

Supplementary Information

Mononuclear $[\text{Ni}^{\text{II}}(\text{L})(\text{P}-\text{o-C}_6\text{H}_4\text{S})_2(\text{o-C}_6\text{H}_4\text{SH})]^{0/1-}$ ($\text{L} = \text{Thiolate, Selenolate, PPh}_3$, and Cl) Complexes with Intramolecular [Ni - S - H - S]/[Ni - H - S] Interactions Modulated by the Coordinated Ligand L: Relevance to the [NiFe] Hydrogenases

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Fig S1. ^1H NMR spectra of $[\text{Ni}^{\text{II}}(\text{PPh}_3)(\text{P}(\text{o-C}_6\text{H}_4\text{S})_2(\text{o-C}_6\text{H}_4\text{-SCH}_3))]^-$ (**8**) with variable temperature (δ 1.820 at -60 to 2.109 ppm at 60 in $\text{C}_4\text{D}_8\text{O}$).

Fig S2. ORTEP drawing and labeling scheme of $[\text{Ni}^{\text{II}}(\text{SePh})(\text{P}(\text{o-C}_6\text{H}_4\text{S})_2(\text{o-C}_6\text{H}_4\text{-SCH}_3))]^-$ anion (**10**).

Fig S1. ^1H NMR spectra of $[\text{Ni}^{\text{II}}(\text{PPh}_3)(\text{P}(o\text{-C}_6\text{H}_4\text{S})_2(o\text{-C}_6\text{H}_4\text{-SCH}_3))]$ (**8**) with variable temperature (δ 1.820 at -60 to 2.109 ppm at 60 in $\text{C}_4\text{D}_8\text{O}$).

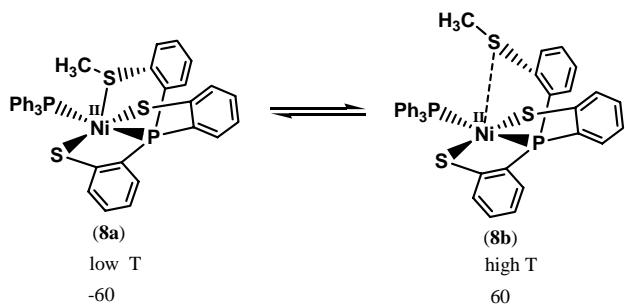
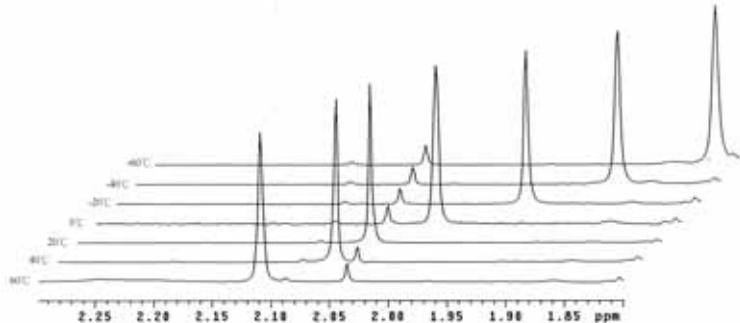


Fig S2. ORTEP drawing and labeling scheme of $[\text{Ni}^{\text{II}}(\text{SePh})(\text{P}(o\text{-C}_6\text{H}_4\text{S})_2(o\text{-C}_6\text{H}_4\text{-SCH}_3))]$ (**10**)⁻ anion. Selected bond distances (\AA) and angles (deg): Ni—S(1) 2.2204(5); Ni—S(2) 2.1706(5); Ni—P(1) 2.1019(5); Ni—Se 2.3452(3); Ni—S(3) 3.229(7); S(1)—Ni—S(2) 159.61(3); P(1)—Ni—Se 176.847(17); S(1)—Ni—Se 91.268(14); S(2)—Ni—Se 93.635(14); C(12)—P(1)—Ni 106.74(6); C(18)—P(1)—Ni 110.40(6); C(19)—P(1)—Ni 118.80(6); C(24)—S(3)—C(25) 100.54(9); Ni—S(3)—C(25) 102.55(8).

