Dihydrogen activation by sulfido-bridged dinuclear Ru/Ge complexes: insight to the [NiFe] hydrogenase unready state
Tsuyoshi Matsumoto,* Naohisa Itakura, Yukiko Nakaya, and Kazuyuki Tatsumi*

Department of Chemistry, Graduate School of Science, and Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

Supporting Information
General. All reactions and manipulations of air-sensitive compounds were conducted under an inert atmosphere of dry nitrogen employing standard Schlenk techniques. Toluene, THF, hexane, dichloromethane, and hexamethyldisiloxane (HMDSO) were degassed and dried according to the Grubbs’ report, where the solvents were passed over columns of activated alumina and a supported copper catalyst supplied from Hansen & Co. Ltd. C$_6$D$_6$ was dried over sodium and distilled prior to use. $^1$H NMR (500 or 600 MHz) and $^{31}$P NMR spectra (202 or 243 MHz) were recorded on a JEOL JNM-ECP500 or ECA600 spectrometer. $^1$H NMR chemical shifts were quoted in ppm relative to the residual protons of deuterated solvents. $^{31}$P{$_1^H$} NMR chemical shifts were referenced to signals of external 85% H$_3$PO$_4$. Elemental analyses were performed on a LECO CHNS-932 microanalyzer. The synthesis and spectroscopic data of [Dmp(Dep)Ge($\mu$–S($\mu$–OH)Ru(PEt$_3$)](BArF$_4$) (2b), Dmp(Dep)Ge($\mu$–S)$_2$Ru(PR$_3$) (3a; R = Ph, 3b; R = Et), [Dmp(Dep)Ge($\mu$–S($\mu$–SH)Ru(PR$_3$)](BArF$_4$) (4a; R = Ph, 4b; R = Et), [Dmp(Dep)Ge($\mu$–S($\mu$–H)Ru(PPh$_3$)](BArF$_4$) (5a), and Dmp(Dep)Ge($\mu$–S)Ru(PPh$_3$) (6a) were reported in our previous papers.

Synthesis of [Dmp(Dep)Ge($\mu$–S($\mu$–H)Ru(PEt$_3$)](BArF$_4$) (5b). A toluene solution of 2b (120.0 mg, 0.0720 mmol) was stirred under an atmospheric pressure of H$_2$ for 6 h at r.t. The solution was evaporated to dryness, and the yellow residue was crystallized from HMDSO/CH$_2$Cl$_2$ at –30 $^\circ$C to give 5b as yellow crystals in 84% yield. When the same reaction was performed in C$_6$D$_6$ and monitored by $^1$H NMR analysis, a quantitative formation of 5b and H$_2$O ($\delta$ 0.34) was observed within 5 min at r.t. Data for 5b: $^1$H NMR (600 MHz, C$_6$D$_6$): $\delta$ 8.63 (s, 8H, $o$–CH of BAr$_2^+$), 7.47 (s, 4H, $p$–CH of BAr$_2^+$), 7.54 (t, $J$ = 7.8 Hz, 1H, $p$–CH of Dmp), 7.17 (t, $J$ = 7.8 Hz, 1H, $p$–CH of Dmp), 7.12 (d, $J$ = 7.8 Hz, 1H, $m$–CH of Dmp), 6.95 (d, $J$ = 7.8 Hz, 1H, $m$–CH of Dmp), 7.66 (d, $J$ = 7.8 Hz, 1H, $m$–CH of Dmp), 6.69 (s, 1H, $m$–CH of Mes), 6.16 (d, $J$ = 7.8 Hz, 1H, $m$–CH of Dmp), 6.13 (s, 1H, $m$–CH of Mes), 5.85 (s, 1H, $m$–CH of Mes), 5.19 (s, 1H, $m$–CH of Mes), 2.93 (dq, $J_i$ = 7.8 Hz, $J_{J_i}$ = 14.2 Hz, 1H, CH$_2$CH$_3$ of Dep), 2.65 (dq, $J_i$ = 7.8 Hz, $J_{J_i}$ = 14.2 Hz, 1H, CH$_2$CH$_3$ of Dep), 2.61 (dq, $J_i$ = 7.8 Hz, $J_{J_i}$ = 14.2 Hz, 1H, CH$_2$CH$_3$ of Dep), 2.17 (s, 3H, CH$_3$ of Mes), 2.15 (s, 3H, CH$_3$ of Mes), 2.08 (s, 3H, CH$_3$ of Mes), 2.02 (dq, $J_i$ = 7.8 Hz, $J_{J_i}$ = 14.2 Hz, 1H, CH$_2$CH$_3$ of Dep), 1.92 (s, 3H, CH$_3$ of Mes), 1.83 (s, 3H, CH$_3$ of Mes), 1.57 (s, 3H, CH$_3$ of Mes), 1.40 (dq, $J_{J_i}$ = 155.4 Hz, $J_{J_{J_i}}$ = 7.5 Hz, 6H, PCH$_2$CH$_3$), 1.20 (t, $J$ = 7.8 Hz, 3H, CH$_2$CH$_3$ of Dep), 0.92 (t, $J$ = 7.8 Hz, 3H, CH$_2$CH$_3$ of Dep), 0.78 (dt, $J_{J_i}$ = 16.2 Hz, $J_{J_{J_i}}$ = 7.5 Hz, 9H, PCH$_2$CH$_3$), –10.50 (d, $J_i$ = 7.2 Hz, 1H, Ru–H). $^{31}$P{$_1^H$} NMR (243 Hz, C$_6$D$_6$) $\delta$ 27.4. Anal. Caled for C$_{72}$H$_{66}$BF$_{24}$GePRuS: C, 52.90; H, 4.07; S, 1.96. Found: C, 52.65; H, 3.89; S, 2.01.
**Reaction of 4b and H2.** A benzene-$d_6$ solution of 4b (50.0 mg, 0.0300 mmol) was placed into a 5mmφ NMR tube with a gas inlet, and the solution was degassed with three freeze–pump–thaw cycles. The tube was connected to a balloon filled with H2 gas, and the solution was warmed to 80 °C. After 3 days, the products were analysed by $^1$H NMR spectra, which showed the solution contained 4b and 5b in a 17 : 83 ratio.

**Reaction of 4a and H2O.** A THF-$d_{10}$ solution of 4a (50.0 mg, 0.0282 mmol) and 10 equiv H2O was placed into a 5mmφ NMR tube. The solution was stirred at 298 K for 1 day and analysed by $^1$H NMR spectra, which displays the signals of 4a and 2a in 98 : 2 ratio.

**Reaction of 4a and H2 in the presence of H2O.** A THF solution of 4a (100.0 mg, 0.0564 mmol) was refluxed under an atmospheric pressure of H2 for 1 day. The solution was evaporated to dryness, and the yellow residue was crystallized from HMDSO/CH2Cl2 to give 5b as yellow crystals in 68% yield.

**Deprotonation Reaction of 5b.** To an acetonitrile solution of 5b (100 mg, 0.0612 mmol) was added NaH (5.0 mg, 0.21 mmol) and stirred for 10 h at r.t. All the volatiles were removed in vacuo and the residue was extracted by toluene. Complex 6b was obtained quantitatively as a yellow powder.

**Protonation Reaction of 6b.** To a THF solution of 6b (50.0 mg, 0.0649 mmol) was added H(OEt$_2$)$_2$BAF$_4$ (80 mg, 0.079 mmol) and stirred for 10 h at r.t. All the volatiles were removed in vacuo and the residue was extracted by toluene. Complex 5b was obtained quantitatively as a yellow powder. Data for 6b; $^1$H NMR (600 MHz, C$_6$D$_6$): δ 7.10 (d, $J$ = 6.4 Hz, 1H, $m$–CH of Dmp), 6.96 (t, $J$ = 7.8 Hz, 1H, $p$–CH of Dmp), 6.82 (d, $J$ = 6.4 Hz, 1H, $m$–CH of Dmp), 6.74 (s, 1H, $m$–CH of Mes), 6.70 (d, $J$ = 7.8 Hz, 1H, $m$–CH of Dep), 6.58 (d, $J$ = 7.8 Hz, 1H, $m$–CH of Dep), 6.31 (s, 1H, $m$–CH of Mes), 5.77 (s, 1H, $m$–CH of Mes), 3.73 (dq, $J_1$ = 7.8 Hz, $J_2$ = 14.2 Hz, 1H, $CH_2$CH$_3$ of Dep), 3.54 (s, 1H, $m$–CH of Mes), 3.31 (dq, $J_1$ = 7.8 Hz, $J_2$ = 14.2 Hz, 1H, $CH_2$CH$_3$ of Dep), 2.97 (dq, $J_1$ = 7.8 Hz, $J_2$ = 14.2 Hz, 1H, $CH_2$CH$_3$ of Dep), 2.30 (s, 3H, CH$_3$ of Mes), 2.28 (s, 3H, CH$_3$ of Mes), 2.20 (dq, $J_1$ = 7.8 Hz, $J_2$ = 14.2 Hz, 1H, $CH_2$CH$_3$ of Dep), 2.19 (s, 3H, CH$_3$ of Mes), 1.89 (s, 3H, CH$_3$ of Mes), 1.73 (s, 3H, CH$_3$ of Mes), 1.44 (s, 3H, CH$_3$ of Mes), 1.37 (dq, $J_{H-P}$ =
155.4 Hz, $J_{H,H} = 7.5$ Hz, 6H, PCH$_2$CH$_3$), 1.15 (t, $J = 7.3$ Hz, 3H, CH$_2$CH$_3$ of Dep), 1.08 (t, $J = 7.3$ Hz, 3H, CH$_2$CH$_3$ of Dep), 0.75 (dt, $J_{P,H} = 16.2$ Hz, $J_{H,H} = 7.5$ Hz, 9H, PCH$_2$CH$_3$).
Anal. Calcd for C$_{40}$H$_{53}$GePRuS: C, 62.34; H, 6.93; S, 4.16. Found: C, 61.97; H, 6.70; S, 4.25.

References