

**Dihydrogen activation by sulfido-bridged dinuclear Ru/Ge complexes:
insight to the [NiFe] hydrogenase unready state**

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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,¹ where the solvents were passed over columns of activated alumina and a supported copper catalyst supplied from Hansen & Co. Ltd. C₆D₆ was dried over sodium and distilled prior to use. ¹H NMR (500 or 600 MHz) and ³¹P NMR spectra (202 or 243 MHz) were recorded on a JEOL JNM-ECP500 or ECA600 spectrometer. ¹H NMR chemical shifts were quoted in ppm relative to the residual protons of deuterated solvents. ³¹P{¹H} NMR chemical shifts were referenced to signals of external 85% H₃PO₄. Elemental analyses were performed on a LECO CHNS-932 microanalyzer. The synthesis and spectroscopic data of [Dmp(Dep)Ge(μ -S)(μ -OH)Ru(PEt₃)](BAR^F₄) (**2b**), Dmp(Dep)Ge(μ -S)₂Ru(PR₃) (**3a**; R = Ph, **3b**; R = Et), [Dmp(Dep)Ge(μ -S)(μ -SH)Ru(PR₃)](BAR^F₄) (**4a**; R = Ph, **4b**; R = Et), [Dmp(Dep)Ge(μ -S)(μ -H)Ru(PPh₃)](BAR^F₄) (**5a**), and Dmp(Dep)Ge(μ -S)Ru(PPh₃) (**6a**) were reported in our previous papers.^{2,3}

Synthesis of [Dmp(Dep)Ge(μ -S)(μ -H)Ru(PEt₃)](BAR^F₄) (5b**).** A toluene solution of **2b** (120.0 mg, 0.0720 mmol) was stirred under an atmospheric pressure of H₂ for 6 h at r.t. The solution was evaporated to dryness, and the yellow residue was crystallized from HMDSO/CH₂Cl₂ at -30 °C to give **5b** as yellow crystals in 84% yield. When the same reaction was performed in C₆D₆ and monitored by ¹H NMR analysis, a quantitative formation of **5b** and H₂O (δ 0.34) was observed within 5 min at r.t. Data for **5b**; ¹H NMR (600 MHz, C₆D₆): δ 8.63 (s, 8H, *o*-CH of BAR^F), 7.47 (s, 4H, *p*-CH of BAR^F), 7.54 (t, *J* = 7.8 Hz, 1H, *p*-CH of Dmp), 7.17 (t, *J* = 7.8 Hz, 1H, *p*-CH of Dep), 7.12 (d, *J* = 7.8 Hz, 1H, *m*-CH of Dmp), 6.95 (d, *J* = 7.8 Hz, 1H, *m*-CH of Dmp), 6.76 (d, *J* = 7.8 Hz, 1H, *m*-CH of Dep), 6.69 (s, 1H, *m*-CH of Mes), 6.16 (d, *J* = 7.8 Hz, 1H, *m*-CH of Dep), 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*₁ = 7.8 Hz, *J*₂ = 14.2 Hz, 1H, CH₂CH₃ of Dep), 2.65 (dq, *J*₁ = 7.8 Hz, *J*₂ = 14.2 Hz, 1H, CH₂CH₃ of Dep), 2.61 (dq, *J*₁ = 7.8 Hz, *J*₂ = 14.2 Hz, 1H, CH₂CH₃ of Dep), 2.17 (s, 3H, CH₃ of Mes), 2.15 (s, 3H, CH₃ of Mes), 2.08 (s, 3H, CH₃ of Mes), 2.02 (dq, *J*₁ = 7.8 Hz, *J*₂ = 14.2 Hz, 1H, CH₂CH₃ of Dep), 1.92 (s, 3H, CH₃ of Mes), 1.83 (s, 3H, CH₃ of Mes), 1.57 (s, 3H, CH₃ of Mes), 1.40 (dq, *J*_{H-P} = 155.4 Hz, *J*_{H-H} = 7.5 Hz, 6H, PCH₂CH₃), 1.20 (t, *J* = 7.8 Hz, 3H, CH₂CH₃ of Dep), 0.92 (t, *J* = 7.8 Hz, 3H, CH₂CH₃ of Dep), 0.78 (dt, *J*_{P-H} = 16.2 Hz, *J*_{H-H} = 7.5 Hz, 9H, PCH₂CH₃), -10.50 (d, *J*_{H-P} = 7.2 Hz, 1H, Ru-H). ³¹P{¹H} NMR (243 Hz, C₆D₆) δ 27.4. Anal. Calcd for C₇₂H₆₆BF₂₄GePRuS: 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-d₆ 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 ¹H 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 ¹H 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(OEt₂)₂BAR^F₄ (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**; ¹H NMR (600 MHz, C₆D₆): 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, CH₂CH₃ of Dep), 3.54 (s, 1H, *m*-CH of Mes), 3.31 (dq, *J*₁ = 7.8 Hz, *J*₂ = 14.2 Hz, 1H, CH₂CH₃ of Dep), 2.97 (dq, *J*₁ = 7.8 Hz, *J*₂ = 14.2 Hz, 1H, CH₂CH₃ of Dep), 2.30 (s, 3H, CH₃ of Mes), 2.28 (s, 3H, CH₃ of Mes), 2.20 (dq, *J*₁ = 7.8 Hz, *J*₂ = 14.2 Hz, 1H, CH₂CH₃ of Dep), 2.19 (s, 3H, CH₃ of Mes), 1.89 (s, 3H, CH₃ of Mes), 1.73 (s, 3H, CH₃ of Mes), 1.44 (s, 3H, CH₃ of Mes), 1.37 (dq, *J*_{H-P} =

155.4 Hz, $J_{H-H} = 7.5$ Hz, 6H, PCH₂CH₃), 1.15 (t, $J = 7.3$ Hz, 3H, CH₂CH₃ of Dep), 1.08 (t, $J = 7.3$ Hz, 3H, CH₂CH₃ of Dep), 0.75 (dt, $J_{P-H} = 16.2$ Hz, $J_{H-H} = 7.5$ Hz, 9H, PCH₂CH₃).
Anal. Calcd for C₄₀H₅₃GePRuS: C, 62.34; H, 6.93; S, 4.16. Found: C, 61.97; H, 6.70; S, 4.25.

References

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