Mechanistic Investigation of the Hydration Reaction of [Cr(η^6-silabenzene)(CO)$_3$]: Hydrido(silacyclohexadienyl)chromium Complex as an Intermediate

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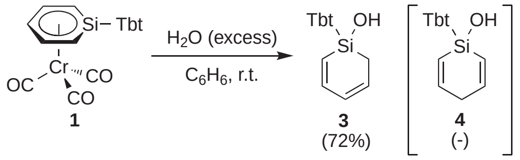
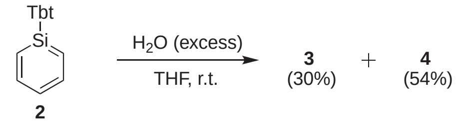
A key intermediate for the hydration reaction of [Cr(η^6-silabenzene)(CO)$_3$], hydrido(η^5-silacyclohexadienyl)chromium complex, was successfully synthesized by the reaction of silabenzene complex with 2 mol equiv of H_2O. X-ray diffraction study revealed that the hydroxy group on the central silicon atom is located at the endo position to the metal moiety. The treatment of the endo adduct with excess of D_2O resulted in the stereoselective formation of 1-silacyclohexa-2,4-diene bearing a deuterium atom at the methylene position.

The chemistry of chromium tricarbonyl complexes having an arene ligand has been extensively studied, and their unique reactivities have been revealed.[1] For example, the reactions of [Cr(η^6-benzene)(CO)$_3$] with alkyllithiums as a nucleophile are known to produce exo adducts, Li[Cr(η^5-cyclohexadienyl)(CO)$_3$], stereoselectively.[2] Further reactions of the anionic complexes with electrophiles resulted in the stereoselective formations of the corresponding cyclohexa-1,3-dienes.[3] On the other hand, we have already reported the syntheses of various metallaaromatic compounds containing a heavier group 14 element by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt) and their applications as an arene ligand for group 6 transition metal complexes.[4] We have synthesized a stable silabenzene complex, [Cr(η^6-silabenzene)(CO)$_3$] **1**, and found that the reaction of **1** with excess of water gave silanol **3** regioselectively (eq 1).[4h] This result was in sharp contrast with that for the similar reaction of free silabenzene **2**,[5] which resulted in the competitive 1,2- and 1,4-addition of water (eq 2). Herein, we report the detailed mechanistic studies on the hydration and related reactions of the silabenzene complex **1**, which revealed that hydrido(silacyclohexadienyl) complex **5** is a key intermediate for the reaction.

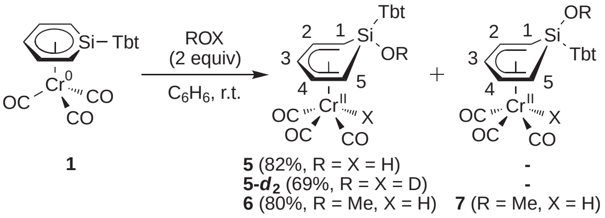


(1)



(2)

First of all, the reaction of **1** with 2 mol equiv of H_2O was performed. As shown in eq 3, the reaction afforded the hydrido(silacyclohexadienyl) complex **5** in 82% yield stereoselectively.[6,7] This is the first chromium complex bearing a silacyclohexadienyl ligand. The complex **5** was characterized based on the results of ^{1}H, ^{13}C, and ^{29}Si NMR and IR spectroscopic studies together with elemental analysis. In addition, the stereochemistry around the central silicon atom was confirmed by the NOE experiments and X-ray crystallographic analysis (Figure 1a).[8] Both studies indicated that the OH group was oriented at the endo position toward the Cr(CO)$_3$ unit. In the ^{1}H NMR spectrum of **5** in C_6D_6, the signals assignable to the protons of the silacyclohexadienyl ring were observed at 5.30 (t, H3), 4.97 (dd, H2 and H4), and 2.15 (dd, H1 and H5) ppm, which were similar to those reported for silacyclohexadienyl complexes.[9] The characteristic signal assignable to that of Cr–H was observed at −9.04 ppm (t), which was reasonable for the chemical shift of a terminal hydride bound to a chromium atom.[10] Interestingly, H1 and H5 protons and Cr–H are coupling with each other ($J = 9.0$ Hz), indicating that the hydrido(silacyclohexadienyl) complex **5** could be regarded as an agostic complex (eq 4).[11] In the ^{13}C NMR spectrum of **5**, the signal of the carbons in the carbonyl ligands was observed as only one signal at 231.3 ppm, suggesting the existence of rapid rotation of Cr(CO)$_3$ unit. In IR spectrum of **5**, the frequencies of the carbonyl stretchings (1991, 1910, and 1889 cm^{-1}) are smaller than those observed for the related complex [Cr(η^5-cyclopentadienyl)(CO)$_3$(H)][10] (2018, 1947, and 1938 cm^{-1}). This result indicated that the electron-donating ability of the η^5-silacyclohexadienyl ligand was higher than that of the η^5-cyclopentadienyl ligand.



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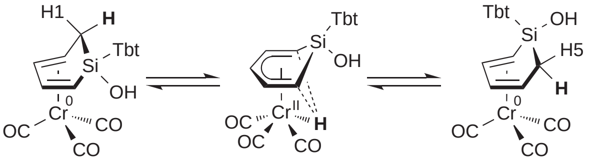


(4)

The reaction of **1** with 2 mol equiv of D_2O gave deuteride(silacyclohexadienyl)chromium complex **5**-d_2 in 69% yield. ^{1}H and ^{2}H NMR studies showed the product contained 81% deuterium at the OH group and Cr–H moiety, suggesting those H atoms were surely derived from water. The treatment of **1** with 2 mol equiv of methanol resulted in the formation of the endo and exo adducts, **6** and **7**, respectively, in the ratio of 10:1.[12] The structure of endo adduct **6** was determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectra, elemental analysis, and X-ray diffraction study (Figure 1b).[8]

In general, nucleophilic attack to η^6-benzene chromium tricarbonyl complexes are known to afford the corresponding exo adducts due to the steric hindrance of Cr(CO)$_3$ unit.[2] Therefore, the fact that the endo adduct was obtained as a major product

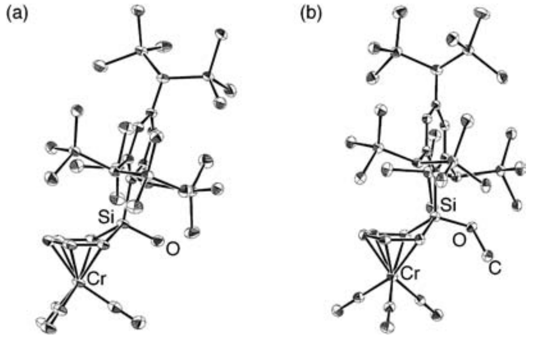
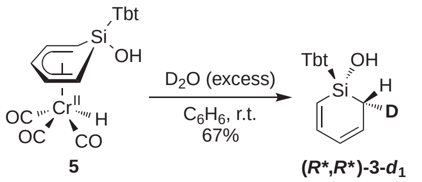


Figure 1. ORTEP drawings of **5** (a) and [**6**•$0.5C_6H_6$] (b) (30% probability). The hydrogen atoms and benzene molecule were omitted for clarity.

even in the reaction with a larger molecule than water such as methanol suggested the selectivity observed for the hydration reaction of **1** is most likely due to the interaction between the ROX and $Cr(CO)_3$ units.

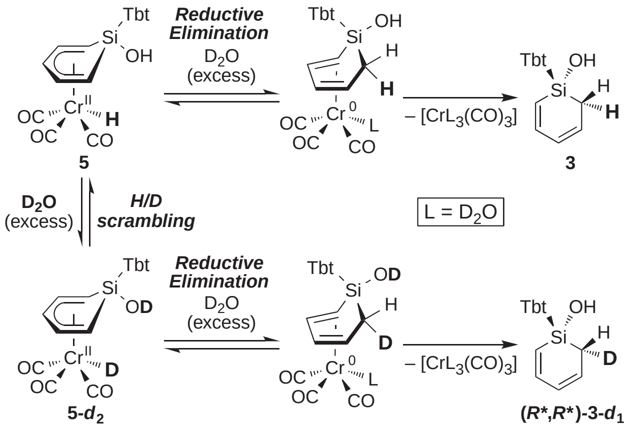
As an alternative mechanism for the conversion of **1** to **5**, the reaction pathway including the demetallation/recombination steps can be conceivable. However, the fact that [Cr(η^6-benzene)$(CO)_3$] did not react with **3** in benzene clearly showed that this is not the case but the Cr–H complex **5** is derived from **1** without dissociation of the SiC_5 ring from the Cr center.[13]

When the isolated **5** was treated with excess of D_2O, the reaction furnished the final product, 1-silacyclohexa-2,4-diene (R^*,R^*)-**3**-d_1 stereo- and regioselectively (eq 5). This result strongly suggests that the conversion of **1** to **3** proceeds via the hydrido(silacyclohexadienyl) complex **5**. The regioselective formation of 1,2-adduct would be derived from the high contribution of the conjugated 1,3-diene intermediate as well as the equilibrium of complex **5** (eq 4). ^1H and ^2H NMR studies of (R^*,R^*)-**3**-d_1 in benzene-d_6 and benzene showed 90% incorporation of D atom for the methylene position in the SiC_5 ring. On the other hand, the reaction of **5**-d_2 (81% deuterium incorporation at each position) with excess of H_2O afforded (R^*,R^*)-**3**-d_1 with 30% deuterium content at the methylene position. A plausible mechanism for the reaction of **5** with D_2O was postulated as Scheme 1. Formal reductive elimination of **5** leading to the formation of **3**-d_1 induced by D_2O may occur with a rapid H/D scrambling of Cr–H in **5**. Actually, during the reaction of **5** with slight excess of D_2O in a sealed tube, ^1H NMR monitoring showed the conversion of unreacted starting complex **5** to **5**-d_2.[12]



(5)

In summary, we have revealed the reactivity of the silabenzene complex **1** toward water in detail and succeeded in the isolation of the first chromium complex bearing a silacyclohexadienyl ligand as an intermediate in the conversion of **1** to **3**. The present studies clearly showed the unique reactivities of **1** compared with its carbon analogues. Further study on the reactivities of **1** toward various reagents is underway.



Scheme 1.

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6 The reaction of **1** with 1 mol equiv of H_2O in C_6D_6 resulted in the 50% conversion of **1** to **5**.

7 When the reaction of **1** with 2 mol equiv of H_2O in THF was performed, 1:1 mixture of endo and exo adducts was obtained.

8 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-687315 (**5**) and 687314 ([**6**•$0.5C_6H_6$]).

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

13 The reaction of [Cr(η^6-benzene)$(CO)_3$] with silacyclohexa-1,4-diene **4** did not proceed.