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Synthesis and Structure of Novel Organo(siloxo)platinum Complexes. Facile Reduction by Dihydrogen

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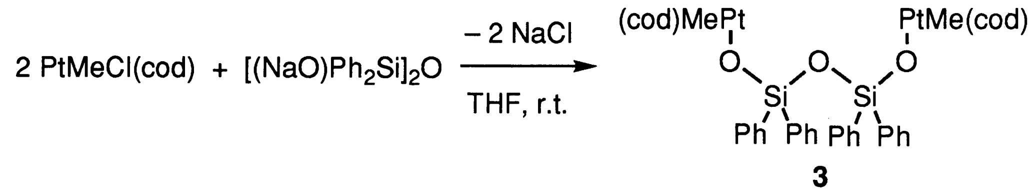
Novel mono- and dinuclear organo(siloxo)platinum complexes $PtR(OSiPh_3)(cod)$ (R = Me, Ph) and $[\{PtMe(cod)O\}Ph_2Si]_2O$ have been prepared and characterized. The molecular structure of $PtPh(OSiPh_3)(cod)$ has been determined by X-ray structure analysis. The activity for reduction of $PtMe(OSiPh_3)(cod)$ and $PtMe(OPh)(cod)$ by H_2 is higher than that of $PtMe_2(cod)$.

It is well known that heterogeneous catalysis by transition metals supported on oxides is greatly influenced by the so-called metal-support interaction.1) However, the exact nature of the interaction is less explored at the molecular level. In the course of our study on the relationship between homogeneous and heterogeneous catalyses, we have been studying the chemistry of model complexes of the supported metal catalysts, where the complexes have bonds of R–M–O–M' (R = organic group; M = transition metal; M' = Si,2) Al, Ti, Zr, Mg, etc.). In this paper, we describe the synthesis and reactivity of novel organo(siloxo)platinum complexes as possible models of R–Pt–O–Si interface in Pt/SiO_2 catalysts, which are widely used in heterogeneous hydrogenolysis of hydrocarbons. Although several organo(alkoxo)platinum complexes are known,3) examples of the siloxo complexes have not been reported to our knowledge.

A metathetical reaction of PtMeCl(cod)4) (cod = 1,5-cyclooctadiene) with $NaOSiPh_3$5) in THF at –20 °C gave $PtMe(OSiPh_3)(cod)$ (**1**) (Eq. 1). Colorless crystals of **1** were obtained by recrystallization from ether/hexane. The phenyl analogue **2** was prepared by the similar method using PtPhCl(cod), too. Dinuclear complex $[\{PtMe(cod)O\}]Ph_2Si]_2O$ (**3**) was also synthesized from PtMeCl(cod) and a sodium salt of disiloxanediol $[(NaO)Ph_2Si]_2O$6) (Eq. 2).

$$\mathrm{PtRCl(cod)} + \mathrm{NaOSiPh_3} \xrightarrow[\text{THF, r.t.}]{-\,\mathrm{NaCl}} \mathrm{PtR(OSiPh_3)(cod)} \qquad (1)$$

$$\mathrm{R = Me}\ (\mathbf{1}),\ \mathrm{Ph}\ (\mathbf{2})$$



3 (2)

Complexes **1**–**3** were characterized by IR, NMR, and elemental analysis.[7)] IR spectrum of **1** showed a strong ν(Si–O) band at 990 cm^{-1}. In ^{1}H NMR of **1** in C_6D_6, olefinic protons of COD gave two broad signals having ^{195}Pt satellites at δ 3.5 and 5.2. This indicates a substantial difference of the trans influence of Me and $OSiPh_3$ in a square planar geometry at Pt; the higher field signal is assignable to the olefinic protons trans to $OSiPh_3$ and the lower one to those trans to Me. When Ph_3SiOH (3 equiv) was added to the C_6D_6 solution of **1**, the signals of *o*–H (δ 8.0, br) and *m*, *p*–H (δ 7.3, br) in OSi*Ph*$_3$ shifted to higher field (*o*–H: δ 7.7, br; *m*, *p*–H: δ 7.2, br), thus approaching to the chemical shift of free Ph_3SiOH (*o*–H: δ 7.6, m; *m*, *p*–H: δ 7.1, m) with increase in the peak intensity. This shows that the $OSiPh_3$ ligand exchanges rapidly with free Ph_3SiOH in the solution.

The molecular structure of the phenyl analogue **2** has been determined by X-ray structure analysis.[8)] Figure 1 depicts an ORTEP drawing, where **2** has a square planar geometry at Pt. The Pt–O bond distance is 1.997(5) Å, being in the typical range of Pt–O bonds (1.99–2.07 Å) reported for alkoxoplatinum complexes such as $Pt(OMe)_2$(dpe), PtMe(OMe)(dpe), and $PtMe(OCH(CF_3)_2)(PMe_3)_2(HOCH(CF_3)_2)$.[3c, 3e)] The Pt–O–Si angle of 144.1(3)° is larger than the Pt–O–C angles for the alkoxoplatinum complexes (117–123°). This may be in part due to the steric repulsion between Ph and bulky $OSiPh_3$, since the Pt–O is a single bond.[9)] The Pt–C(10) and Pt–C(11) bond lengths trans to Ph are longer than the Pt–C(7) and Pt–C(14) trans to $OSiPh_3$, reflecting stronger trans influence of Ph than that of $OSiPh_3$.

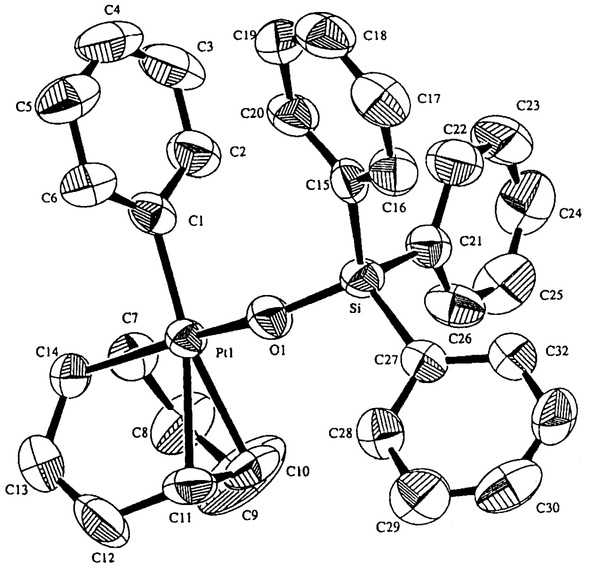


Fig. 1. An ORTEP drawing of **2**. Selected bond lengths (Å) and angle (°): Pt–O 1.997(5), Pt–C(1) 2.021(8), Pt–C(7) 2.115(8), Pt–C(14) 2.102(7), Pt–C(10) 2.307(8), Pt–C(11) 2.301(7), Si–O 1.590(5), Pt–O–Si 144.1(3).

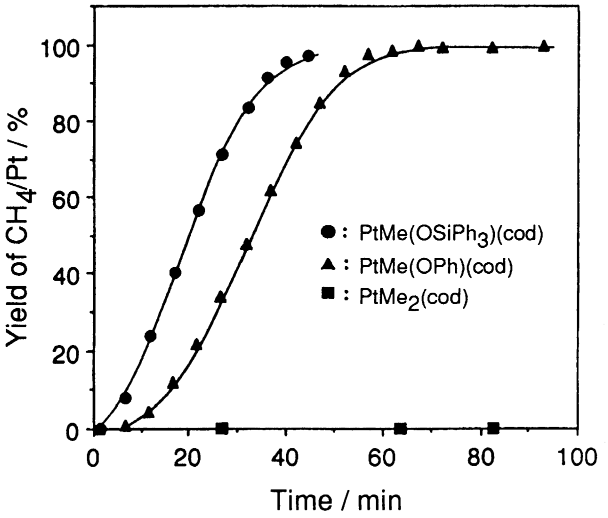


Fig. 2. Plot of yield of CH_4 versus time in the reaction of Pt complexes with H_2. Complex: 0.020 mmol, THF: 1 cm^3, 1 °C.

$$\underset{\mathbf{1}}{PtMe(OSiPh_3)(cod)} + 3\,H_2 \longrightarrow CH_4 + Ph_3SiOH + cyclo\text{-}C_8H_{16} + Pt(0) \qquad (3)$$

Treatment of a THF solution of **1** with H_2 (1 atm) at 1 °C for 1 h quantitatively liberated CH_4, Ph_3SiOH, cyclooctane with concomitant formation of colloidal Pt(0) metal (Eq. 3).10) Figure 2 shows a plot of yield of CH_4 versus time, where the reaction for $PtMe_2$(cod) was much slower than for **1** and PtMe(OPh)(cod) (**4**). It should be noted that **1** is more susceptible to the reduction than **4**. In addition, induction periods were observed for **1** and **4** in Fig. 2. In the similar plots for other products, cyclooctane was always formed behind CH_4 and Ph_3SiOH, and free COD and cyclooctene were detected at the early stage of the reaction. It is thus likely that **1** is initially reduced into CH_4, Ph_3SiOH, COD, and Pt(0), followed by the stepwise reduction of COD to cyclooctane via cyclooctene. To clarify the role of the Pt colloids in reduction of **1**, the following experiment was performed. In the reaction of **1** with H_2 in diglyme ([**1**] = 0.020 mol dm^{-3}) at –19 °C, the reaction was stopped after 115min when the conversion of **1** was ca. 50% and the Pt colloids were suspended. To the resulting mixture was added 1 or 2 equiv of the diglyme solution of **1** of the same concentration at –19 °C. In this case, the induction period was not observed. Accordingly, we suggest that the reduction of **1** is catalyzed by the Pt colloids formed during the reaction. Whitesides reported that the reduction of PtR_2(diolefin) with H_2 is catalyzed on the surface of Pt black.11) Further mechanistic study is now under way.

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7) **1**: Yield 59%; mp 134–135 °C (dec.); IR (KBr): ν(Si–O) 990 cm^{-1}; ^1H NMR (200 MHz, C_6D_6): δ 0.95 (s, ^2J(Pt–H) 75 Hz, 3H, CH_3), 1.0–2.0 (m, 8H, COD CH_2), 3.5 (br, ^2J(Pt–H) 68 Hz, 2H, COD =CH trans to $OSiPh_3$), 5.2 (br, ^2J(Pt–H) 27 Hz, 2H, COD =CH trans to Me), 7.2–8.0 (m, $OSi(C_6H_5)_3$). Anal. Found: C, 54.08; H, 5.37%. Calcd for $C_{27}H_{30}OSiPt$: C, 54.62; H, 5.09%. **2**: Yield, 21%; mp 145–146 °C (dec.); IR (KBr): ν(Si–O) 990 cm^{-1}; ^1H NMR (200 MHz, C_6D_6): δ 1.0–2.0 (m, 8H, COD CH_2), 3.8 (br, ^2J(Pt–H) 68 Hz, 2H, COD =CH trans to $OSiPh_3$), 5.4 (br, ^2J(Pt–H) 26 Hz, 2H, COD =CH trans to Ph), 6.8–7.5 (m, Pt–C_6H_5), 7.2–8.0 (m, $OSi(C_6H_5)_3$). **3**: Yield, 14%; IR (KBr): ν(Si–O) 1069, 1050, 1023 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.66 (s, ^2J(Pt–H) 74 Hz, 3H, CH_3), 1.5–2.5 (m, 8H, COD CH_2), 4.0 (br, ^2J(Pt–H) 70 Hz, 2H, COD =CH trans to $OSiPh_3$), 5.2 (br, ^2J(Pt–H) 28 Hz, 2H, COD =CH trans to Me), 7.2–8.0 (m, $OSi(C_6H_5)_3$). Anal. Found: C, 48.18; H, 4.69%. Calcd for $C_{42}H_{50}O_3Si_2Pt_2$: C, 48.08; H, 4.80%.

8) Crystal data for **2**: $C_{32}H_{32}OSiPt$, M = 655.78, triclinic, space group $P\bar{1}$ (#2), a = 10.571(1) Å, b = 13.724(2) Å, c = 10.350(1) Å, α = 104.91(1)°, β = 99.319(10)°, γ = 69.80(1)°, V = 1357.4(3) $Å^3$, Z = 2, D_c = 1.60 g cm^{-3}. Intensity data were collected at 23 °C on a Rigaku AFC5R diffractometer with graphite monochromated Mo–Kα radiation in the $6° < 2\theta < 55°$ range, a total of 6566 reflections being collected. Absorption correction was not applied. The structure was solved by heavy-atom methods. The non-hydrogen atoms were refined anisotropically by a full-matrix least-squares procedure. Hydrogen atoms were included in the calculation but not refined. The final R and R_w values are 0.045 and 0.028 for 4015 reflections with $|F_o| > 3\sigma|F_o|$. All the calculations were performed using the teXan crystalographic software package of Molecular Structure Corporation.

9) However, M–O–Si systems frequently have wide angles at oxygen. See: K. Young, E. D. Simhon, and R. H. Holm, *Inorg. Chem.*, **24**, 1831 (1985).

10) The rate of reaction of **1** with H_2 was independent of the rate of rotation of the magnetic stirring bar, confirming that the rate was not limited by the diffusion of H_2.

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