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Synthetic Designs and Structural Investigations of Biomimetic Ni-Fe Thiolates

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Abstract

Described are the syntheses of several $\text{Ni}(\mu\text{-SR})_2\text{Fe}$ complexes, including hydride derivatives, in a search for improved models for the active site of [NiFe]-hydrogenases. The nickel(II) precursors include (i) nickel with tripodal ligands: $\text{Ni}(\text{PS}_3)^-$ and $\text{Ni}(\text{NS}_3)^-$ (PS_3^{3-} = tris(phenyl-2-thiolato)phosphine, NS_3^{3-} = tris(benzyl-2-thiolato)amine) (ii) traditional diphosphine-dithiolates, including chiral diphosphine *R,R*-DIPAMP, (iii) cationic Ni(phosphine-imine/amine) complexes, (iv) organonickel precursors $\text{Ni}(\text{o-tolyl})\text{Cl}(\text{tmeda})$ and $\text{Ni}(\text{C}_6\text{F}_5)_2$. The following new nickel precursor complexes were characterized: $\text{PPh}_4[\text{Ni}(\text{NS}_3)]$ and the dimeric imino/amino-phosphine complexes $[\text{NiCl}_2(\text{PCH}=\text{N}^{\text{An}})]_2$ and $[\text{NiCl}_2(\text{PCH}_2\text{NH}^{\text{An}})]_2$ ($\text{P} = \text{Ph}_2\text{PC}_6\text{H}_4\text{-2-}$). The iron(II) reagents include $[\text{CpFe}(\text{CO})_2(\text{thf})]\text{BF}_4$, $[\text{Cp}^*\text{Fe}(\text{CO})(\text{MeCN})_2]\text{BF}_4$, $\text{FeI}_2(\text{CO})_4$, $\text{FeCl}_2(\text{diphos})(\text{CO})_2$, and $\text{Fe}(\text{pdt})(\text{CO})_2(\text{diphos})$ (diphos = chelating diphosphines). Reactions of the nickel and iron complexes gave the following new Ni-Fe compounds: $\text{Cp}^*\text{Fe}(\text{CO})\text{Ni}(\text{NS}_3)$, $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-pdt})\text{Ni}(\text{dppbz})]\text{BF}_4$, $[(\text{R,R-DIPAMP})\text{Ni}(\mu\text{-pdt})(\text{H})\text{Fe}(\text{CO})_3]\text{BAR}^{\text{F}}_4$, $[(\text{PCH}=\text{N}^{\text{An}})\text{Ni}(\mu\text{-pdt})(\text{Cl})\text{Fe}(\text{dppbz})(\text{CO})]\text{BF}_4$, $[(\text{PCH}_2\text{NH}^{\text{An}})\text{Ni}(\mu\text{-pdt})(\text{Cl})\text{Fe}(\text{dppbz})(\text{CO})]\text{BF}_4$, $[(\text{PCH}=\text{N}^{\text{An}})\text{Ni}(\mu\text{-pdt})(\text{H})\text{Fe}(\text{dppbz})(\text{CO})]\text{BF}_4$, $[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})_2\text{Ni}]\text{BF}_4$, $[\text{H}[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})_2\text{Ni}]]\text{BF}_4$, and $(\text{C}_6\text{F}_5)_2\text{Ni}(\mu\text{-pdt})\text{Fe}(\text{CO})_2(\text{dppv})$ ($\text{DIPAMP} = (\text{CH}_2\text{P}(\text{C}_6\text{H}_4\text{-2-OMe})_2)_2$; $\text{BAR}^{\text{F}}_4 = [\text{B}(\text{C}_6\text{H}_3\text{-3,5-(CF}_3)_2)_4]^-$). Within the context of $\text{Ni}(\text{-SR})_2\text{-Fe}$ complexes, these new complexes feature new microenvironments for the nickel center: tetrahedral Ni, chirality, imine and amine coligands, and Ni-C bonds. In the case of $[\text{H}[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})_2\text{Ni}]]^+$, four low-energy isomers are separated by 3 kcal/mol, one of which features a biomimetic $\text{HNi}(\text{SR})_4$ site, as supported by DFT calculations.

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Supporting Information

Spectroscopic data, selected reaction schemes, selected procedures.

SUPPORTING INFORMATION

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CCDC 1527147, 1873034, 1873035, 1873036, 1873037, 1873038, 1873039, 1527148 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table of Contents Synopsis and Graphic

The nickel complex of tris(benzy-2-thiolato)amine (NS_3^{3-}) is a robust air-stable tetrahedral nickel thiolate that failed to give suitably reactive active site models. A more traditional [NiFe]-models is the chiral [(*R,R*-DIPAMP)Ni(pdt)(H)Fe(CO) $_3$] $^+$. The iminophosphine and amino-phosphine [NiCl $_2$ (P-N)] complexes are precursors to the bimetallic derivatives [(P-N)Ni(pdt)(Cl)Fe(dppbz)(CO)] $^+$. The organonickel precursors Ni(*o*-tolyl)Cl(tmeda) was used to prepare the basic mixed valence [(dppv)(CO)Fe(μ -pdt)] $_2$ Ni, featuring a tetrahedral NiS $_4$ core. From Ni(C $_6$ F $_5$) $_2$ (dioxane) $_2$ was obtained (C $_6$ F $_5$) $_2$ Ni(pdt)Fe(CO) $_2$ (dppv).

Introduction

[NiFe] hydrogenases are enzymes that catalyze the reversible oxidation of H $_2$, a process that is relevant to the metabolism of many microorganisms.¹ Motivated by the implications of H $_2$ redox and related reactions,² much effort has been expended on replicating the active site of these enzymes.³ Progress in modeling the active site can be measured by the structural similarity of models and the various catalytically significant states. These states include Ni-SI, Ni-R, Ni-L, and Ni-C. Structural models for the first three states have been described although they lack biomimetic terminal ligands. Analysis of models for the Ni(II)-Fe(II)-hydride state, Ni-R, is presented in Figure 1. The figure highlights aspects where synthetic models are deficient or differ strongly from the natural system.

From the synthetic perspective, models either manipulate the Ni site or the Fe site. In this report we continue this approach, emphasizing expanding the range of ligands on nickel. We address, sometimes with only incremental progress, the following deficiencies in modeling: (1) nonplanar Ni(II) sites, (2) the rarity of Ni(SR) $_x$ sites ($x > 2$), (3) the asymmetry of the Ni...H-Fe interactions, and (4) the introduction of exchangeable terminal ligand sites on Ni, specifically those based on Ni-C sigma bonds.

Problems 1 and 2: Nonplanar Ni(II) sites and nonbridging NiSR sites.

The Ni-center in the Ni-SI $_a$ is a distorted tetrahedron with four cysteine-thiolate ligands, two terminal and two bridging. The terminal thiolates are implicated as bases in proton transfer reactions,^{4,5} such as the heterolysis of H $_2$. In the two models with terminal Ni-SR centers, the corresponding hydride derivatives could not be prepared.^{6,7} All Ni(II)-containing models feature square planar or five-coordinate Ni. Thus, one goal in this work focused on incorporating Ni centers with rigidly nonplanar coordination sphere and at least one terminal thiolate.

Problem 3: the Asymmetry of the Ni...H-Fe Interactions.

Several hydride-containing NiFe complexes are known.³ They are all of the type $L_2Ni(SR)_2FeHL_3$. In these models the Fe-H bond is usually⁸ shorter than the Ni-H bond,^{9–12} whereas in the enzyme, the $d_{Ni-H} < d_{Fe-H}$.¹³ The shorter Ni-H distance underscores the role of Ni as the hydride carrier, whereas Fe center serves as a redox-inactive Lewis acid. In this paper, the Ni coordination sphere is manipulated in an effort to strengthen the Ni-H interaction.

Results and Discussion

1. Ni(II) complexes of tripodal PS_3 and NS_3 ligand and their [NiFe] derivatives.

Nonplanar Ni(II) thiolate complexes were targeted several years ago by Liaw, Koch and Millar, and their coworkers.^{14–19} They described several complexes of tripodal phosphine trithiolates^{20,21} (Figure S1), but not the corresponding Ni-Fe derivatives. Our efforts initially focused on the phosphine trithiolates, but quickly turned to amine trithiolates.

Ni(PS_3)- and Ni(NS_3)-Based Models.—Using $P(C_6H_4-2-SH)_3$, Liaw, Millar, and their coworkers described promising nickel precursors with terminal thiolates. Our experiments showed however that in its reactions with iron reagents, $[Ni(PS_3H)PPh_3]$ ¹⁶ (Scheme S1, Figures S2–11) serves as a source of PPh_3 or transfers the PS_3^{3-} chelate to Fe. One solution to the transfer of the PPh_3 involves use of $[Ni(PS_3)]^-$, but this species does not exist *per se*.

In view of the challenges with the $Ni(PS_3)$ -based models, we turned to complexes derived from $N(CH_2C_6H_4-2-SH)_3$, (abbreviated $N(SH)_3$). This tripodal ligand was developed by Koch *et al.*, who characterized the tetrahedral complexes $[M(NS_3)]^-$ ($M = Ga(III), Zn(II), Fe(II)$).^{22–24} Considerable progress has also been reported on the synthesis of $N(SH)_3$.^{25,26} As shown schematically in eq 1, the NS_3 ligand envelops the metal center because it features *six*-membered chelate rings. In contrast the PS_3^{3-} ligands, forming only five-membered chelate rings, leave one site open for coordination of a fifth ligand.²⁰

The complex $[Ni(NS_3)]^-$ was synthesized by combining $[N(SNa)_3]$ with $NiCl_2 \cdot 6H_2O$ in ethanol solution (eq 1).

(1)

The salt $\text{PPh}_4[\text{Ni}(\text{NS}_3)]$ was isolated as green crystals. The solid is soluble in polar organic solvents to give air-stable solutions that are intensely green owing to strong absorptions at 477 ($\epsilon = 3800$) and 637 nm ($\epsilon = 1200 \text{ cm}^{-1}\text{M}^{-1}$, Figure S12), consistent with tetrahedral Ni(II). This salt was characterized by X-ray crystallography, ESI-MS, ^1H -NMR spectroscopy, and elemental analyses. Its ^1H -NMR spectrum in CD_2Cl_2 solution spanned from $\delta 300$ to -20 (Figure S13), consistent with the paramagnetic nature of this complex. ESI-MS in negative mode displayed the molecular ion peak (Figure S14).

According to X-ray crystallography, $\text{PPh}_4[\text{Ni}(\text{NS}_3)]$ consists of a pseudo-tetrahedral Ni complex (Figure 2). The S-Ni-S bond angles range from 105 to 136° , perhaps due to the Jahn-Teller distortion arising from the $(e_2)^4(t_2)^4$ configuration. A related $[\text{Ga}(\text{NS}_3)]$ complex exhibited average S-Ga-S and N-Ga-S angles of 115 and 102° , respectively.²² The Ni-N bond length is $\sim 2.03 \text{ \AA}$, whereas the Ni-S bond-lengths range from ~ 2.26 – $2.28 \text{ \AA}$. Solutions of $\text{Ph}_4\text{P}[\text{Ni}(\text{NS}_3)]$ are unreactive toward CO and PPh_3 . In contrast, adducts of the type $[\text{Ni}(\text{PS}_3)\text{CO}]^-$ have been characterized crystallographically.²⁰

To generate Fe-Ni complexes, reactions of $[\text{Ni}(\text{NS}_3)]^-$ with cyclopentadienyl iron complexes were investigated.^{27,28} Treatment of $\text{Na}[\text{Ni}(\text{NS}_3)]$ or $\text{Ph}_4\text{P}[\text{Ni}(\text{NS}_3)]$ with $[\text{CpFe}(\text{CO})_2(\text{thf})]\text{BF}_4$ gave an immediate reaction. The deep brown product exhibited a pair of ν_{CO} bands, shifted by 25 – 30 cm^{-1} to lower energy with respect to the cationic precursor (Figure S15). This initial product is assigned as the 1:1 adduct $\text{Ni}(\text{NS}_3)\text{Fe}(\text{CO})_2\text{Cp}$. Allowing solutions of this adduct to stand in ambient light, the pair of ν_{CO} bands is replaced by a new broad peak at 1952 cm^{-1} . Similar shifts are observed for other $\text{L}_x\text{Ni}(\text{SR})_2\text{Fe}(\text{CO})\text{Cp}$ complexes from (planar) Ni-thiolates and $\text{Cp}(\text{CO})_2\text{Fe}$ -based precursors.²⁶ The positive-ion ESI-mass spectrum of the decarbonylated product (despite its being charge-neutral) shows an intense peak envelope centered at $m/Z = 1173.9$, which corresponds to $[\text{Ni}(\text{NS}_3)\text{Fe}(\text{CO})\text{Cp}]_2$ (Figure S16). The same product was obtained from the reaction of $[\text{Ni}(\text{NS}_3)]^-$ with $[\text{CpFe}(\text{CO})(\text{MeCN})_2]\text{BF}_4$ ($\nu_{\text{CO}} = 2013 \text{ cm}^{-1}$, Figure S17–19). The experimental peak envelope was well simulated with theoretical values. The ^1H NMR spectrum of the product was broad.

Experiments were also conducted on related $\text{Cp}^*\text{Fe}(\text{CO})$ -based complexes ($\text{Cp}^* = \text{C}_5\text{Me}_5$). Being bulky, the Cp^*Fe -based reagent was expected to favor formation of a 1:1 Ni-Fe derivative.²⁹ Indeed, treating a CH_2Cl_2 solution of $[\text{Ni}(\text{NS}_3)]^-$ salts with $[\text{Cp}^*\text{Fe}(\text{CO})(\text{MeCN})_2]\text{BF}_4$ generated a new complex with a single ν_{CO} band shifted to lower energy vs the cationic iron precursor (Figure S20). Based on the relative positions of CO and Cp^* ligands, two stereoisomers are possible (Scheme 1), as have been observed for other Ni(μ -

$\text{SR})_2\text{Fe}(\text{CO})\text{Cp}^*$ complexes.^{30,31} The positive-ESI-mass spectrum shows intense peaks corresponding to M^+ and $[\text{M}-\text{CO}]^+$ (Figure S21). The isotopic distributions for both peak envelopes match simulated spectra (Figure S22, S23).

2. $\text{Ni}(\text{P}_2\text{S}_2) + \text{Fe}(\text{II})$ Reagents

The addition of electrophilic iron reagents to nickel-(diphos)-dithiolates is a traditional route to $\text{Ni}(\text{SR})_2\text{-Fe}$ complexes (diphos = chelating diphosphine ligand).^{3,27} Analogous methods using planar NiN_2S_2 complexes have been well investigated, where $\text{N}_2\text{S}_2^{2-}$ is a tetradentate diaminedithiolate.^{32,33} Relative to NiN_2S_2 , $\text{Ni}(\text{dithiolate})(\text{diphos})$ complexes are advantageous because the geometry at Ni is less restrained, which allows the generation of tetrahedral $\text{Ni}(\text{I})$ derivatives.³

(a) $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-pdt})\text{Ni}(\text{diphosphine})]^+$.—Reinvestigation of Schroeder's synthesis of $[\text{Cp}(\text{CO})\text{Fe}(\text{pdt})\text{Ni}(\text{dppe})]^+$,³⁴ although mainly confirmatory, is briefly described because the stepwise refinement of methodology is instructive. According to Schroeder, the reaction of $\text{Ni}(\text{pdt})(\text{dppe})$ and $\text{CpFe}(\text{CO})_2\text{I}$ gives $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-pdt})\text{Ni}(\text{dppe})]^+$ as well as a considerable amount of $[\text{Ni}_2(\mu\text{-pdt})(\mu\text{-I})(\text{dppe})_2]^+$. The salt $[\text{CpFe}(\text{CO})_2(\text{thf})]\text{BF}_4$ was found to react with $\text{Ni}(\text{pdt})(\text{dppe})$ in a less complicated manner (Scheme 2, Figure S26–27). As revealed by *in situ* ^{31}P NMR spectroscopy, however $[\text{Ni}_2(\mu\text{-pdt})(\mu\text{-Cl})(\text{dppe})_2]^+$ was a byproduct. When performed in THF (Figure S28), the reaction produced $[\text{CpFe}(\text{CO})(\text{dppe})]^+$ as a side product. The lability of the diphosphine was suppressed by replacing $\text{Ni}(\text{pdt})(\text{dppe})$ with $\text{Ni}(\text{pdt})(\text{dppv})$ ($\text{dppv} = \text{cis-1,2-C}_2\text{H}_2(\text{PPh}_2)_2$, Figure S29–32). With this optimized protocol, the reaction $\text{Ni}(\text{pdt})(\text{dppv}) + [\text{CpFe}(\text{CO})_2(\text{thf})]^+$ was found to produce a previously undetected intermediate. With two equally intense ^{31}P NMR signals, this new species is assigned as $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-pdt})\text{Ni}(\text{dppv})]^+$, wherein only one thiolate bridges Ni and Fe.²⁰ The related reaction $\text{Ni}(\text{pdt})(\text{dppbz}) + [\text{CpFe}(\text{CO})(\text{NCMe})_2]^+$ produced high yields of $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-pdt})\text{Ni}(\text{dppbz})]^+$, which was characterized by X-ray crystallography as its BF_4^- salt (Figure 3, S33–S35).

$[(\text{CO})_3\text{Fe}(\text{H})(\mu\text{-pdt})\text{Ni}(\text{R,R-DIPAMP})]^+$.—Another route from $\text{Ni}(\text{dithiolate})(\text{diphos})$ to $\text{Ni}(\text{SR})_2\text{-Fe}$ complexes involves use of $\text{FeI}_2(\text{CO})_4$ as a source of $[\text{FeI}(\text{CO})_3]^+$.¹⁰ This approach was adopted to prepare a complex containing *R,R*-DIPAMP (DIPAMP = 1,2-bis[(2-methoxyphenyl)(phenyl)phosphino]ethane). In addition to being chiral, *R,R*-DIPAMP features 2-methoxyphenyl groups, which are suitably positioned to coordinate³⁵ to nickel, although this aspect was not manifested. As summarized in Scheme 3, $\text{NiCl}_2(\text{R,R-DIPAMP})$ was converted to $\text{Ni}(\text{pdt})(\text{R,R-DIPAMP})$. ^{31}P and ^1H NMR spectra confirm the diamagnetic nature of the complex (Figure S36–S37). Treatment of $\text{Ni}(\text{pdt})(\text{R,R-DIPAMP})$ with $\text{FeI}_2(\text{CO})_4$ yielded the corresponding iodo-bridged $[\text{NiFe}]$ complex $[(\text{R,R-DIPAMP})\text{Ni}(\mu\text{-$

$\text{pdt}(\mu\text{-I})\text{Fe}(\text{CO})_3]^+$, which was characterized *in situ* by FTIR spectrum. Reduction of this cationic iodo complex with Cp_2Co generated $(R,R\text{-DIPAMP})\text{Ni}(\mu\text{-pdt})\text{Fe}(\text{CO})_3$, which was also characterized *in situ* by its FT-IR spectrum. Reaction of this reduced species with $\text{H}(\text{OEt}_2)_2\text{BAr}^{\text{F}}_4$ gave $[(R,R\text{-DIPAMP})\text{Ni}(\mu\text{-pdt})(\text{H})\text{Fe}(\text{CO})_3]\text{BAr}^{\text{F}}_4$, which was fully characterized ($\text{BAr}^{\text{F}}_4^- = [\text{B}(\text{C}_6\text{H}_3\text{-3,5-(CF}_3)_2)_4]$, Scheme 3, Figure S36–S41). The pattern of the ν_{CO} bands in the FT-IR spectrum product and the intermediates (Figure 4, Figure S38–39) match those observed for related (achiral) complexes.¹⁰

The crystallographically determined structure of $[(R,R\text{-DIPAMP})\text{Ni}(\mu\text{-pdt})(\text{H})\text{Fe}(\text{CO})_3]\text{BAr}^{\text{F}}_4$ is shown in Figure 5. The Ni-Fe distance is 2.65 Å. The Ni and Fe centers adopt square-pyramidal and pseudo-octahedral geometries, respectively. The Ni-H and Fe-H distances are 1.94(4) and 1.58(4) Å, respectively. ^{31}P -NMR spectrum of $[(R,R\text{-DIPAMP})\text{Ni}(\mu\text{-pdt})(\text{H})\text{Fe}(\text{CO})_3]\text{BAr}^{\text{F}}_4$ exhibited two slightly broad peaks (865.0, 70.2), indicating the P's on Ni are nonequivalent as required by the presence of the chiral diphosphine (Figure S40–S41).

3. $\text{NiCl}_2(\text{N-chelate}) + \text{Fe}(\text{pdt})(\text{CO})_2(\text{diphosphine})$

An established route to nickel-iron dithiolates involves the reaction $\text{NiCl}_2\text{L}_2 + \text{Fe}(\text{pdt})(\text{CO})_2\text{L}'_2$. This method is useful when the corresponding $\text{Ni}(\text{SR})_2\text{L}_2$ building block is not available, as illustrated by Song's synthesis of models containing $\text{Ni}(\text{dppp})^{2+}$ centers ($\text{dppp} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$).³⁶ We applied this approach to the preparation of Ni-Fe complexes with Ni(phosphine-amine/imine) centers. The majority of Ni-Fe-H complexes are derived from nickel diphosphine centers.³ Since NiCl_2 derivatives of P-N ligands tend to be pentacoordinate,³⁷ Ni(PN)-based models were anticipated to adopt novel structures.

[Ni(P-imine)]-Based Models.—This effort focused on complexes of the iminephosphine $\text{PCH}=\text{N}^{\text{An}}$ derived from 2-diphenylphosphinobenzaldehyde and anisidine ($\text{H}_2\text{NC}_6\text{H}_4\text{OMe}$).³⁸ The reaction of equimolar $\text{NiCl}_2(\text{DME})$ and $\text{PCH}=\text{N}^{\text{An}}$ gave a yellow paramagnetic 1:1 complex (DME = 1,2-dimethoxyethane). As shown by X-ray crystallography, the complex is the dimer $[\text{NiCl}_2(\text{PCH}=\text{N}^{\text{An}})]_2$ (Figure 6). It features a pair of pentacoordinate Ni centers with two bridging chloride ligands. This dimeric motif is

well-precedented in other $[\text{NiCl}_2(\text{P-N})]_2$ complexes.^{39–41} The 5-coordinated paramagnetic high-spin nickel(II) centers adopt pseudo square pyramidal geometry ($\tau = 0.26$ ⁴²) with apical phosphines.

The targeted $\text{Ni}(\text{SR})_2\text{Fe}$ complex was prepared by combining $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppbz})$ and $[\text{NiCl}_2(\text{PCH}=\text{N}^{\text{An}})]_2$. When conducted in acetone solution at 0 °C in the presence of NaBF_4 , the reaction gave $[(\text{PCH}=\text{N}^{\text{An}})\text{Ni}(\mu\text{-pdt})\text{ClFe}(\text{dppbz})(\text{CO})]\text{BF}_4$ as the exclusive product (eq 2). With $\nu_{\text{CO}} = 1946 \text{ cm}^{-1}$ (Figure S42), the cation resembles related complexes such as $[(\text{dppe})\text{Ni}(\mu\text{-pdt})\text{ClFe}(\text{dppe})(\text{CO})]^+$.⁴³ The (+)-ESI-mass spectrum displayed peak envelopes for both the molecular ion ($[\text{M}]^+$) and $[\text{M-CO}]^+$ (Figure S43). The ^{31}P -NMR spectrum exhibits three doublet of doublets (Figure S44). Signals at $\delta 67.7$ and 72.6 are assigned to the FeP centers, and that at $\delta 19.4$ is assigned to the NiP centers. Three nonequivalent phosphine sites indicates that the diphosphine on Fe is apical-basal, as is observed in other complexes of the type $[(\text{diphos})\text{Ni}(\mu\text{-pdt})\text{ClFe}(\text{diphos})(\text{CO})]^+$.⁸ The ^1H -NMR spectrum is well resolved (Figure S45).

The reduced complex $(\text{PCH}=\text{N}^{\text{An}})\text{Ni}(\mu\text{-pdt})\text{Fe}(\text{dppbz})(\text{CO})$ was obtained by treating $[(\text{PCH}=\text{N}^{\text{An}})\text{Ni}(\mu\text{-pdt})\text{ClFe}(\text{dppbz})(\text{CO})]\text{BF}_4$ with Cp^*_2Co . Yellow solids that precipitated from the reaction solution are presumed to be salts of $[\text{Cp}^*_2\text{Co}]^+$. The targeted $(\text{PCH}=\text{N}^{\text{An}})\text{Ni}(\mu\text{-pdt})\text{Fe}(\text{dppbz})(\text{CO})$ was isolated as a brown solid, which is soluble in THF, toluene, and CH_2Cl_2 . In the IR spectrum of this $[\text{Ni}^{\text{I}}\text{Fe}^{\text{I}}]$ derivative, ν_{CO} appears at 1919 cm^{-1} vs 1946 cm^{-1} for $[(\text{PCH}=\text{N}^{\text{An}})\text{Ni}(\mu\text{-pdt})\text{ClFe}(\text{dppbz})(\text{CO})]\text{BF}_4$ (Figure S46). The ^{31}P -NMR spectrum revealed three new sets of peaks, indicating that the diphosphine on Fe is apical-basal (Figure S47).

(3)

Protonation of $(\text{PCH}=\text{N}^{\text{An}})\text{Ni}(\mu\text{-pdt})\text{Fe}(\text{dppbz})(\text{CO})$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ yielded the corresponding hydride. This product is characterized by a ν_{CO} band at 1945 cm^{-1} (Figure S49), which is shifted by 26 cm^{-1} vs its precursor (eq 3). The ^{31}P -NMR spectrum consisted of two sets of three equi-intensity peaks, indicating the presence of two species (Figure S50). ESI-MS in the positive mode displayed peak envelopes for both the molecular ion ($[\text{M}]^+$) and $[\text{M-CO}]^+$ for $[(\text{PCH}=\text{N}^{\text{An}})\text{Ni}(\text{pdt})(\text{H})\text{Fe}(\text{dppbz})(\text{CO})]^+$ (Figure S52–S53). The ^1H -NMR spectrum revealed one hydride peak (triplet) at $\delta -0.7$ (Figure S54). Although the complex is stable in solid state, the hydride signal disappears over a period of days in CD_2Cl_2 solution. We tentatively assigned the product as $[(\text{PCH}=\text{N}^{\text{An}})\text{Ni}(\mu\text{-pdt})(\text{H})\text{Fe}(\text{dppbz})(\text{CO})]\text{BF}_4$; whereas the two set of peaks in ^{31}P -NMR can be attributed to (i) the hydride complex ($\delta 26.8, 91.21, 94.6$), and (ii) the decomposition product ($\delta 19.8, 72.9, 75.8$) in CH_2Cl_2 .

[Ni(P-amine)]-Based Models.—Using method completely analogous to the preceding section, Ni-Fe complexes were pursued with *amino*-phosphines. The required nickel amino-

phosphine precursor was prepared from the phosphine-amine chelate $\text{PCH}_2\text{NH}^{\text{An}}$, which in turn was obtained by borohydride reduction of $\text{PCH}=\text{N}^{\text{An}}$ (Figure S55–S56). Treating $\text{PCH}_2\text{NH}^{\text{An}}$ with $\text{NiCl}_2(\text{DME})$ gave $[\text{NiCl}_2(\text{PCH}_2\text{NH}^{\text{An}})]_2$, isolated in analytical purity as a yellow paramagnetic solid. X-ray crystallography established that the complex is dimeric, consisting of a pair of pentacoordinate Ni centers with bridging chloride ligands (Figure 7).²⁴ The 5-coordinated nickel(II) centers adopt pseudo square pyramidal geometry ($T = 0.13 - 0.17$).

The preparation of the amine-supported Ni-Fe complex followed the method for the aforementioned $(\text{PCH}=\text{N}^{\text{An}})\text{Ni-Fe}$ complex. Combining $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppbz})$ and $[\text{NiCl}_2(\text{PCH}_2\text{NH}^{\text{An}})]_2$ in acetone in the presence of NaBF_4 gave $[(\text{PCH}_2\text{NH}^{\text{An}})\text{Ni}(\mu\text{-pdt})\text{ClFe}(\text{dppbz})(\text{CO})]\text{BF}_4$ in excellent yield (eq 4). The (+)-ESI-mass spectrum displayed peak envelopes for both the molecular ion ($[\text{M}]^+$) and $[\text{M}-\text{CO}]^+$ (Figure S57). Judging from its IR spectrum ($\nu_{\text{CO}} = 1949 \text{ cm}^{-1}$), the cation resembles the analogous $\text{PCH}=\text{N}^{\text{An}}$ complex (Figure S58). The ^{31}P NMR spectrum revealed a single species (3 peaks), showing that the secondary amine coordinates diastereoselectively (Figure S59).

Attempted reduction of $[(\text{PCH}_2\text{NH}^{\text{An}})\text{Ni}(\mu\text{-pdt})\text{ClFe}(\text{dppbz})(\text{CO})]\text{BF}_4$ with Cp^*_2Co produced $[\text{Cp}^*_2\text{Co}]^+$ as well as a large amount of free $\text{PCH}_2\text{NH}^{\text{An}}$, as verified respectively by ^1H and ^{31}P NMR spectroscopy (Figure S61). The formation of free phosphine indicates that the $\text{PCH}_2\text{NH}^{\text{An}}$ does not stabilize the reduced complex. Attempted dehydrohalogenation of $[(\text{PCH}_2\text{NH}^{\text{An}})\text{Ni}(\mu\text{-pdt})\text{ClFe}(\text{dppbz})(\text{CO})]^+$ using with NaOMe also yielded a large amount of free $\text{PCH}_2\text{NH}^{\text{An}}$ (Figure S62).

(4)

4. $\text{NiR}_2 + \text{Fe}(\text{pdt})(\text{CO})_2(\text{diphosphine})$

The modeling of the active site would be facilitated if it were possible to introduce ligands at nickel *after* formation of the $\text{Ni}(\mu\text{-SR})_2\text{Fe}$ or $\text{Ni}(\mu\text{-SR})_2(\mu\text{-H})\text{Fe}$ core. One specific idea was that terminal thiolates could be introduced by protonolysis of Ni-carbon sigma bonds using thiols.^{44,45} $\text{Ni}(\text{SR})_2\text{-Fe}$ complexes with Ni-carbon sigma-bonds are however unknown. To simplify the synthetic chemistry, we chose to focus on nickel aryl complexes.

(a) Ni(tolyl)Cl(tmeda) + Fe(pdt)(CO)₂(dppv).—Experiments aimed at generating Ni-aryl substituents entailed reaction of Fe(pdt)(CO)₂(dppv) and NiCl(2-tolyl)(tmeda) (tmeda = tetramethylethylenediamine).^{46,47} With a labile diamine ligand, this Ni complex was expected to serve as a source of Ni(C₆H₄-2-Me)Cl. In practice, the reaction proved more complicated. Chromatographic work-up reliably gave yields of ~30% of [(dppv)(CO)Fe(μ-pdt)]₂Ni, isolated as a chocolate brown, air-stable solid (eq 5).

(5)

This complex is one of several with the Fe(SR)₂Ni(SR)₂Fe core.^{27,48} The distinctive aspect of our Fe(SR)₂Ni(SR)₂Fe complex is that the constituent metals are not all divalent. The metal centers have a collective formal charge of 4+. The tetrahedral geometry of the Ni center is appropriate for Ni(0) or Ni(I), leading to descriptions of the complex as Fe(1.5)Ni(I)Fe(1.5) or Fe(II)Ni(0)Fe(II). The Fe(1.5)Ni(I)Fe(1.5) description is favored because the ν_{CO} band at 1914 cm⁻¹ is within 3 cm⁻¹ of that for (dppv)(CO)Fe(μ-pdt)Ni(dppv), which we had previously assigned as Fe(I)-Ni(I).⁸ The formation of a reduced complex is consistent with NiCl(2-tolyl)(tmeda) functioning as a source of Ni(0) via ligand redistribution and reductive elimination of bitolyl.⁴⁷ The complex undergoes reversible oxidation at -1.2 V.

The complex [(dppv)(CO)Fe(μ-pdt)]₂Ni is C₂-symmetric, consisting of a central [Ni(pdt)₂]²⁺ center attached to a pair of [(dppv)(CO)Fe]⁺ modules (Figure 8). The S-Ni-S angles range from 88 to 138°, with an average of 114°. The two Fe centers are equivalent, as imposed by the crystallographic site symmetry. Counting Ni-Fe bond as a sixth ligand, the Fe centers are pseudo-octahedral, which is also consistent with the SFe-P and P-Fe-C angles. The dppv ligands span apical and basal coordination site on Fe, which is typical for Fe(I)Ni(I) derivatives such as (dppv)(CO)Fe(μ-pdt)Ni(dppv).⁸

The ³¹P NMR spectrum [(dppv)(CO)Fe(μ-pdt)]₂Ni features two broad singlets, assigned to phosphorus centers attached to apical and basal sites on each Fe as observed also for (dppv)(CO)Fe(μ-pdt)Ni(dppv).⁸ Upon warming the sample to 80 °C, the two ³¹P NMR singlets broadened into the baseline, but coalescence was not observed.

The crystallographic structure of [(dppv)(CO)Fe(μ-pdt)]₂Ni matches the low-energy DFT result, although the computed bond distances are about 5% longer than those observed experimentally. The stereochemistry of the (dppv)(CO)Fe(pdt)NiL₂ core for the low energy structures follow structural patterns for related NiFe complexes:⁸ lower energy isomers differ with respect to apical-basal dppv vs basal-basal dppv (6.7 kcal/mol). A structure with planar NiS₄ center is observed only at 12.7 kcal/mol. This planar nickel structure can also be described with a dihedral angle (θ) of 0° between the S1-Ni1-S2 and S1'-Ni1-S2' planes.

High spin (triplet) states are high energy, especially for larger values of θ . Attempts to antiferromagnetically localize spins on metal centers (through the Broken Symmetry approximation) failed. NBO charges on Fe1, Ni, and Fe2 are -0.20 , $+0.61$ and -0.20 , respectively in **1A** and -0.18 , $+0.53$ and -0.18 in **1B**. In other words, Fe centers carry more negative charge than Ni independent of θ . The frontier molecular orbitals are localized almost entirely on metal and sulfur centers. The HOMO is predominantly Fe1-Ni1-Fe2 σ bonding, whereas the LUMO is Fe1-Ni1 and Ni1-Fe2 σ^* antibonding (Figure 9).

With oxidation states assigned as Fe(1.5)Ni(I)Fe(1.5) or Fe(I)Ni(II)Fe(I), [(dppv)(CO)Fe(μ -pdt)]₂Ni has two reducing equivalents and may therefore be expected to protonate. Indeed, as a CH₂Cl₂ solution, the complex reacts with HBF₄ to give the dark purple cation H[(dppv)(CO)Fe(μ -pdt)]₂Ni⁺ (eq 6). This hydride complex was initially identified by its ESI-MS spectrum. The new species features ν_{CO} bands at 1943 and 1961 cm⁻¹ in CH₂Cl₂ solution assigned to unprotonated and protonated FeCO centers, respectively. Like other Ni(SR)₂Fe hydrides, {H[(dppv)(CO)Fe(μ -pdt)]₂Ni}⁺ is an active catalyst for hydrogen evolution from HBF₄, as demonstrated by cyclic voltammetry (Fig. S67–68).

The structure of {H[(dppv)(CO)Fe(μ -pdt)]₂Ni}BF₄ was elucidated by single crystal X-ray diffraction (Figure 9). The connectivity in [(dppv)(CO)Fe(μ -pdt)]₂Ni is retained, however protonation induces Ni to convert from tetrahedral to square planar geometry.⁴⁹ The Fe-H and Ni-H distances are 1.65(4) and 1.82(4) Å, respectively. Such unsymmetrically bridging hydrides are typical for other Ni-Fe hydrides.⁹ The HFe-Ni distance is only slightly elongated (2.5653(9) Å) compared with the neighboring unprotonated Ni-Fe fragment (2.5327(9) Å). The Fe(1)-P and Fe(2)-P distances are almost the same, but the Fe-S distances for unprotonated Fe are 0.05 Å shorter than the ~ 2.28 Å HFe-S distances.

According to ¹H NMR spectra, solutions of {H[(dppv)(CO)Fe(μ -pdt)]₂Ni}⁺ exist as a mixture of three isomers as revealed by three sets of signals in the hydride region (Figure 10). These signals are centered at δ -4.9 (t, $J(\text{H,P}) = 36$ Hz), -6.6 (broad), and -15.5 (s) with respective integrated intensities of 1:1.5:2.5 at room temperature. The broad signal at δ -6.6 sharpens to a singlet at elevated temperatures. The ³¹P NMR spectrum of {H[(dppv)(CO)Fe(μ -pdt)]₂Ni}BF₄ consists of five peaks, which can be assigned to the three isomeric hydrides (Figure S64). The relative intensities of the ¹H and ³¹P NMR signals are mutually consistent. In addition to {H[(dppv)(CO)Fe(μ -pdt)]₂Ni}BF₄, the salt {H[(dppv)(CO)Fe(μ -pdt)]₂Ni}BARF₄ was also prepared. The change in counteranion did not noticeably affect the NMR results, indicating that the isomer distribution is unaffected by ion pairing.

Additional insight into the structures of and relationships between the isomeric hydrides was provided by low temperature NMR studies (Figure S65). Solutions prepared by dissolving crystals of {H[(dppv)(CO)Fe(μ -pdt)]₂Ni}BF₄ in CD₂Cl₂ at -80 °C contain exclusively the isomer with a hydride signal at δ -4.9 . At -80 °C, the ³¹P NMR spectrum consists of four equally intense signals, which are decoalesced daughters of the δ 86 and 72 signals observed in the thermally equilibrated room temperature spectrum. The relative frequencies of these four signals indicate that the splitting does not arise from spin-spin coupling; instead, these signals are assigned to four nonequivalent phosphine sites. Because the cation {H[(dppv)(CO)Fe(μ -pdt)]₂Ni}⁺ is C_s-symmetric, the observation of four signals may be attributed to

frozen conformations of the pdt^{2-} backbones. Upon warming the solution to $-45\text{ }^{\circ}\text{C}$, the four ^{31}P NMR signals coalesce into two broad singlets, which continue to sharpen as the solution is warmed to room temperature. These two singlets are assigned to protonated and unprotonated $\text{Fe}(\text{dppv})(\text{CO})$ sites. These data provide some insight into the slowness of the degenerate hydride (or proton) transfer between two equivalent FeNi sites. Also appearing in the $-45\text{ }^{\circ}\text{C}$ spectrum are three signals in intensity 1:1:2 (the latter intensity from accidental degeneracy), assigned to second isomer. Near room temperature these three signals coalesce into the singlet at $\delta\ 86.8$, indicating again that two $\text{Fe}(\text{dppv})$ sites are equilibrating rapidly on the NMR timescale. At $-15\text{ }^{\circ}\text{C}$ two broad singlets appear at low field, assigned to a third isomer. These signals appear concomitant with the appearance of the hydride signal at $\delta\ 15.5$.

The crystallographic structure for $\{\text{H}[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})]_2\text{Ni}\}^+$ matches the low-energy DFT result. The DFT structure is one of four isomers that are separated by $\sim 3\text{ kcal/mol}$. These isomeric hydrides differ in terms of the stereochemistry of the $\text{Fe}(\text{dppv})(\text{CO})$ site and θ , the dihedral or “twist” angle defined by the S1NiS2 and S3NiS4 planes. All stable isomers feature bridging hydrides. The two lowest-energy isomers are depicted in eq 6 and Figure 12.

(6)

The DFT-calculated chemical shifts of the hydride ligand, δ_H correlate with the twist angle. When $\theta = 0$, $\sim \delta_H - 2$ (e.g., in $[\mathbf{1A}]^+$) vs the observed chemical shift of $\delta - 4.9$. For the isomers with $\theta \sim 60^\circ$, δ_H ranges from $\sim \delta - 9.1$ to -10.2 .

(b) $\text{Ni}(\text{C}_6\text{F}_5)_2(\text{dioxane})_2 + \text{Fe}(\text{pdt})(\text{CO})_2(\text{diphos})$.—The previous experiment using $\text{NiCl}(\text{2-tolyl})(\text{tmeda})$ failed to deliver Ni-Fe complexes with Ni-C sigma bonds. The methodology was revised with a focus on $\text{Ni}(\text{C}_6\text{F}_5)_2(\text{dioxane})_2$, which is known to have labile ether ligands and robust Ni-C bonds.⁵⁰ Indeed, this complex was found to react readily with $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppv})$ to form a ruby-red 1:1 adduct $(\text{C}_6\text{F}_5)_2\text{Ni}(\mu\text{-pdt})\text{Fe}(\text{CO})_2(\text{dppv})$ (eq 7, Figure S66–69).

(7)

The ^{31}P and ^{19}F NMR data are consistent with a C_s -symmetric Ni-Fe complex with a square planar Ni center and octahedral Fe site (Figure S68–69). X-ray crystallographic characterization confirms these findings (Figure 13).

Summary and Conclusions

Many properties of the active site of the [NiFe]-hydrogenases remain to be simulated with models (Fig. 1). Addressing these gaps requires the development of new and the evolution of established synthetic methods. This report describes both approaches to complexes with $\text{Ni}(\mu\text{-SR})_2\text{Fe}$ cores.

The boldest approach to active site models entailed the use of the tetrahedral $[\text{Ni}(\text{NS}_3)]^-$ building block. The starting complex $[\text{Ni}(\text{NS}_3)]^-$ is a remarkable example of a robust, air-stable tetrahedral nickel(II) thiolate. Many nickel tri- and tetrathiulates are known, including the iconic $[\text{Ni}(\text{SPh})_4]^{2-}$,⁵¹ but they are either exchange-labile, oligomerize, or both.⁵² The complex $[\text{Ni}(\text{NS}_3)]^-$ was deployed in an attempt to approximate the geometry of the $\text{Ni}(\text{SR})_4$ site, as seen in the enzyme. One barrier to producing $\text{Ni}(\text{SR})_2\text{-Fe}$ ensembles, suggested by the formation of tetrametallic complexes with $[\text{Ni}(\text{NS}_3)]_2\text{Fe}_2$ cores, is the wide S-Ni-S angle in $[\text{Ni}(\text{NS}_3)]^-$. An associated deficiency in this Ni-containing building block is that the Ni center exhibits no Lewis acidity, which is a requirement for Ni(II)-Fe(II) models.

The active sites of the hydrogenases are chiral owing to the asymmetric distribution of ligands around the metal centers. Using chiral ancillary ligands, e.g. *R,R*-DIPAMP, represents one method to impose asymmetry. The twisting introduced by the C_2 -symmetric ligand is not however transmitted to the geometry at the Ni site, which adopts a planar NiS_2P_2 coordination sphere. Furthermore, neither the Ni center nor the hydride exhibited any affinity for the methoxy substituent. In the enzyme, water is assumed to bind to Ni(II) and especially Ni(III).⁴ The work does however demonstrate the utility of chiral ligands to probe the stereodynamics of $\text{Ni}(\text{SR})_2\text{-Fe}$ models. In a related modelling effort, phosphine-imine and phosphine-amine ligands were installed in rare examples of models with Ni-N bonds.

The final phase of this study examined nickel-aryl reagents. The original idea was to introduce alkyl/aryl ligands that would be susceptible to protonolysis by thiols. In one case, this approach afforded the first $\text{Ni}(\text{SR})_4$ -hydrides. As active site models, these NiFe_2 complexes have incorrect metal stoichiometry. Nonetheless DFT calculations support the existence of Fe-H-Ni(SR)₄ centers where the geometry at Ni approaches that in the enzyme.¹³ The preparation of Fe-H-Ni(SR)₄ centers with terminal thiolates remains an unsolved challenge.

Experimental

General.—Literature procedures were followed for the preparation of $\text{P}(\text{SH})_3$ from thiophenol.⁵³ For the preparation of $\text{N}(\text{SH})_3$, $\text{N}(\text{CH}_2\text{C}_6\text{H}_4\text{-2-Br})_3$ was prepared using aqueous ammonia method,²⁶ followed by lithiation and sulfidation.^{54,55} PCH=N^{An} was prepared by a modification of the published route,⁵⁶ as described in the Supporting Information. The complexes $\text{Ni}(\text{pdt})(\text{dppe})$, $\text{Ni}(\text{pdt})(\text{dppv})$, and $\text{Ni}(\text{pdt})(\text{dppbz})$ were

prepared from the corresponding $\text{NiCl}_2(\text{diphosphine})$ by treatment with propanedithiol and two equiv of NaOMe in a mixture of CH_2Cl_2 and MeOH. The following organometallic reagents were prepared according to literature procedures: $[\text{CpFe}(\text{CO})_2(\text{thf})]\text{BF}_4$,⁵⁷ $[\text{CpFe}(\text{CO})(\text{MeCN})_2]\text{BF}_4$ and $[\text{Cp}^*\text{Fe}(\text{CO})(\text{MeCN})_2]\text{BF}_4$,⁵⁸ $\text{NiCl}_2(\text{DME})$,⁵⁹ $\text{Fe}(\text{dppv})(\text{CO})_2\text{Cl}_2$,⁶⁰ $\text{FeI}_2(\text{CO})_4$,⁶¹ and $\text{Ni}(\text{C}_6\text{F}_5)_2(\text{dioxane})_2$.⁵⁰ $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppv})$ and $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppbz})$ were prepared as we previously described.⁶² Efforts to improve the yields were fruitless. Other methods have been described recently.⁶³

$\text{Ph}_4\text{P}[\text{Ni}(\text{NS}_3)]$.—A solution of NaOMe (0.216 g, 4 mmol) in MeOH (10 mL) was added to a slurry of $[\text{NH}(\text{SH})_3]^+\text{Cl}^-$ (0.420 g, 1 mmol), also in MeOH (20 mL). The resulting homogeneous solution of $\text{N}(\text{SNa})_3$ was allowed to stir for 30 min. before being evaporated. A solution of this white residue in 10 mL of EtOH was treated with a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.240 g, 1 mmol) in 10 mL of EtOH. The color of the solution immediately changed to dark green. After 1 h, solvent was removed, leaving a green-colored residue of $\text{Na}[\text{Ni}(\text{NS}_3)]$. Alternatively, addition of Ph_4PBr (0.630 g, 1.5 mmol) to the dark green $\text{Na}[\text{Ni}(\text{NS}_3)]$ solution precipitated a green solid. Yield: 662 mg (85%). X-ray quality crystals of $\text{Ph}_4\text{P}[\text{Ni}(\text{NS}_3)]$ were obtained from vapor diffusion of pentane into CH_2Cl_2 solution of the complex at -30°C . ^1H NMR (500 MHz, CD_2Cl_2): δ -11.50, -10.85, 7.70, 7.95, 8.05, 13.33, 19.40, 96.99, 287.43. ^{31}P NMR (202 MHz, CH_2Cl_2): δ 23.58. ESI-MS (negative, CH_2Cl_2): 437.9965 ($[\text{M}]^-$, 100%). UV-Vis (CH_2Cl_2): $\lambda = 373$ nm ($\epsilon = 6367 \text{ cm}^{-1}\text{M}^{-1}$), 435 ($\epsilon = 3681$), 477 ($\epsilon = 3766$), 637 ($\epsilon = 1185$). Anal. Calcd for $\text{C}_{46}\text{H}_{40}\text{Cl}_2\text{NNiPS}_3$ [$\text{Ph}_4\text{P}[\text{Ni}(\text{NS}_3)]$ CH_2Cl_2 (found): C, 63.98 (64.08); H, 4.67 (4.71); N, 1.62 (1.81).

$[\text{Ni}(\text{NS}_3)\text{Fe}(\text{CO})_2\text{Cp}]$ and $[\text{Ni}(\text{NS}_3)\text{Fe}(\text{CO})\text{Cp}]_2$.—A solution of $\text{Na}[\text{Ni}(\text{NS}_3)]$ (0.462 g, 1 mmol) (or $\text{Ph}_4\text{P}[\text{Ni}(\text{NS}_3)]$ (0.779 g, 1 mmol)) in 15 mL of THF was treated with a solution of $[\text{CpFe}(\text{CO})_2(\text{thf})]\text{BF}_4$ (0.336 g, 1 mmol) in 15 mL of THF. The resulting dark brownish solution was stirred for 2 h. Addition of pentane to the reaction mixture precipitated $[\text{Ni}(\text{NS}_3)\text{Fe}(\text{CO})_2\text{Cp}]$ as a brown solid (IR (THF): $\nu_{\text{CO}} = 2046, 2002 \text{ cm}^{-1}$). A THF solution of this crude product was stirred for a few days in daylight. Vapor diffusion of pentane into the THF solution of the complex yielded crude $[\text{Ni}(\text{NS}_3)\text{Fe}(\text{CO})\text{Cp}]_2$. This complex was purified by extraction into CH_2Cl_2 . The filtered extract was evaporated to dryness to yield the desired product. This $[\text{Ni}(\text{NS}_3)\text{Fe}(\text{CO})\text{Cp}]_2$ complex can also be synthesized upon reaction between $\text{Na}[\text{Ni}(\text{NS}_3)]$ (0.462 g, 1 mmol) (or $\text{Ph}_4\text{P}[\text{Ni}(\text{NS}_3)]$ (0.779 g, 1 mmol)) and $[\text{CpFe}(\text{CO})(\text{MeCN})_2]\text{BF}_4$ (0.318 g, 1 mmol) in 20 mL of CH_2Cl_2 . After 1 day, the solution was filtered, and the filtrate was evaporated, leaving a residue of $[\text{Ni}(\text{NS}_3)\text{Fe}(\text{CO})\text{Cp}]_2$. Low quality crystals could be obtained by layering a CH_2Cl_2 solution of the complex with pentane in an NMR tube at room temperature. Yield: 441 mg (75%). IR (CH_2Cl_2): $\nu_{\text{CO}} = 1957 \text{ cm}^{-1}$. ESI-MS (positive, CH_2Cl_2): 1173.9290 ($[\text{M}]^+$, 100%). Anal. Calcd for $\text{C}_{57}\text{H}_{52}\text{Cl}_6\text{Fe}_2\text{N}_2\text{Ni}_2\text{O}_2\text{S}_6$ [$[\text{Ni}(\text{NS}_3)\text{Fe}(\text{CO})\text{Cp}]_2 \cdot 3\text{CH}_2\text{Cl}_2$] (found): C, 47.84 (47.52); H, 3.66 (3.46); N, 1.96 (1.67).

$\text{Ni}(\text{NS}_3)\text{Fe}(\text{CO})\text{Cp}^*$.—A solution of $\text{Na}[\text{Ni}(\text{NS}_3)]$ (0.462 g, 1 mmol) (or $\text{Ph}_4\text{P}[\text{Ni}(\text{NS}_3)]$ (0.779 g, 1 mmol)) in 15 mL of CH_2Cl_2 was treated with a solution of $[\text{Cp}^*\text{Fe}(\text{CO})(\text{MeCN})_2]\text{BF}_4$ (0.388 g, 1 mmol) in 15 mL of CH_2Cl_2 . After being stirred for 24 h, the reaction solution was filtered, and the filtrate was evaporated to leave a brown residue.

Yield: 461 mg (70%). IR (CH₂Cl₂): ν_{CO} = 1954, 1925 cm⁻¹. ESI-MS (CH₂Cl₂): 657.0421 ([M]⁺, 100%), 629.0474 ([M-CO]⁺, 77%). Anal. Calcd for C₃₆H₄₁Cl₈FeNNiOS₃ [[Ni(NS₃)Fe(CO)Cp*]·4CH₂Cl₂] (found): C, 43.32 (43.28); H, 4.14 (4.34); N, 1.40 (1.92).

Reaction of [CpFe(CO)₂(thf)]BF₄ with Ni(pdt)(dppe).—A solution of [CpFe(CO)₂(thf)]BF₄ (0.336 g, 1 mmol) in 15 mL of CH₂Cl₂ was added to a solution of Ni(pdt)(dppe) (0.563 g, 1 mmol) in 25 mL of CH₂Cl₂. The reaction mixture was stirred for 72 h and then filtered. Dilution of the filtrate with pentane precipitated a mixture of [Cp(CO)Fe(μ-pdt)Ni(dppe)]BF₄ and [Ni₂(μ-pdt)(μ-Cl)(dppe)₂]BF₄, which were identified spectroscopically. ³¹P NMR (202 MHz, CH₂Cl₂): 856.58, 56.95, 57.81; IR (CH₂Cl₂): ν_{CO} = 1953 cm⁻¹. X-ray quality crystals of [Cp(CO)Fe(μ-pdt)Ni(dppe)]BF₄ were obtained by vapor diffusion of pentane into CH₂Cl₂ solution of the mixture. When the reaction was repeated using THF in place of CH₂Cl₂, the pentane-precipitate was a mixture of [Cp(CO)Fe(μ-pdt)Ni(dppe)]BF₄ and [CpFe(CO)(dppe)]BF₄, which were identified spectroscopically. ¹H NMR (500 MHz, CH₂Cl₂): 82.51 – 2.67 (2H, m), 2.67 – 2.82 (2H, m), 4.75 (5H, s), 7.11 – 7.22 (4H, m), 7.45 (4H, d, *J* = 6.71), 7.48 – 7.64 (12H, m). ³¹P NMR (202 MHz, THF): 892.93. IR (CH₂Cl₂): ν_{CO} = 1980 cm⁻¹.

Reaction of [CpFe(CO)₂(thf)]BF₄ with Ni(pdt)(dppv).—A solution of [CpFe(CO)₂(thf)]BF₄ (0.336 g, 1 mmol) in 15 mL of CH₂Cl₂ was added into a solution of Ni(dppv)(pdt) (0.561 g, 1 mmol) in 25 mL of CH₂Cl₂. After stirring for 3 days, the mixture was filtered, and the filtrate was diluted with pentane to precipitate a mixture of [Cp(CO)Fe(μ-pdt)Ni(dppv)]BF₄ and [Ni₂(pdt)(μ-Cl)(dppv)₂]BF₄, which were identified spectroscopically. ³¹P NMR (202 MHz, CH₂Cl₂): 864.61, 65.97, 66.58, 59.07. The last two signals are assigned to [Cp(CO)Fe(μ-pdt)Ni(dppv)]BF₄ and [Ni₂(pdt)(μ-Cl)(dppv)₂]BF₄, respectively. When the same reaction was repeated in THF, the exclusive product precipitated with pentane was [Cp(CO)Fe(μ-pdt)Ni(dppv)]BF₄. Yield: 558 mg (70%). ³¹P NMR (202 MHz, THF): δ 64.6 (major), 66.0, 66.6. (weak) IR (THF): ν_{CO} = 1946 cm⁻¹.

[Cp(CO)Fe(μ-pdt)Ni(dppbz)]BF₄.—A solution of [CpFe(CO)(MeCN)₂]BF₄ (0.032 g, 0.1 mmol) in 5 mL of THF was added into a solution of Ni(pdt)(dppbz) (0.061 g, 0.1 mmol) in 5 mL of THF. As the reaction mixture stirred for 24 h, green solid precipitated. X-ray quality crystals were grown by vapor diffusion of pentane into CH₂Cl₂ solution of the salt at -29 °C. Yield: 72 mg (85%). ³¹P NMR (202 MHz, CH₂Cl₂): 856.4 (major), 57.3 (small peak, may be due to a stereoisomer based on the position of Cp and CO) IR (CH₂Cl₂): ν_{CO} = 1953 cm⁻¹. ESI-MS (positive, CH₂Cl₂): 759.0300 ([M]⁺), 731.0234 ([M-CO]⁺). Anal. Calcd for C_{39.5}H₃₆BClF₄FeNiOP₂S₂ [[Cp(CO)Fe(μ-pdt)Ni(dppbz)]BF₄]·0.5CH₂Cl₂] (found): C, 53.33 (53.8); H, 4.08 (4.52).

NiCl₂(*R,R*-DIPAMP).—A slurry of NiCl₂·6H₂O (0.65 mmol, 85 mg) and *R,R*-DIPAMP (0.65 mmol, 300 mg) in 5 mL of EtOH was heated at reflux for 15 min. After cooling the mixture to 0 °C, an orange solid precipitated. The solid product was washed with EtOH and Et₂O. Yield: 360 mg (94%). Anal. Calcd for C_{28.2}H_{28.4}Cl_{2.4}NiO₂P₂ [NiCl₂(*R,R*-DIPAMP)·0.2 CH₂Cl₂] (found): C, 55.98 (55.97); H, 4.73 (4.6).

Ni(pdt)(*R,R*-DIPAMP).—A suspension of NiCl₂(*R,R*-DIPAMP) (0.61 mmol, 360 mg) and 1,3-propanedithiol (0.61 mmol) in CH₂Cl₂ was treated dropwise with a solution of NaOMe (1.22 mmol) in 1 mL of MeOH. The resulting mixture was stirred for 30 min. Solvent was removed, and the residue was extracted into CH₂Cl₂. The extract was filtered through a pad of Celite and then evaporated to afford Ni(pdt)(*R,R*-DIPAMP) as a brown-red solid. Yield: 350 mg (92%). ¹H NMR (500 MHz, CD₂Cl₂) δ 8.33 (s, 4H), 7.58 (s, 6H), 7.38 (t, *J* = 7.7 Hz, 2H), 6.99 – 6.79 (m, 6H), 3.39 (s, 6H), 2.41–2.35 (m, 4H), 2.30–2.25 (m, 2H), 2.24–2.20 (m, 2H), 1.89 (q, *J* = 6.0 Hz, 2H). ³¹P NMR (202 MHz, CD₂Cl₂): δ 53.4 (s).

[(*R,R*-DIPAMP)Ni(μ-pdt)(H)Fe(CO)₃]BAr^F₄.—At –80 °C, a stirred mixture of FeI₂(CO)₄ (236 mg, 0.56 mmol) and Ni(pdt)(*R,R*-DIPAMP) (350 mg, 0.56 mmol) was treated with 7 mL of CH₂Cl₂, resulting in a dark brown homogeneous solution. After 2 min, the IR spectrum of the mixture showed ν_{CO} = 2094, 2076, 2050 and 2021 cm^{–1}, consistent with the formation of the μ-iodo intermediate [(*R,R*-DIPAMP)Ni(μ-pdt)(I)Fe(CO)₃]⁺. The cold reaction mixture was treated with 2 equiv (212 mg, 1.12 mmol) of Cp₂Co. The reaction solution became dark green. After stirring for 1 h at room temperature, the reaction mixture was evaporated, and the resulting green solid was washed with MeCN. The solid was extracted into 5 mL of CH₂Cl₂, and the extract was filtered through Celite. The CH₂Cl₂ solution was evaporated, leaving (*R,R*-DIPAMP)Ni(μ-pdt)Fe(CO)₃ as a green solid. Yield: 215 mg (50%). ¹H NMR (500 MHz, CD₂Cl₂): δ 7.78 (s, 6H), 7.37 (s, 8H), 7.13 – 6.73 (m, 4H), 3.67 (s, 6H), 2.62 (s, 2H), 2.43–2.27 (m, 4H), 2.05 – 1.61 (m, 4H). ³¹P NMR (202 MHz, CD₂Cl₂): δ 60.0 (s). IR (CH₂Cl₂): ν_{CO} = 2024, 1950 cm^{–1}. A stirred solution of (*R,R*-DIPAMP)Ni(μ-pdt)Fe(CO)₃ (100 mg, 0.13 mmol) in 3 mL of CH₂Cl₂ was treated with H(OEt₂)₂BAr^F₄ (121 mg, 0.12 mmol). An immediate color change from green to red was observed. The solution was concentrated to ~ 1 mL. The concentrate was layered with pentane and cooled to –20 °C to give [(*R,R*-DIPAMP)Ni(μ-pdt)(H)Fe(CO)₃]BAr^F₄ as red colored solid. Yield: 82 mg (42%). ³¹P NMR (202 MHz, CD₂Cl₂): δ 66.8 (br. s). ¹H NMR (500 MHz, CD₂Cl₂): δ –3.06 (s, 1H, hydride). IR (CH₂Cl₂): ν_{CO} = 2078, 2016 cm^{–1}. Anal. Calcd for C₆₇H₄₉Cl₂BF₂₄FeNiO₅P₂S₂ [(*R,R*-DIPAMP)Ni(μ-pdt)(H)Fe(CO)₃]BAr^F₄·CH₂Cl₂] (found): C, 46.99 (47.31); H, 2.88 (2.89).

[NiCl₂(PCH=N^{An})]₂.—A slurry of NiCl₂(DME) (0.220 g, 1 mmol) in 15 mL of CH₂Cl₂ was added into a stirred solution of PCH=N^{An} (0.395 g, 1 mmol) in 20 mL of CH₂Cl₂. After 2 h, the solution was concentrated to 10 mL. Dilution with pentane gave yellow-brown crystals. X-ray quality crystals were obtained upon layering a CH₂Cl₂ solution of the complex with pentane. Yield: 420 mg (80%). Anal. Calcd for C₅₃H₄₆Cl₆N₂Ni₂O₂P₂ [[NiCl₂(PCH=N^{An})]₂·CH₂Cl₂] (found): C, 56.09 (55.87); H, 4.09 (3.81); N, 2.47 (2.49).

PCH₂NH^{An}.—To a solution of PCH=N^{An} (0.490 g, 1.24 mmol) in 30 mL of MeOH at 0 °C was added NaBH₄ (0.180 g, 4.76 mmol) over the course of a few minutes. After the addition was complete, the reaction mixture was stirred for 15 min. The reaction mixture was treated with aqueous 1M NaOH solution (5 mL). The mixture was extracted into CH₂Cl₂. After drying the extract over MgSO₄, solvent was removed leaving a colorless oil. Yield: 443 mg (90%). ³¹P NMR (202 MHz, CD₂Cl₂): δ –15.88 (s). ¹H NMR (500 MHz, CD₂Cl₂): 3.74 (s,

3H), 4.48 (d, 2H), 6.41 (d, 2H), 6.72 (d, 2H), 6.95 (t, 1H), 7.21 (t, 1H), 7.29 – 7.38 (m, 12 H), 7.53 (q, 1H).

[NiCl₂(PCH₂NH^{An})]₂.—A slurry of NiCl₂(DME) (0.110 g, 0.5 mmol) in 15 mL of CH₂Cl₂ was added into a solution of PCH₂NH^{An} (0.199 g, 0.5 mmol) in 20 mL of CH₂Cl₂. From the initially homogeneous solution precipitated a yellow solid. The reaction was continued for 2 h before the solid was collected by filtration. This compound is insoluble in CH₂Cl₂ but soluble in THF. X-ray quality crystals were obtained upon vapor diffusion of pentane into THF solution of the complex at room temp. Yield: 210 mg (80%). Anal. Calcd for C₅₃H₅₀Cl₆N₂Ni₂O₂P₂ [[NiCl₂(PCH₂NH^{An})]₂·CH₂Cl₂] (found): C, 55.89 (56.33); H, 4.42 (5.00); N, 2.46 (2.44).

[(PCH=N^{An})Ni(μ-pdt)ClFe(dppbz)(CO)]BF₄.—A slurry of [NiCl₂(PCH=N^{An})]₂ (0.050 g, 0.05 mmol) in 10 mL of acetone was treated with a solution of NaBF₄ (0.017 g, 0.15 mmol) in 10 mL of acetone followed by a slurry of Fe(pdt)(CO)₂(dppbz) (0.066 g, 0.1 mmol) also in 10 mL of acetone. The mixture immediately became dark brown. After stirring the mixture for 2 h at 0 °C, solvent was removed under vacuum. The solid residue was extracted into CH₂Cl₂, and this extract was filtered through glass wool. The filtrate was evaporated to give a brown-colored solid. Crystals were obtained from vapor diffusion of pentane into a CH₂Cl₂ solution of the salt at –30 °C. Yield: 115 mg (95%). IR (CH₂Cl₂): ν_{CO} = 1946 cm^{–1}. ESI-MS (positive, CH₂Cl₂): 1124.1044 [M]⁺, 1096.1278 [MCO]⁺. ³¹P NMR (202 MHz, CH₂Cl₂): 872.66 (dd, 1P, Fe-P), 67.80 (dd, 1P, Fe-P), 19.43 (dd, 1P, Ni-P). ¹H-NMR (500 MHz, CD₂Cl₂): 87.76–6.54 (overlapping signals, 43H), 3.80 (s, 3H), 3.62 (dt, J = 13.73, 4.58 Hz, 1 H), 2.89 (d, J = 13.73 Hz, 1 H), 2.27 (d, J = 13.73 Hz, 1 H), 2.01 – 2.10 (m, 1 H), 1.92 – 2.01 (m, 1 H), 1.86 (d, J = 7.63 Hz, 1 H). Anal. Calcd for C_{62.5}H₅₇BCl₆F₄FeNNiO₂P₃S₂ [(PCH=N^{An})Ni(μ-pdt)ClFe(dppbz)(CO)]BF₄·2.5 CH₂Cl₂] (found): C, 52.67 (52.39); H, 4.03 (4.2); N, 0.98 (1.0).

[(PCH=N^{An})Ni(μ-pdt)(H)Fe(dppbz)(CO)]BF₄.—A solution of Cp*₂Co (0.066 g, 0.2 mmol) in 5 mL of THF was added into a slurry of [(PCH=N^{An})Ni(μ-pdt)ClFe(dppbz)(CO)]BF₄ (0.121 g, 0.1 mmol) in 5 mL of THF. The resulting mixture was stirred for 2 h at room temperature. The yellow solid precipitate ([Cp*₂Co]Cl/[Cp*₂Co]BF₄) was filtered off. The filtrate was evaporated to dryness to obtain the (PCH=N^{An})Ni(μ-pdt)Fe(dppbz)(CO) as a brown solid. This compound is soluble in THF, toluene, and CH₂Cl₂. IR (CH₂Cl₂): ν_{CO} = 1919 cm^{–1}. ³¹P NMR (202 MHz, THF): 888.35 (dd, 1P, Fe-P), 80.74 (dd, 1P, Fe-P), 36.13 (q, 1P, Ni-P). ¹H-NMR (500 MHz, THF-d⁸): 88.22 – 6.16 (overlapping signals, 43H), 3.49 (s, 3H), 2.17 (m, 1H), 1.92 (m, 1H), 1.84 (m, 1H), 1.66 (m, 1H), 1.13 (m, 1H), 1.04 (m, 1H). Crude (PCH=N^{An})Ni(μ-pdt)Fe(dppbz)(CO) (0.087 g, 0.08 mmol) was dissolved in 10 mL of THF, and HBF₄·Et₂O (11 μL, 0.08 mmol) was added dropwise to this solution. The resulting dark brown mixture was stirred for 2 h. The solvent was evaporated to dryness to obtain [(PCH=N^{An})Ni(μ-pdt)(H)Fe(dppbz)(CO)]BF₄. Crystals were obtained upon vapor diffusion of pentane into CH₂Cl₂ solution of the salt. Yield: 85 mg (90%). IR (CH₂Cl₂): ν_{CO} = 1945 cm^{–1}. ESI-MS (positive, CH₂Cl₂): 1090.1417 [M]⁺, 1062.1503 [M-CO]⁺. ³¹P NMR (202 MHz, THF): 894.47 (1P, Fe-P), 91.58 (1P, Fe-P), 76.78 – 77.30 (2P, Fe-P), 28.01 (d, 1P, Ni-P), 21.50 (t, 1P, Ni-P). ³¹P NMR (202 MHz, CD₂Cl₂): 8 94.55 (1P, Fe-P), 91.01 (1P, Fe-P),

75.83 (0.5P, Fe-P), 72.92 (0.5P, Fe-P), 26.75 (1P, Ni-P), 19.83 (0.5P, Ni-P). ^1H NMR (CD_2Cl_2): $-\text{0.66}$ (t, hydride, 1H). Anal. Calcd for $\text{C}_{61}\text{H}_{55}\text{BCl}_2\text{F}_4\text{FeNNiO}_2\text{P}_3\text{S}_2$ $[(\text{PCH}=\text{N}^{\text{An}})\text{Ni}(\mu\text{-pdt})(\text{H})\text{Fe}(\text{dppbz})(\text{CO})]\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$ (found): C, 57.99 (58.13); H, 4.39 (5.05); N, 1.11 (1.12).

$[(\text{PCH}_2\text{NH}^{\text{An}})\text{Ni}(\mu\text{-pdt})\text{ClFe}(\text{dppbz})(\text{CO})]\text{BF}_4$.—A slurry of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppbz})$ (0.066 g, 0.1 mmol) in 10 mL of acetone was treated with a slurry of $[\text{NiCl}_2(\text{PCH}_2\text{NH}^{\text{An}})]_2$ (0.050 g, 0.05 mmol) in 10 mL of acetone and a solution of NaBF_4 (0.017 g, 0.15 mmol) also in 10 mL of acetone. The solution immediately turned dark brown. The resulting mixture was stirred for 2 h at 0°C . Solvent was removed, and the solid residue was extracted with CH_2Cl_2 . After filtering through glass wool, this extract was evaporated, leaving brown-black solid product. Yield: 110 mg (91%). IR (CH_2Cl_2): $\nu_{\text{CO}} = 1949\text{ cm}^{-1}$. ESI-MS (positive, CH_2Cl_2): 1126.1201 $[\text{M}]^+$, 1098.1071 $[\text{M}-\text{CO}]^+$. ^{31}P NMR (202 MHz, CH_2Cl_2): 874.07 (dd, 1P, Fe-P), 71.43 (dd, 1P, Fe-P), -3.25 (dd, 1P, Ni-P). ^1H -NMR (500 MHz, CD_2Cl_2): 87.82–6.50 (overlapping signals, 42H), 3.89–4.05 (m, 2 H), 3.78 (s, 3H), 3.50 (m, 1 H), 3.04 (m, 1 H), 2.49 (d, $J = 9.16\text{ Hz}$, 1 H), 2.04 (m, 1 H), 1.90 (m, 1 H), 1.44 (m, 1 H), 0.62 (d, $J = 7.63\text{ Hz}$, 1 H). Anal. Calcd for $\text{C}_{61}\text{H}_{56}\text{BCl}_3\text{F}_4\text{FeNNiO}_2\text{P}_3\text{S}_2$ $[(\text{PCH}_2\text{NH}^{\text{An}})\text{Ni}(\mu\text{-pdt})\text{ClFe}(\text{dppbz})(\text{CO})]\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$ (found): C, 56.37 (56.32); H, 4.34 (4.56); N, 1.08 (1.18).

$[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})]_2\text{Ni}$.—To a solution of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppv})$ (1.02 g, 1.66 mmol, 1 equiv) in 10 mL of THF was added a solution of $\text{Ni}(\text{o-tol})\text{Cl}(\text{tmeda})$ (0.50 g, 1.66 mmol, 1 equiv) in 5 mL of THF. The reaction was stirred at room temperature for 8 h. A dark brown solution developed. The solvent was removed under vacuum. The solid residue was extracted into 3 mL of CH_2Cl_2 , and this extract was filtered through a $5 \times 15\text{ cm}$ column of silica gel using additional CH_2Cl_2 as an eluent. The brown-colored band was collected and reduced in volume. Addition of 60 mL of pentane to the concentrated CH_2Cl_2 solution precipitated $[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})]_2\text{Ni}$ as a brown solid. Yield: 0.362 g (35%). Vapor diffusion of pentane into a concentrated solution of $[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})]_2\text{Ni}$ in CH_2Cl_2 gave red-orange prisms suitable for X-ray crystallography. ^1H NMR (500 MHz, C_6D_6): δ 8.34 (br s, 8H), 7.74–7.55 (m, 12H), 7.32 (br s, 8H), 7.11 (m, 4H), 7.03 (m, 8H), 6.97 (m, 4H), 2.16–1.77 (m, 8H), 1.32–1.07 (m, 4H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C_6D_6): δ 100.19 (br s, 2P), 81.51 (br s, 2P). IR (THF): $\nu_{\text{CO}} = 1914\text{ (s) cm}^{-1}$. Anal. Calcd for $\text{C}_{60}\text{H}_{58}\text{Fe}_2\text{NiO}_2\text{P}_4\text{S}_4$: C, 58.42; H, 4.74. Found: C, 57.65; H, 4.44.

$\{\text{H}[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})]_2\text{Ni}\}\text{BF}_4$.—A solution of $[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})]_2\text{Ni}$ (200 mg, $1.62 \times 10^{-4}\text{ mmol}$, 1 equiv) in 4 mL of CH_2Cl_2 was treated with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (22 μL , 26 mg, $1.62 \times 10^{-4}\text{ mol}$, 1 equiv). The mixture was stirred at room temperature for 30 min. A dark red solution developed. The solvent was removed under vacuum. The solid residue was washed with dry Et_2O ($3 \times 5\text{ mL}$) and dried under vacuum. Crystals of this were grown by vapor diffusion of pentane into CH_2Cl_2 solutions of the salt at room temperature. Yield: 152 mg (71%). ^1H NMR (500 MHz, CD_2Cl_2 , basal-basal isomer, -60°C): δ 8.27 (ddd, $J = 85, 45, 12\text{ Hz}$, 4H), 7.73 (s, 4H), 7.32 (br s, 8H), 7.64–7.05 (m, 36H), 2.52–1.22 (overlapping signals, 6H), 1.10 (s, 2H), 0.31 (br s, 1H), 0.25 (br s, 2H), -0.28 (br s, 1H), -5.10 (br s, 1H). ^1H NMR (500 MHz, CD_2Cl_2 , mixture of isomers, 20°C): δ 8.56–7.05 (overlapping signals,

40H), 2.48 (m, 0.74 H), 2.04 (t, $J = 13$ Hz, 0.91H). 1.97 (m, 0.44H), 1.75 (m, 2.75H), 1.59 (m, 1.31H), 1.27 (m, 0.8H), 1.15 (m, 0.75H), 1.08 (m, 1.36H), 0.82 (m, 1.63H), 0.51 (m, 0.49H), 0.27 (m, 0.77H), -0.15 (q, $J = 13$ Hz), -4.87 (t, $J = 38$ Hz, 0.15H), -6.67 (br s, 0.23H), -15.50 (s, 0.36H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 20 °C): 895.23 (br s, 2P, apical-basal isomer), 91.49 (br s, 2P, apical-basal isomer), 87.43 (s, 4P, Ni-H), 86.72 (s, 2P, basal-basal isomer), 71.70 (s, 2P, basal-basal isomer). IR (THF): $\nu_{\text{CO}} = 1965, 1943\text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{61}\text{H}_{59}\text{B Cl}_2\text{F}_4\text{Fe}_2\text{NiO}_2\text{P}_4\text{S}_4$: C, 52.17; H, 4.23. Found: C 52.09; H, 4.35. $\{\text{H}[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})_2\text{Ni}]\}\text{BAR}^{\text{F}}_4$ was prepared similarly. ^1H NMR (500 MHz, CD_2Cl_2 , mixture of isomers, 20 °C): δ 8.56–7.05 (overlapping signals, 48H), 2.48 (m, 0.74 H), 2.04 (t, $J = 13$ Hz, 0.91H). 1.97 (m, 0.44H), 1.75 (m, 2.75H), 1.59 (m, 1.31H), 1.27 (m, 0.8H), 1.15 (m, 0.75H), 1.08 (m, 1.36H), 0.82 (m, 1.63H), 0.51 (m, 0.49H), 0.27 (m, 0.77H), -0.15 (q, $J = 13$ Hz), -4.87 (t, $J = 38$ Hz, 0.15H), -6.67 (br s, 0.23H), -15.50 (s, 0.36H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 20 °C): 95.23 (br s, 2P, apical-basal isomer), 91.49 (br s, 2P, apical-basal isomer), 87.43 (s, 4P, Ni-H), 86.72 (s, 2P, basal-basal isomer), 71.70 (s, 2P, basal-basal isomer). IR (THF): $\nu_{\text{CO}} = 1965, 1943\text{ cm}^{-1}$.

$(\text{C}_6\text{F}_5)_2\text{Ni}(\mu\text{-pdt})\text{Fe}(\text{CO})_2(\text{dppv})$.—In the glove box a solution of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppv})$ (370.0 mg, 0.602 mmol) in 30 mL of THF was added dropwise to a stirred solution of $\text{Ni}(\text{C}_6\text{F}_5)_2(\text{dioxane})_2$ (342.5 mg, 0.602 mmol) in 10 mL of THF over 20 min at room temperature. The solution quickly changed from orange to a very dark red. The reaction was judged complete based on ^{31}P NMR measurements. The volume of the reaction mixture was reduced to ~10 mL under vacuum. Addition of 20 mL of pentane to this filtrate produced a bright red powder. Slow diffusion of pentane into a THF solution of the complex resulted in long ruby-red needles. Yield: 480 mg (79%). ^1H NMR (500 MHz, d_8 -THF, 20 °C): δ 8.56–7.05 (overlapping signals, 48H), 2.48 (m, 0.74 H), 2.04 (t, $J = 13$ Hz, 0.91H). 1.97 (m, 0.44H), 1.75 (m, 2.75H), 1.59 (m, 1.31H), 1.27 (m, 0.8H), 1.15 (m, 0.75H), 1.08 (m, 1.36H), 0.82 (m, 1.63H), 0.51 (m, 0.49H), 0.27 (m, 0.77H), -0.15 (q, $J = 13$ Hz), -4.87 (t, $J = 38$ Hz, 0.15H), -6.67 (br s, 0.23H), -15.50 (s, 0.36H). $^{19}\text{F}\{^1\text{H}\}$ NMR (470.4 MHz, d_8 -THF, 20 °C): δ 119.2 (d, $J = 30.8$ Hz, 2F), 120.8 (d, $J = 30.8$ Hz, 2F), 169.75 (t, $J = 20.2$ Hz, 2F), 171.0 (br, 2F), 171.2 (br, 2F). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, d_8 -THF, 20 °C): 870.5 (s, 2P). IR (THF): $\nu_{\text{CO}} = 2059, 1990\text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{43}\text{H}_{28}\text{F}_{10}\text{FeNiO}_2\text{P}_2\text{S}_2$: C, 51.27; H, 2.80. Found: C 50.95; H, 3.00.

X-ray Crystallographic Determinations.—Crystallographic Data for $\text{Ph}_4\text{P}[\text{Ni}(\text{NS}_3)]$, $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-pdt})\text{Ni}(\text{dppbz})]\text{BF}_4$, $[(R,R\text{-DIPAMP})\text{Ni}(\mu\text{-pdt})(\text{H})\text{Fe}(\text{CO})_3]\text{BAR}^{\text{F}}_4$, $[\text{NiCl}_2(\text{PCH}=\text{N}^{\text{An}})]_2$, $[\text{NiCl}_2(\text{PCH}_2\text{NH}^{\text{An}})]_2$, $\{(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})_2\text{Ni}\}$, $\{\text{H}[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})_2\text{Ni}]\}\text{BF}_4$, and $(\text{C}_6\text{F}_5)_2\text{Ni}(\mu\text{-pdt})\text{Fe}(\text{CO})_2(\text{dppv})$ were collected on a Bruker D8 Venture instrument equipped with a four-circle kappa diffractometer and Photon 100 detector. An I μ s microfocus Mo ($\lambda = 0.71073\text{ \AA}$) source was supplied the multi-mirror monochromated incident beam. The samples were mounted on a 0.3 mm loop with the minimal amount of Paratone-N oil. Data were collected as a series of φ and/or ω scans. Data were collected at 100K and integrated and filtered for statistical outliers using SAINT,⁶⁴ and corrected for absorption by multi-scan methods using SADABS⁶⁵ v2014/7. The structures were phased using direct methods or intrinsic phasing methods and then refined with the SHELX software package SHELX-2014–7.⁶⁶

Density Functional Theory (DFT).—Computations were carried out according to the TZVP/B97-D scheme, as implemented in the TURBOMOLE 7.2 programs suite.^{67–69} The pure B97-D functional, which intrinsically accounts for dispersive effects, has been chosen since it proved to reliably reproduce both geometries and reactive behavior of hydrogenase-like models.⁷⁰ The Resolution-of-the-Identity (RI) technique has been used to reduce the computational costs deriving by the treatment of the classical electron-electron repulsive contribution to the total energy.⁷¹ Both low ($S = 0$) and high ($S = 1$) spin forms of [(dppv)(CO)Fe(μ -pdt)]₂Ni have been characterized. With the attempt of localizing opposite spins of the monodeterminant wave function in different parts of the molecule, the Broken Symmetry approximation has been adopted, to detect (eventual) antiferromagnetic spin couplings.⁷² Nuclear magnetic shielding tensors for ¹H NMR chemical shifts were computed according to the Gauge Including Atomic Orbital (GIAO) method^{73,74} on TZVP/BP86 geometries, a very popular scheme for the reproduction of spectroscopic and stereoelectronic features of transition metal complexes relevant to hydrogenases.^{63,75,76}

Supplementary Material

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Figure 1.
Active site of [NiFe]-hydrogenase core in the Ni-R state.

Figure 2. ORTEP (50 % probability) of the anion in PPh₄[Ni(NS₃)]. Ni(1)-N(1), 2.0310(15) Å; Ni(1)-S(1), 2.2621(5) Å; Ni(1)-S(3), 2.2705(5) Å; Ni(1)-S(2), 2.2829(5) Å. Selected angles: N(1)-Ni(1)-S(1): 100.49(4)°; N(1)-Ni(1)-S(3), 101.02(4)°; N(1)-Ni(1)-S(2), 100.83(4)°; S(1)-Ni(1)-S(3), 105.03(2)°; S(1)-Ni(1)-S(2), 136.60(2)°; S(3)-Ni(1)-S(2), 107.36(2)°.

Figure 4.

IR spectra (CH_2Cl_2) of $[(R,R\text{-DIPAMP})\text{Ni}(\mu\text{-pdt})(\text{I})\text{Fe}(\text{CO})_3]\text{I}$ (top), $[(R,R\text{-DIPAMP})\text{Ni}(\mu\text{-pdt})\text{Fe}(\text{CO})_3]$ (middle), and $[(R,R\text{-DIPAMP})\text{Ni}(\mu\text{-pdt})(\text{H})\text{Fe}(\text{CO})_3]\text{BAr}^{\text{F}}_4$ (bottom).

Figure 5.

ORTEP diagram (50 % probability) of $[(R,R\text{-DIPAMP})\text{Ni}(\mu\text{-pdt})(\text{H})\text{Fe}(\text{CO})_3]\text{BARF}_4$ (H atoms were removed for clarity. Selected distances (Å): Ni(1)-H(1): 1.94(4); Fe(1)-H(1): 1.58(4); Ni(1)-Fe(1): 2.6589(5); Ni(1)-S(1): 2.2153(8); Ni(1)-S(2): 2.2174(9); Ni(1)-P(1): 2.1629(8); Ni(1)-P(2): 2.1669(9); Fe(1)-S(1): 2.3119(9); Fe(1)-S(2): 2.3136(8).

Figure 6.

ORTEP diagram (50 % probability) of [Ni Cl₂(PCH=N^{An})]₂; H atoms were removed for clarity Selected distances (Å): Ni(1)-Cl(1): 2.3638(5); Ni(1)-Cl(2): 2.3128(5); Ni(1)-Cl(1): 2.4033(6); Ni(1)-P(1): 2.2842(3); Ni(1)-N(1): 2.074(1).

Figure 7. ORTEP diagram (50 % probability) of $[\text{NiCl}_2(\text{PCH}_2\text{NH}^{\text{An}})]_2$. H atoms were removed for clarity except N-H. Selected distances (Å): Ni(1)-N(1), 2.1173(11); Ni(1)-Cl(2), 2.3065(3); Ni(1)-P(1), 2.3271(4); Ni(1)-Cl(1), 2.3544(3); Ni(1)-Cl(1)1', 2.3584(3).

Figure 8.

ORTEP diagram (50 % probability) of $[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})]_2\text{Ni}$. H atoms were removed for clarity. Selected distances ($\text{\AA}$) [DFT-calculated values]: Fe(1)-Ni(1), 2.4532(3) [2.523]; Fe(1)-P(1), 2.2134(7); Fe(1)-P(2), 2.1871(6); Fe(1)-S(1), 2.2589(6) [2.314]; Fe(1)-S(2), 2.2925(7) [2.271]; Ni(1)-S(1), 2.2459 [2.290]; Ni(1)-S(2), 2.2612 [2.235].

Figure 9.
Frontier MOs of $[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})]_2\text{Ni}$ (isosurface cutoff = 0.05 a.u.).

Figure 10.

ORTEP diagram (50 % probability) of the cation in $\{H[(dppv)(CO)Fe(\mu\text{-pdt})]_2Ni\}BF_4$. H atoms were removed for clarity. Selected distances (Å): Fe(1)-Ni(1), 2.5327(9) [2.572]; Fe(2)-Ni(1), 2.5653(9) [2.598]; Fe(2)-H, 1.65(4) [1.635]; Ni(1)-H, 1.82(4) [1.745]; Fe(2)-S(3), 2.285(1) [2.264]; Fe(2)-S(4), 2.274(1) [2.262]; Ni(1)-S(1), 2.197(1) [2.249]; Ni(1)-S(2), 2.203(1) [2.248]; Ni(1)-S(3), 2.223(1) [2.263]; Ni(1)-S(4), 2.217(1) [2.264].

Figure 11. ^1H -NMR spectra of $\{\text{H}[(\text{dppv})(\text{CO})\text{Fe}(\mu\text{-pdt})]_2\text{Ni}\}\text{BF}_4$ (CD_2Cl_2 solution) providing evidence for three isomers.

Figure 12.

Optimized structures of the low-energy isomers of $\{H[(dppv)(CO)Fe(\mu-pdt)]_2Ni\}^+$. Selected distances ($\text{\AA}$): Fe(2)-H, 1.635 in $[H1A]^+$ and 1.654 in $[H1B]^+$; Ni(1)-H, 1.745 in $[H1A]^+$ and 1.643 in $[H1B]^+$.

Figure 13. ORTEP diagram (50 % probability) of (C₆F₅)₂Ni(μ-pdt)Fe(CO)₂(dppv). H atoms were removed for clarity. Selected distances (Å): Ni(1)-S(1), 2.2596(8); Ni(1)-S(2), 2.2335(8); Fe(1)-S(1), 2.3313(8); Fe(1)-S(2), 2.3313(7); Fe(1)-P(1), 2.2246(8); Fe(1)-P(2), 2.2183(9).

Scheme 1.
Structures proposed for isomers of $\text{Ni}(\text{NS}_3)\text{Fe}(\text{CO})\text{Cp}^*$.

Scheme 2.

Reaction of $\text{Ni}(\text{pdt})(\text{diphos})$ and $[\text{CpFe}(\text{CO})_2(\text{thf})]^+$.

Scheme 3. Synthesis of $[(R,R\text{-DIPAMP})\text{Ni}(\mu\text{-pdt})(\text{H})\text{Fe}(\text{CO})_3]^+$.