction. Under these conditions, a high effective concentration of the rather less reactive ethylene as well as of carbon monoxide would be expected.

The catalysts examined with substrate **1a**, which are all soluble in supercritical ethylene—for example, $[Co_2(CO)_8]$ (**I**), $[Co_4(CO)_{11}\{P(OPh)_3\}]$ (**II**), or $[Co_4(CO)_{12}]$ (**III**), worked well although the efficiency of each catalyst varied from case to case. On the other hand, $[Co_2(CO)_6\{P(OPh)_3\}_2]$ (**IV**), which is a reliable catalyst in organic solvents,[5d] did not work because of its low solubility in supercritical ethylene.

We optimized the reaction conditions with catalysts **II** and **III** in most cases.[11] Ethylene (110 atm at 34 °C) and CO (5 atm at 34 °C) were charged into a mixture of phenylacetylene (3 mmol) and catalyst **II** (0.09 mmol) in a stainless-steel reactor (80 mL). The reaction mixture was gradually warmed to 85 °C over 6 h, where the pressure in the reactor usually reached 200 – 210 atm. The reaction mixture was allowed to react at that temperature for 46 h. 2-Phenylcyclopentenone (**1b**) was obtained in 80 % yield (Table 1, entry 1). Only 2-substituted cyclopentenone was obtained.

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