Coordinatively Unsaturated Ru(II) Species Ru(xantsil)(CO): A New Active Catalyst for Oligomerization/Deoligomerization of $HSiMe_2SiMe_3$ [xantsil = (9,9-Dimethylxanthene-4,5-diyl)bis(dimethylsilyl)]. Isolation of a Stabilized Form of the Silyl(silylene) Intermediates

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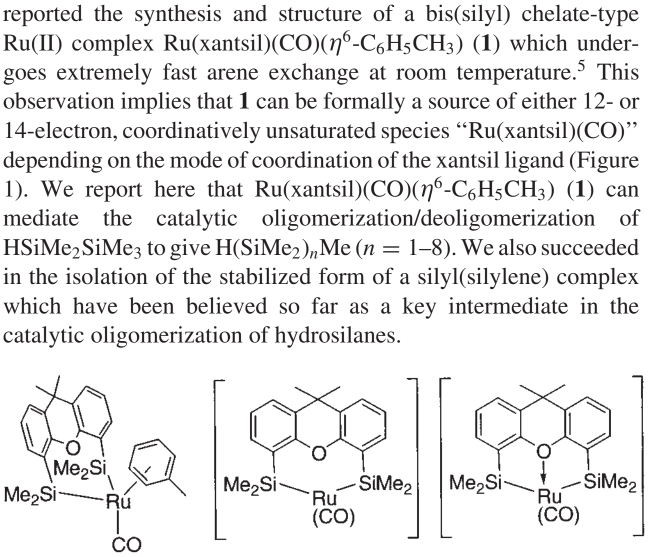
Ru(xantsil)(CO)(η^6-$C_6H_5CH_3$) (**1**) was found to be a catalyst for the oligomerization/deoligomerization of $HSiMe_2SiMe_3$ to give $H(SiMe_2)_nMe$ ($n = 1$–8). A possible mechanism involving a silyl(silylene) intermediate was strongly supported by the isolation of its stabilized form, i.e., alkoxy-bridged bis(silylene) complex which was characterized by X-ray crystal structure analysis.

Transition-metal chloro complexes such as $RhCl(PR_3)_3$, $IrCl(CO)(PR_3)_2$, $RuCl_2(PR_3)_3$, and $MCl_2(PR_3)_2$ (M=Pd, Pt) have been widely employed as active homogeneous catalysts for the various transformation reactions of organic compounds.[1] Recently, our study[2] has been focused on the exceptionally strong σ-donor character and high *trans* influencing ability of silyl ligands.[3] Introduction of a silyl ligand instead of the chloro ligand could enhance or change the reactivity and catalytic performance of transition metal complexes. However, facile elimination of silyl ligands from the metal center has retarded the progress of such application.[4] To avoid this drawback of silyl ligands, we designed a chelate ligand "xantsil" [xantsil = (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)]. Because of the rigid backbone of the xanthene core and electron-releasing character of silyl groups, xantsil can be an ideal supporting ligand for coordinatively unsaturated transition-metal complexes. In a previous paper, we reported the synthesis and structure of a bis(silyl) chelate-type Ru(II) complex Ru(xantsil)(CO)(η^6-$C_6H_5CH_3$) (**1**) which undergoes extremely fast arene exchange at room temperature.[5] This observation implies that **1** can be formally a source of either 12- or 14-electron, coordinatively unsaturated species "Ru(xantsil)(CO)" depending on the mode of coordination of the xantsil ligand (Figure 1). We report here that Ru(xantsil)(CO)(η^6-$C_6H_5CH_3$) (**1**) can mediate the catalytic oligomerization/deoligomerization of $HSiMe_2SiMe_3$ to give $H(SiMe_2)_nMe$ ($n = 1$–8). We also succeeded in the isolation of the stabilized form of a silyl(silylene) complex which have been believed so far as a key intermediate in the catalytic oligomerization of hydrosilanes.



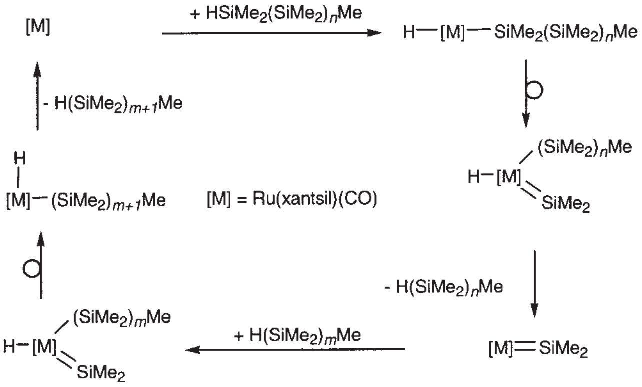
1 **A** **B**

Figure 1. Coordination modes of xantsil.

The ruthenium(II) xantsil complex **1** (0.1 mol%) catalyzed the oligomerization/deoligomerization of $HSiMe_2SiMe_3$ at room temperature to give $H(SiMe_2)_nMe$ ($n = 1$–5) after 2 days reaction with the molar ratios of $81\,(n = 1) : 56\,(n = 2) : 11\,(n = 3) : 3\,(n = 4) : 1\,(n = 5)$ based on the peak areas of the GC(FID). The products were confirmed by ^1H NMR and GC-Mass spectroscopy (eq 1). When the reaction was carried out at 90 °C for 2 days, formation of products with n up to 8 was observed with the molar ratios of $346\,(n = 1) : 96\,(n = 2) : 82\,(n = 3) : 64\,(n = 4) : 35\,(n = 5) : 13\,(n = 6) : 4\,(n = 7) : 1\,(n = 8)$ (eq 1).

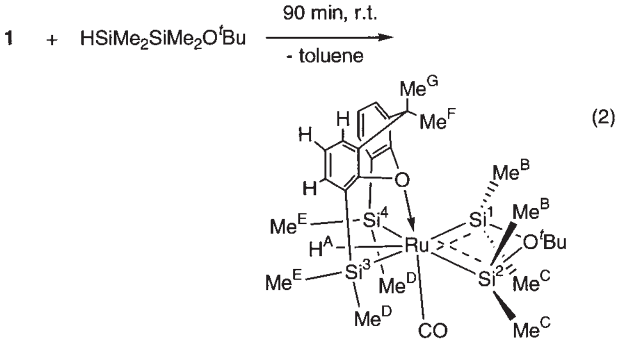
$$HSiMe_2SiMe_3 \xrightarrow[\text{2 days}]{\text{0.1 mol\% } \mathbf{1}} \underset{\substack{(\text{r.t., } n = 1\text{-}5) \\ (90\ ^\circ\text{C, } n = 1\text{-}8)}}{H(SiMe_2)_nMe} \qquad (1)$$

A plausible mechanism for the ruthenium-mediated oligomerization/deoligomerization is illustrated in Scheme 1.



Scheme 1. A plausible mechanism for the Ru(II) mediated oligomerization/deoligomerization of hydrodisilane.

The reaction could proceed via repeated oxidative additions of Si-H, 1,2-silyl migration,[6] and reductive elimination processes. The silyl(silylene) intermediates can be indirectly confirmed by replacing a methyl group of the disilane with a ^{t}BuO group. When **1** was allowed to react with a stoichiometric amount of $HSiMe_2SiMe_2O^tBu$ at room temperature, a bis(silylene) ruthenium(IV) complex **2** was formed almost quantitatively (eq 2). Workup of the resulting solution and crystallization from toluene afforded colorless needles of **2** (84%).[7] The elemental analysis and mass spectral data are consistent with the formula of **2**.



(2)

2

The structure of **2** was unequivocally determined by the X-ray crystal structure analysis.[8] The crystal contains two independent molecules, but there is no essential difference. The ORTEP view of one of them is shown in Figure 2. Although the hydrido ligand could not be located crystallographically, NMR data clearly indicates its existence. It might be found along the unusually widened Si3-Ru1-Si4 angle (119.4(1)°). Thus, **2** takes a distorted seven-coordinate pentagonal bipyramid with the nearly planar arrangement of all four silicon atoms with ruthenium (mean deviation from the least square Si_4 plane: 0.0161 Å). The bond lengths of Ru-Si (silylene) (ave. 2.399 Å) are shorter than those of Ru-Si (silyl) (ave. 2.434 Å) but about 0.09 Å longer than those of the previously reported ruthenium bis(silylene) complexes, probably due to the *trans*-influence of the silyl ligands. The length between Ru1 and O2 is 2.289(8) Å, indicating the coordination of the oxygen atom O2 to the ruthenium center to satisfy the 18-electron rule. Thus, the xantsil works as a tridentate ligand.

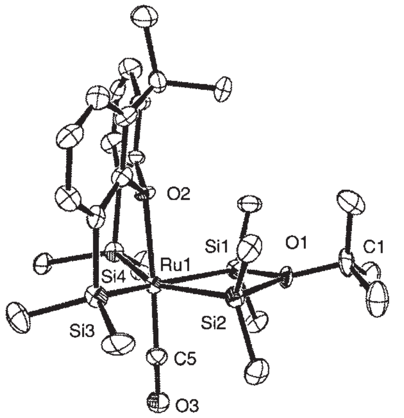


Figure 2. ORTEP drawing of **2**. Selected bond lengths (Å) and angles (°): Ru1-Si1 2.395(4), Ru1-Si2 2.402(4), Ru1-Si3 2.443(4), Ru1-Si4 2.424(4), Ru1-C5 1.79(1), Ru1-O2 2.289(8), Si1-O1 1.813(9), Si2-O1 1.827(9), O1-C1 1.52(1), Si1-Ru1-Si2 67.9(1), Si3-Ru1-Si4 119.4(1), O2-Ru1-C5 175.2(6).

The NMR spectroscopic data of **2** are consistent with the crystal structure. The ^{1}H NMR spectrum of **2** shows a singlet at −2.23 ppm assignable to Ru-H. Four singlet signals of the methyl groups appear at 0.13 (6H), 0.59 (6H), 0.62 (6H), and 0.88 (6H) which are assigned to SiMe^B, SiMe^D, SiMe^E, and SiMe^C, respectively (see eq 2). The signals of two 9-Me groups on xantsil appear inequivalently at 1.24 (9-Me^F) and 1.75 (9-Me^G). These assignments are established by the NOESY technique. In the two-dimensional NOESY spectrum, a correlation peak is present between Ru-H and SiMe^E resonances, indicating that the hydrido hydrogen atom is located along the Si^3-Ru1-Si^4 angle. The NOESY spectrum also shows the intramolecular exchange process of the methyl groups on the silylene ligands. The dynamic process could involve the cleavage of a Si-O bond followed by rotation of the resulting donor-free silylene moiety about the Ru=Si double bond to interchange the methyl group environments. This mechanism is essentially the same as those of the exchange of Si-Me groups in $Cp(CO)_2W\{SiMe_2 \cdots Do \cdots SiMe_2\}$ (Do=OMe, NEt_2)[9] and $Cp^*(Me_3P)Ru\{SiMe_2 \cdots OR \cdots SiMe_2\}$ (R=Me, ^{t}Bu).[10] In the ^{29}Si{^{1}H} NMR spectrum, the signal of two silylene ligands appeared equivalently at 107.6 ppm, which is shifted significantly to downfield from that of the xantsil silyl groups (15.4 ppm). The ^{29}Si chemical shift of silylene ligands is characteristic of base-stabilized silylene complexes.

Disproportionation of pentamethyldisilane has been reported by Yamamoto et al. in which a catalytic amount of $(Et_3P)_2PtCl_2$ was employed.[11] The reaction requires relatively severe conditions and proceeds at 90 °C (18 h) to give $H(SiMe_2)_nMe$ ($n = 1$–6).

This paper demonstrated that our bis(silyl)ruthenium complex **1** generates a 12- or 14-electron coordinatively unsaturated **A** or **B** species and works as an active catalyst for the metal-mediated oligomerization/deoligomerization of hydrodisilanes. Over the past few decades, silyl(silylene) complexes have been postulated in the metal-mediated oligomerization of hydrosilanes and hydrodisilanes. In this paper, we offered a convincing evidence in support of the existence of silyl(silylene) complexes in the catalytic reaction.

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7 Data for **2**: ^{1}H NMR (CD_2Cl_2) $\delta - 2.23$ (s, 1H, RuH), 0.13 (s, 6H, SiMe^B), 0.59 (s, 6H, SiMe^D), 0.62 (s, 6H, SiMe^E), 0.88 (s, 6H, SiMe^C), 1.24 (s, 3H, 9-Me^F), 1.38 (s, 9H, ^{t}Bu), 1.75 (s, 3H, 9-Me^G), 7.12, 7.23, 7.48 (m, 6H, Ar). ^{13}C{^{1}H} NMR (CD_2Cl_2) 6.2, 7.2, 10.0, 14.0 (SiMe), 22.6 (OC*Me*$_3$), 30.7, 30.9 (9-Me), 35.8 (*C*-Me$_2$), 92.3 (O*C*Me$_3$), 123.5, 124.9, 130.7, 134.4, 136.0, 161.9 (Ar), 204.2 (CO). ^{29}Si{^{1}H} NMR (CD_2Cl_2) 15.4 (xantsil Si), 107.6 (silylene Si), IR (KBr pellet) 1923 cm^{-1} (ν_{CO}), Mass (EI, 70 eV) m/z 587 (M$^+$-^{t}Bu, 26), 513 (M$^+$-^{t}Bu-Me$_2$SiO, 41), 325 (100). Anal. Calcd for $C_{28}H_{46}RuO_3Si_4$: C, 52.21; H, 7.20%. Found: C, 51.71; H, 7.16%.

8 Crystallographic data for **2**: $C_{28}H_{46}O_3RuSi_4$, $M = 644.08$, *monoclinic*, space group $P2_1$, $a = 18.216(3)$ Å, $b = 9.634(1)$ Å, $c = 19.327(2)$ Å, $\beta = 109.647(6)°$, $V = 3194.2(7)$ Å^3, $T = -123$ °C, $Z = 4$, $D_c = 1.339$ g cm^{-3}, μ(Mo-Kα) = 6.67 cm^{-1}, $R1 = 0.075$ ($I > 2\sigma$ (I)), $R = 0.114$, $Rw = 0.216$ (all data). Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-177653. 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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