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Structure of 4-Sila-3-platinacyclobutene and Its Formation via Pt-Promoted γ-Si−H Bond Activation of 3-Sila-1-propenylplatinum Precursor

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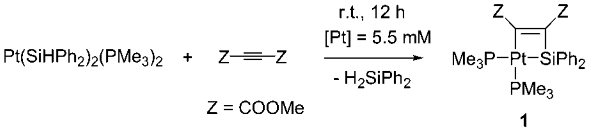
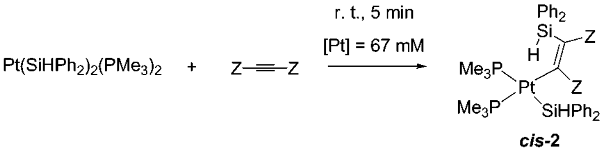
Complexes of group 10 metals catalyze various C−Si bond-forming reactions of organosilicon compounds with unsaturated molecules such as alkenes, alkynes, and dienes.[1] Many Si-containing cyclic compounds were prepared by this approach, using diorganosilanes, tetraorganodisilanes, silacyclopropenes, and silacyclopropanes.[2−7] These reactions have been considered to involve 4-sila-3-metallacyclobutene as the common intermediate that plays an important role in forming a new C−Si bond. This four-membered metallacycle, however, has not been isolated or structurally characterized. Ishikawa et al. reported the preparation of a 4-sila-3-nickelacyclobutene in situ, although it is too unstable to be isolated or characterized by crystallography.[8] The Pt-complex-promoted reactions of organosilanes and disilanes with alkynes were postulated to involve a silylene-coordinated platinum complex[9] as a precursor to the metallacyclobutene intermediate.[6,7] In this paper, we report the first isolation and crystallographic results of a Pt-containing silacyclobutene and demonstrate its formation pathway via an unexpected precursor.

$Pt(SiHPh_2)_2(PMe_3)_2$[10] reacts with an equimolar mixture of dimethyl acetylenedicarboxylate (DMAD) in THF ([Pt] = 5.5 mM) for 12 h to produce $\mathrm{Pt}\overline{\mathrm{(CZ{=}CZ\text{-}Si}}\mathrm{Ph_2)(PMe_3)_2}$ (Z = COOMe) (**1**) in 85% yield as yellow crystals accompanied by the formation of H_2SiPh_2 (eq 1). Figure 1 shows the molecular structure of **1** by X-ray crystallography.[11] The complex contains a planar four-membered ring with an Si−Pt−C1 angle (65.8(2)°) that is smaller than that of the saturated four-membered 2-sila-1-platinacyclobutane (68.1(3)°).[12] The $^{29}Si\{^1H\}$ NMR signal of **1** at δ −63.6 shows coupling with ^{195}Pt (J_{SiPt} = 778 Hz) and two unequivalent ^{31}P ($^2J_{SiP}$ = 161 and 3 Hz) nuclei.[13]



(1)

The reaction of $Pt(SiHPh_2)_2(PMe_3)_2$ with an equimolar mixture of DMAD in the presence of H_2SiPh_2 for 5 min ([Pt] = 67 mM) results in the isolation of *cis*-$Pt(CZ{=}CZ\text{-}SiHPh_2)(SiHPh_2)(PMe_3)_2$ (*cis*-**2**), which is formed via insertion of DMAD into a Pt−Si bond of $Pt(SiHPh_2)_2(PMe_3)_2$ (eq 2).



(2)

Dissolution of once-isolated *cis*-**2** in benzene-d_6 causes its partial conversion into **1**, producing a mixture of **1**, *cis*-**2**, and H_2SiPh_2.

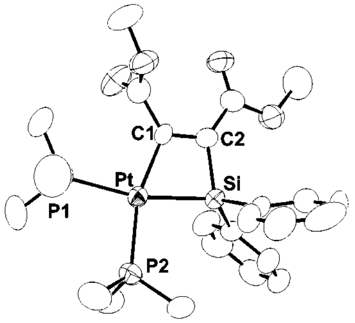


Figure 1. ORTEP drawing of **1** with 50% thermal ellipsoidal plots. The hydrogen atoms are omitted for simplicity.

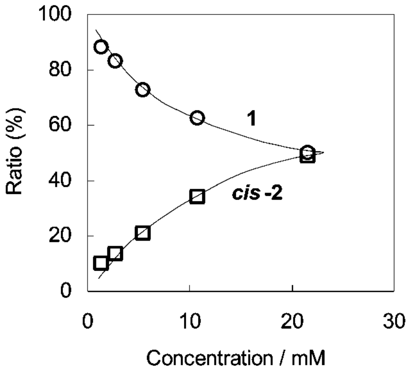
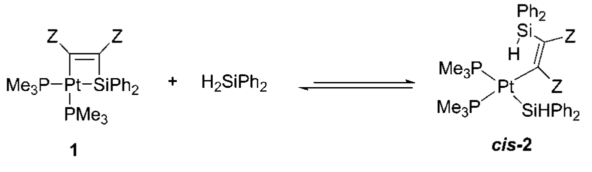


Figure 2. Ratios of **1** and *cis*-**2** of the equilibrated mixtures obtained from equimolar reactions of H_2SiPh_2 and **1** with [Pt] = 1−22 mM (benzene-d_6, 26 °C).

These results suggest that reaction 1 involves *cis*-**2** as the initial product, which is turned into **1** during the reaction. Dissolution of an equimolar mixture of H_2SiPh_2 and **1** in benzene-d_6 causes the partial formation of *cis*-**2** within 1 h. Figure 2 plots the ratios of **1** and *cis*-**2** in the equilibrium mixtures starting from equimolar mixtures of H_2SiPh_2 and **1** with [Pt] = 1−22 mM. Formation of **1** is thermodynamically favored with a low concentration of the complexes. These results suggest that the two complexes are converted easily and reversibly via H_2SiPh_2-promoted ring opening of **1** and γ-Si−H bond activation of *cis*-**2**, followed by elimination of H_2SiPh_2 (eq 3). Slow formation of *trans*-$Pt(CZ{=}CZ\text{-}SiHPh_2)(SiHPh_2)(PMe_3)_2$ (*trans*-**2**) in the reaction mixture prevented the precise determination of the thermodynamic parameters of the above reaction.



(3)

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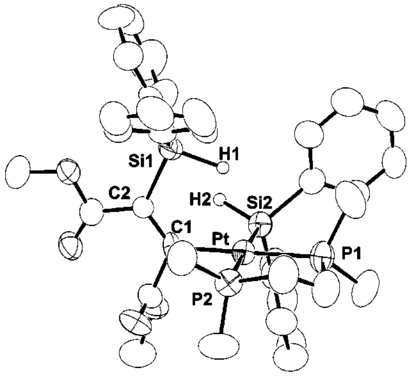
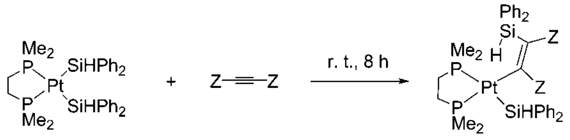


Figure 3. ORTEP drawing of **3** with 50% thermal ellipsoidal plots. The crystal contains solvated THF molecules. Hydrogen atoms, except for SiH, and solvent molecule are omitted for simplicity.

Complex Pt(CZ═CZ-SiHPh$_2$)(SiHPh$_2$)(dmpe) (**3**) (dmpe = 1,2-bis(dimethylphosphino)ethane), which has an analogous structure to *cis*-**2**, is obtained by the reaction of DMAD with Pt(SiHPh$_2$)$_2$-(dmpe) (eq 4). The molecular structure of **3** (Figure 3)[14] shows an

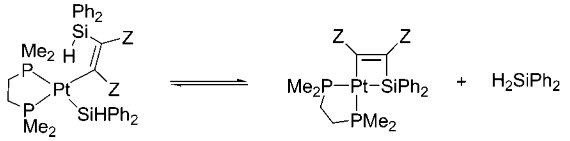


3

(4)

agostic interaction of the γ-hydrogen of the 3-sila-1-propenyl ligand. The hydrogen is located at an apical position of the Pt center. The Pt···H distance, 2.43 Å, is less than the 2.95 Å distance predicted from the sum of van der Waals radii of Pt and H.[15]

Temperature-dependent change of $^1J_{\mathrm{SiH}}$ (198 Hz at 70 °C, 196 Hz at 25 °C, 195 Hz at −30 °C; *cis*-**2**, 197 Hz at 25 °C) of 3-sila-1-propenyl ligand in the NMR spectra of **3** and lower ν(SiH) values of *cis*-**2** (2098 cm^{-1}), *trans*-**2** (2078 cm^{-1}), and **3** (2116 cm^{-1}) than Ph$_2$Si(CH═CH$_2$)H (2124 cm^{-1})[16] indicate the presence of a weak interaction between the SiH hydrogen and Pt in the solid state and in solution. The structure with the cis C═C bond is suited for further strengthening of the interaction, which leads to γ-Si−H bond cleavage promoted by Pt. The ^{1}H NMR spectrum of **3** shows its slow conversion into the corresponding 4-sila-3-platinacyclobutene $\overline{\mathrm{Pt(CZ{=}CZ\text{-}Si}}\mathrm{Ph_2)(dmpe)}$ (**4**) with concomitant formation of H$_2$SiPh$_2$ (eq 5). Although isolation of **4** from the equilibrium



3 **4**

(5)

mixture of **3** and **4** was not feasible,[17] similar NMR parameters between **1** and **4** clearly indicate the 4-sila-3-platinacuclobutene structure of **4**.[18]

Thus, complexes *cis*-**2** and **3** cause intramolecular γ-Si−H bond activation by Pt to afford mixtures with the corresponding 4-sila-3-platinacyclobutenes. Reaction 1 with a low concentration of Pt complex rendered the isolation of **1** possible. Another possible route to 4-sila-3-platinacyclobutene from the reaction of an alkyne with disilylplatinum complexes, involving the initial formation of silylene−platinum complexes,[7] is less plausible for explaining the formation of silaplatinacyclobutene in the reaction of this paper.

In summary, a stable 4-sila-3-platinacyclobutene (**1**) was characterized in both the solid state and solution. The complex is transformed into *cis*-**2** in an equilibrium reaction involving H$_2$SiPh$_2$. Facile and reversible conversion between **1** and *cis*-**2** indicates that *cis*-**2** is the real precursor of **1** in reaction 1.

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Supporting Information Available: Experimental procedures for the synthesis of the complexes and ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and ^{31}P-{^{1}H} NMR spectra of **1**, *cis*-**2**, *trans*-**2**, **3**, and an equilibrated mixture of **3** and **4**, and results of X-ray crystallography for **1**, *trans*-**2**, and **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Crystal data of **1**: C$_{24}$H$_{34}$SiPtP$_2$O$_4$, M_r = 671.65, orthorhombic, $P2_12_12_1$ (No. 19), a = 15.697(2) Å, b = 17.690(5) Å, c = 16.442(2) Å, V = 2719.8(9) Å^3, Z = 4, μ(Mo Kα) = 5.326 mm^{-1}, D_c = 1.640 g cm^{-3}, F(000) = 1328, 3358 unique reflections, 289 variables, R = 0.030, R_w = 0.024, GOF = 1.67, using 2846 reflections with $I > 3\sigma(I)$.

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(13) The 4-sila-3-nickelacyclobutene of ref 8 showed the Si NMR peak at δ −125.3 (corrected as the chemical shift from SiMe$_4$). The higher magnetic field position than **1** may be ascribed to a SiMe$_3$ substituent at the Si atom.

(14) Crystal data for **3**·THF: C$_{36}$H$_{44}$Si$_2$PtP$_2$O$_4$·C$_4$H$_8$O, M_r = 926.06, monoclinic, $P2_1/n$ (No. 14), a = 9.120(2) Å, b = 22.878(4) Å, c = 98.43(2) Å, β = 98.43(2)°, V = 4195(1) Å^3, Z = 4, μ(Mo Kα) = 3.504 mm^{-1}, D_c = 1.466 g cm^{-3}, F(000) = 1872, 10444 unique reflections, 451 variables, R = 0.045, R_w = 0.035, GOF = 1.72, using 5094 reflections with $I > 3\sigma(I)$.

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(17) The solution of **3** is partially converted into **4** and forms an equilibrated mixture of the complexes (75:25) in 2 h at room temperature. Upon raising the temperature to 90 °C, **3** is further converted to **4** to produce the mixture of **3** and **4** in a ratio of 30:70.

(18) ^{31}P{^{1}H} NMR in toluene-d_8: δ 21.2 (J_{PPt} = 2117 Hz) and 37.3 (J_{PPt} = 1345 Hz) for **4** at 90 °C, δ −31.9 (J_{PPt} = 2334 Hz) and −17.5 (J_{PPt} = 1368 Hz) for **1** at 24 °C. ^{1}H NMR in toluene-d_8: δ 3.40 and 3.68 for **4** at 90 °C, δ 3.25 and 3.73 for **1** at 24 °C.

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