Supplementary Material

Mononuclear Ni(III) Complexes \([\text{Ni}^\text{III}(\text{L})(\text{P(C}_6\text{H}_3-3-\text{SiMe}_3-2-S)_3])^{0/1-}\) (L = Thiolate, Selenolate, CH\(_2\)CN, Cl, PPh\(_3\)): Relevance to the Nickel Site of [NiFe] Hydrogenases

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Fig S1. Changes in the \(^2\)H NMR spectra (C\(_4\)H\(_8\)O) observed upon the addition of dry O\(_2\) into the solution of 1-D. The \(^2\)H NMR spectra of 1-D (solid line) and 1-D exposure to dry O\(_2\) (dotted line).

Fig S2. Changes in the UV/vis spectra (THF-CH\(_2\)CN 1:1 volume ratio) occurred upon the addition of O\(_2\) into the solution of complex 1. (a) The reaction was monitored for 6 cycles (the interval between two cycles measured is 5 min.). (b) The reaction was monitored after 6 cycles (the interval between two cycles measured is 12 min.).

Fig. S3. The dechlorination reaction of complex 2 and CH\(_2\)Cl\(_2\) monitored by UV/vis spectra (in CH\(_2\)Cl\(_2\)). The measured intervals between two curves are shown in the diagram.

Fig S4. ORTEP drawing and labeling scheme of \([\text{Ni}^\text{III}(2-S-C_4\text{H}_3\text{S})(\text{P(C}_6\text{H}_3-3-\text{SiMe}_3-2-S)_3])\) (5) anion with thermal ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (deg): Ni—S(1) 2.2769(10); Ni—S(2) 2.2045(9); Ni—S(3) 2.3048(9); Ni—S(4) 2.2554(9); Ni—P(1) 2.1356(9); S(4)—C(28) 1.7511(35); S(1)—Ni—S(2) 123.08(3); S(1)—Ni—S(3) 105.83(3); S(1)—Ni—S(4) 90.77(4); S(1)—Ni—P(1) 87.38(3); S(2)—Ni—S(3) 130.37(4); S(2)—Ni—S(4) 95.41(3); S(2)—Ni—P(1) 87.26(3); S(3)—Ni—S(4) 93.9(3); S(3)—Ni—P(1) 84.69(3); S(4)—Ni—P(1) 177.3(4).
**Fig. S5.** Kinetics data (circle) and fits (solid line) for the reactions of (a) complex 2 with CH$_2$Cl$_2$ ($k_{\text{obs}} = (4.78 \pm 0.02) \times 10^{-5}$ s$^{-1}$, $R^2 = 0.9990$) and (b) complex 4 with CH$_2$Cl$_2$ ($k_{\text{obs}} = (6.01 \pm 0.03) \times 10^{-4}$ s$^{-1}$, $R^2 = 0.9990$).

**Fig. S6.** ORTEP drawing and labeling scheme of [Ni$^{II}$(CO)(P(C$_6$H$_3$-3-SiMe$_3$-2-S)$_3$)]$^-$ (6) anion with thermal ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (deg): Ni—C(1) 1.800(6); Ni—S(1) 2.3047(8); Ni—S(2) 2.3283(8); Ni—S(3) 2.2655(8); Ni—P(1) 2.1075(8); S(1)—Ni—S(2) 109.06(3); S(1)—Ni—S(3) 134.87(3); S(2)—Ni—S(3) 113.03(3); S(1)—Ni—C(1) 96.2(2); S(2)—Ni—C(1) 98.2(2); S(3)—Ni—C(1) 92.6(2); P(1)—Ni—C(1) 175.7(2); P(1)—Ni—S(1) 82.22(3); P(1)—Ni—S(2) 85.10(3); P(1)—Ni—S(3) 85.78(3). Refinement of complex 6 revealed that complexes 6 and 2 were co-crystallization and the occupancy factors of CO and [SePh]$^-$ ligands were 0.9 and 0.1, respectively.

**Fig. S7.** (a) Conversion of complex 2 (0.5 mM in CH$_3$CN) to complex 6 monitored by UV-vis spectrometry under reaction of complex 2 and CO (1 atm) for 78 h at ambient temperature. The absorption band at 711 nm (complex 6) increases with decrease of the bands at 590, 954 nm (complex 2), and two isosbestic points were observed. (b) Conversion of complex 4 (0.5 mM in CH$_3$CN) to complex 6 monitored by UV-vis spectrometry under reaction of complex 4 and CO (1 atm) for 47 h at ambient temperature. The absorption band at 711 nm (complex 6) increases with decrease of the bands at 579, 922 nm (complex 2), and two isosbestic points were observed.

**Fig. S8.** The cyclic voltammograms of [Ni(PPh$_3$)(P(C$_6$H$_3$-3-SiMe$_3$-2-S)$_3$)] (9) in CH$_2$Cl$_2$ (Condition: at room temperature, scan rate 0.1 V/s and referenced to ferrocinium/ferrocene).

**Fig. S9.** The cyclic voltammograms of [Ni(CO)(P(C$_6$H$_3$-3-SiMe$_3$-2-S)$_3$)]$^-$ (6) (dashed line) and [Ni(Cl)(P(C$_6$H$_3$-3-SiMe$_3$-2-S)$_3$)]$^-$ (3) (solid line) (Condition: at room temperature, scan rate 0.1 V/s and referenced to ferrocinium/ferrocene).

**Fig. S10.** ORTEP drawing and labeling scheme of [Ni$^{II}$(PPh$_3$)(P(C$_6$H$_3$-3-SiMe$_3$-2-S)$_2$ (C$_6$H$_3$-3-SiMe$_3$-2-SH))] (8) with thermal ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (deg): Ni—S(1) 2.173(2); Ni—S(2) 2.1901(18); Ni—S(3) 3.314(3); Ni—P(1) 2.1173(19); Ni—P(2) 2.2265(19); S(1)—Ni—S(2) 144.71(9); S(1)—Ni—P(2) 97.49(8); S(1)—Ni—P(1) 88.39(7); S(2)—Ni—P(1) 84.11(7); S(2)—Ni—P(2) 95.87(7); P(2)—Ni—P(1) 169.44(9); Ni—P(1)—C(19) 117.5(2); P(1)—C(19)—C(24) 119.8(5); C(24)—S(3)—H(3) 84.14(23).
**Fig S1.** Changes in the $^2$H NMR spectra ($C_4H_8O$) observed upon the addition of dry $O_2$ into the solution of 1-D. The $^2$H NMR spectra of 1-D (solid line) and 1-D exposure to dry $O_2$ (dotted line).

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