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Formation of $[Ni^{III}(\kappa^1\text{-}S_2CH)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]^-$ via CS_2 Insertion into Nickel(III) Hydride Containing $[Ni^{III}(H)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]^-$

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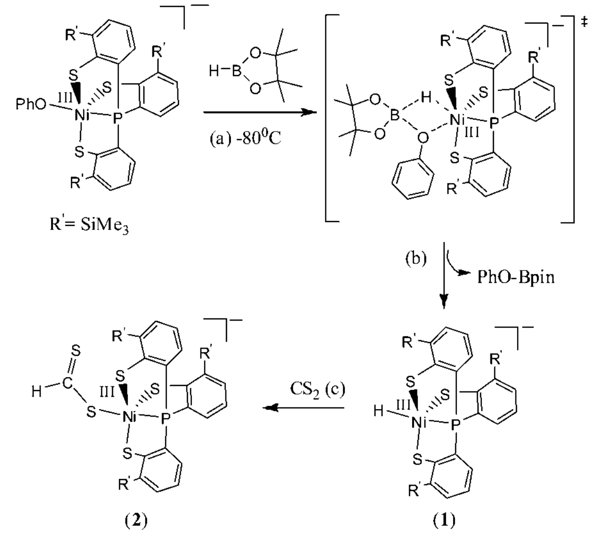
Supporting Information

ABSTRACT: Insertion of CS_2 into the thermally unstable nickel(III) hydride $[PPN][Ni(H)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]$ (**1**), freshly prepared from the reaction of $[PPN][Ni(OC_6H_5)P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3]$ and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin; pin = $OCMe_2CMe_2O$) in tetrahydrofuran at −80 °C via a metathesis reaction, readily affords $[PPN][Ni^{III}(\kappa^1\text{-}S_2CH)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]$ (**2**) featuring a $\kappa^1\text{-}S_2CH$ moiety.

[NiFe] hydrogenase ([NiFe]H_2ase) containing a bimetallic [NiFe] core that is presumed to be the catalytic site for hydrogen activation functions more effectively in the direction of H_2 oxidation.[1−4] The redox-active Ni site was proposed to change between Ni^{III} and Ni^{II}, while the Fe site remains as Fe^{II} in all spectrally defined redox states of the enzyme.[2] The active form Ni−C, an intermediate in the catalytic cycle, of [NiFe]H_2ase was suggested to exist as the $[(S_{cys}H)Ni^{III}(\mu\text{-}SR)_2(\mu\text{-}H)Fe]$ intermediate.[2] Also, X-ray absorption spectroscopy shows that the Ni site of the regulatory hydrogenase (RH) in the presence of hydrogen (RH^{+H_2}), proposed as the Ni−C state, isolated from *Ralstonia eutropha* is a six-coordinate $[Ni^{III}S_2(O/N)_3(H)]$.[3] In the model study, the hydride-containing heterobimetallic $[Ni^{II}(\mu\text{-}H)Fe^{II}]$ $([Ni(\mu\text{-}S(CH_2)_3S)Fe])$ active-site models and hydride-containing bimetallic $[Fe(\mu\text{-}H)(\mu\text{-}pdt)Fe]$ (pdt = 1,3-propanedithiolate) active-site models for the [NiFe] enzymes and [Fe]H_2ase were reported, respectively, recently.[4] Although diverse nickel(II) hydride complexes relevant to the research areas of coordination chemistry and homogeneous catalysis have been well documented,[5] there have been a few reports about the preparation of a $[Ni^{III}H]$-containing complex and no examples of the insertion reaction of small molecule (CS_2) into the Ni^{III}−H bond reported. We are aware that an electrochemical study provided evidence for such a $Ni^{III}H$ species generated by one-electron reduction of a nickel(II) macrocyclic complex accompanied by protonation.[6] Complex $[Ni(psnet)]^+$ {psnet = bis[5-(diphenylphosphino)-3-thiapentanyl]amine} of known structure can stoichiometrically evolve H_2 via the proposed protic oxidation addition to Ni^I, generating $Ni^{III}H$.[7] In this contribution, the reaction of nickel(III) hydride $[PPN][Ni(H)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]$ (**1**) and CS_2, generating $[PPN][Ni^{III}(\kappa^1\text{-}S_2CH)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]$ [**2**; PPN = bis(triphenylphosphoranylidene)ammonium], was described, where complex **1** was prepared by the reaction of $[PPN][Ni(OC_6H_5)P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3]$ and the appropriate hydride donor 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin; pin = $OCMe_2CMe_2O$) in tetrahydrofuran (THF) at −80 °C.

Attempts to prepare complex **1** from $[PPN][Ni(L)P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3]$ (L = OC_6H_5, Cl) with a variety of hydride reagents such as $NaBH_4$, $LiB(Et)_3H$, or $LiAlH_4$ yielded the well-known $[Ni_2^{II}(P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)_2]^{2-}$ as an identifiable product.[8] In contrast to the inertness of $[Ni(SC_6H_5)P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3]^-$ toward HBpin in THF at −80 °C, complex $[Ni(OC_6H_5)P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3]^-$ and 1.3-fold excess of HBpin dissolved in THF were stirred at −80 °C to yield the mononuclear **1** and byproduct PhO-Bpin within less than 30 min (Scheme 1a,b).[9] ^{11}B NMR spectroscopic experiments revealed a broad boron resonance [δ 22.85 (C_6D_6) vs $BF_3{\cdot}OEt_2$; Supporting Information, Figure S1)] that could identify the byproduct PhO-Bpin formed in the $[Ni(OC_6H_5)P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3]^- \rightarrow$ complex **1** conversion.[9]

Scheme 1



Complex **1** is extremely thermally sensitive in solution. At 4 K, complex **1** exhibits a rhombic electron paramagnetic resonance (EPR) spectrum (g = 2.46, 1.96, and 1.92) similar to that (g = 2.44, 2.00, and 1.96) of $[Ni^{III}(CH_3)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]^-$,[10] deviating from complexes $[Ni^{III}(L)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]^-$, displaying EPR signals at g = 2.31, 2.04, and

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1.99 for L = OPh and g = 2.31, 2.09, and 2.00 for L = SEt (77 K),[11] respectively, suggestive of the d^7 Ni^{III} electronic structure (Figure 1a). Monitoring the mixture of $[Ni(OC_6H_5)P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3]^-$ and HBpin in THF by UV−vis spectroscopy revealed a relatively clean conversion of $[Ni(OC_6H_5)P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3]^-$ to complex **1** within 30 min at −80 °C (Figure 2).

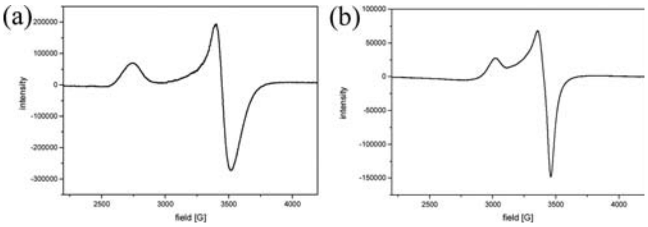

Figure 1. (a) X-band EPR spectrum (g values 2.46, 1.96, and 1.92) of complex **1** in THF at 4 K. (b) X-band EPR spectrum (g values 2.28, 2.03, and 1.99) of complex **2** in THF−CH_3CN (4:1 volume ratio) at 77 K.

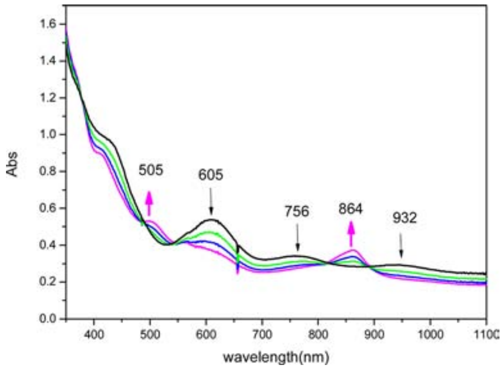

Figure 2. Reaction of $[PPN][Ni(OC_6H_5)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]$ and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (excess) in THF at −80 °C monitored by UV−vis.

As is evidenced by monitoring of the reaction by UV−vis spectroscopy, excess HBpin is required to ensure completeness of the reaction. The increase of the intensity of the absorption bands (505 and 864 nm) and the concomitant decay of the absorption bands (605, 756, and 932 nm) with the presence of isosbestic points indicate the absence of an intermediate during the transformation of $[Ni(OC_6H_5)P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3]^-$ into complex **1**. In comparison with $[Ni^{III}(CH_3)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]^-$ dominated by intense absorption bands at 500 and 825 nm (4:1 volume ratio of THF−CH_3CN),[10] the electronic spectrum of complex **1** coordinated by hydride displays red shifts to 505 and 864 nm (THF). Attempts to detect the ν_{Ni-H} stretching frequency at −80 °C were unsuccessful. Complex **1** exhibits a diagnostic ^1H NMR spectrum with phenyl proton resonances [δ 18.6 (br), 14.5 (br), −10.0 (br)] well-removed from the diamagnetic region at −80 °C. Detection of the signal at a negative chemical shift, which has been interpreted as nickel hydride, was not successful.[5] When a THF solution of complex **1** was stirred above −60 °C, the thermally unstable complex **1** undergoes reductive elimination of the coordinated hydride to yield the well-known $[Ni_2^{II}(P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)_2]^{2-}$ characterized by UV−vis,[8] with concomitant release of H_2 gas identified by milli-Whistle/gas chromatography.[12] With the aid of isotopic experiments, the reaction of a deuterated THF solution of complex **1** and $CDCl_3$ yields the very characteristic $CHDCl_2$ identified by ^1H NMR [δ 5.46 (t, C_4D_8O); SI, Figure S2], and the known $[Ni^{III}(Cl)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]^-$ characterized by UV−vis spectroscopy also supports the existence of complex **1** at −80 °C.[11b] In the present study, the well-characterized complex **1** provides a suitable benchmark toward the synthesis of $[Ni^{III}H]$-containing complexes by means of the metathesis of nickel(III) phenoxide with pinacolborane (HBpin; pin = $OCMe_2CMe_2O$).

In contrast to $NaBH_4$, $LiB(Et)_3H$ or $LiAlH_4$, the transformation of $[Ni(OC_6H_5)P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3]^-$ into complex **1** triggered by HBpin is presumably promoted by the formation of a thermodynamically stable PhO-Bpin bond via the four-center transition state of the metathesis reaction (Scheme 1a,b).[9] That is, PhO-Bpin is generated from the interaction of the lone pair on the phenoxide ligand with the empty p orbital of the B atom of HBpin.[9] A nucleophilic attack of Ni^{III}−H on CS_2 is used to rationalize the preference for the Ni^{III}−H bond to undergo CS_2 insertion, which may also involve a four-center transition state. Despite the high thermodynamic stability of CS_2,[13] it is found that the reaction of complex **1** with CS_2 in THF at −80 °C proceeds to yield green complex **2**, characterized by IR $\nu_{C=S}$, UV−vis, EPR, ^1H NMR, and single-crystal X-ray structure (Scheme 1c). Insertion of CS_2 into the Ni^{III}−H bond of complex **1** yields $[Ni^{III}\text{-}\kappa^1\text{-}S_2CH]$-containing complex **2**, presumably due to the preferential coordination of dithioformate $[S_2CH]^-$ to the Ni^{III} center via the S atom.[11] Consistent with the characteristic g value of $[PPN][Ni(SEt)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]$ (g = 2.31, 2.09, and 2.00),[11] complex **2** displays a rhombic EPR spectrum with g_1 = 2.28, g_2 = 2.03, and g_3 = 1.99 at 77 K (Figure 1b). Further confirmation comes from the presence of the IR $\nu_{as(CS_2)}$ absorption at 1007 cm^{-1} in KBr, assigned to the asymmetric C═S vibration.[13] In comparison with complexes $[PPN][Ni(L)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]$ (L = SEt, SPh) dominated by two intense absorption bands at 577 and 920 nm and 592 and 949 nm, respectively,[11] the electronic spectrum of complex **2** displays a red shift to 604 and 1028 nm. The proton resonances δ 15.7 (br), 10.8 (br), −6.9 (br) (acetone-d_6) were assigned to the $[P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3]^{3-}$ ligand (SI, Figure S3). This result is consistent with the central Ni^{III} possessing a d^7 electronic configuration in a trignoal-bipyramidal ligand field.

To further examine the reactivity of $[Ni^{III}H]$-containing complex **1**, the reaction of **1** and diphenyldisulfide was investigated. The transformation of complex **1** into the known $[Ni^{III}(SPh)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]^-$, characterized by UV−vis and single-crystal X-ray diffraction, was observed when 1 equiv of diphenyldisulfide was added into the THF solution of complex **1**.[11a] In addition, upon the addition of CO gas into the THF solution of complex **1** for 5 h, complex **1** completely transformed into the known $[Ni^{II}(CO)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]^-$, as monitored by UV−vis and IR with a ν_{CO} stretching band [2033 cm^{-1} (KBr)],[11b,14] accompanied by the release of H_2 via reductive elimination.

The structure of the $[Ni^{III}(\kappa^1\text{-}S_2CH)(P(o\text{-}C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)]^-$ unit for complex **2** in $[PPN]^+$ salt is shown in Figure 3. It is noticed that the S5−C64−S4 bond angle of 127.8(2)° is comparable to those [126.4(2)° and 126.8(2)°] of $[Al(OCMeCHCMeNAr)_2(\kappa^1\text{-}S_2CH)]$ and $[Tp^{Ph,Me}Zn(\kappa^1\text{-}S_2CH)]$, respectively.[15] Compared to the C−S bond distance of 1.56 Å in free CS_2,[13] the significantly longer S4−C64 [1.703(2) Å] and S5−C64 [1.645(2) Å] bond lengths reflect that the $[S_2CH]$ ligand of complex **2** acts as a $\kappa^1\text{-}S_2CH$ coordination ligand, as observed in $[Tp^{Ph,Me}Zn(\kappa^1\text{-}S_2CH)]$ [S1−C1 1.694(3) Å and S2−C1 1.623(3) Å].[15b] The Ni1−S4 bond length of 2.261(1) Å

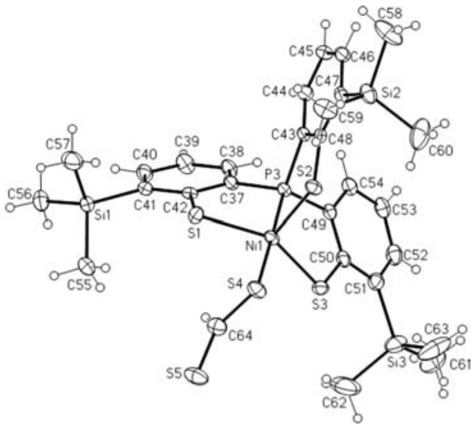

Figure 3. ORTEP drawing and labeling scheme of the **2** anion with thermal ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (deg): Ni1−S4 2.261(1), Ni1−S1 2.247(1), Ni1−S2 2.275(1), Ni1−S3 2.225(1), Ni1−P3 2.126(1), S4−C64 1.703(2), S5−C64 1.645(2); S4−Ni1−P3 178.0(1), S4−Ni1−S1 93.8(1), S4−Ni1−S2 94.4(1), S4−Ni1−S3 91.5(1), S1−Ni1−S2 112.0(1), S2−Ni1−S3 109.7(1), S1−Ni1−S3 137.4(1), S5−C64−S4 127.8(2), C64−S4−Ni1 102.6(1).

falls within the range of 2.246(1)−2.273(1) Å observed in the $[\mathrm{PPN}][\mathrm{Ni(L)(P(}o\text{-}\mathrm{C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3)}]$ (L = SPh, SEt).[11]

In summary, complex $[\mathrm{Ni^{III}(OC_6H_5)P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3}]^-$, inherent with the combination of the electron-deficient $[\mathrm{Ni^{III}P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3}]$ motif and the $[\mathrm{OPh}]^-$ nucleophile, undergoes a HBpin-promoted hydride−phenoxide metathesis reaction to produce the thermally unstable $[\mathrm{Ni^{III}H}]$-containing complex **1**. A comparison of the reactivity of $\mathrm{NaBH_4/LiB(Et)_3H}$ and HBpin highlights the importance of the empty P orbital of the B atom of HBpin in this metathesis reaction, synthesizing $\mathrm{Ni^{III}H}$ complex **1**. Insertion of $\mathrm{CS_2}$ into the $\mathrm{Ni^{III}}$−H bond of complex **1** generates $[\mathrm{Ni^{III}}\text{-}\kappa^1\text{-}\mathrm{S_2CH}]$-containing complex **2**. Our success here in synthesizing $[\mathrm{Ni^{III}H}]$-containing complex **1** may support the existence of an active-site nickel oxidation state of 3+ in $[\mathrm{NiFe}]\mathrm{H_2}$ase.[1−3]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, experimental details concerning the synthesis and characterization of complexes **1** and **2**, EPR experiments, and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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