Nickel-Iron Dithiolates Related to the Deactivated [NiFe]-Hydrogenases

David Schilter and **Thomas B. Rauchfuss**

Thomas B. Rauchfuss: rauchfuz@illinois.edu

aSchool of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA. Tel: 1-217-333-7355

Abstract

Described herein are preparations of synthetic models for the deactivated Ni(II)Fe(II) states of the [NiFe]-hydrogenases. Iodination of the $S = ½$ species $[(dppe)Ni(pdt)Fe(CO)_3]^+$ afforded the diamagnetic iodo complex $[(dppe)Ni(pdt)IFe(CO)_3]^+$. Crystallographic analysis of this species confirmed the presence of square-pyramidal Ni linked to an octahedral Fe centre. The Ni···Fe separation of 3.018 Å indicated the absence of metal-metal bonding. This complex could be reduced to give $(dppe)Ni(pdt)Fe(CO)_3$ and, in the presence of iodide, decarbonylated to afford $(dppe)Ni(pdt)FeI_2$. Derivatives of the type $[(diphosphine)Ni(dithiolate)XFe(CO)_2L]^+$ (X = Cl, Br, I) were prepared by halogenation of mixed-valence precursors $[(diphosphine)Ni(dithiolate)Fe(CO)_2L]^+$ (diphosphine = dppe, dcpe; L = tertiary phosphine or CO). The $Fe(CO)_2(PR_3)$-containing derivatives are more robust than the related tricarbonyl derivatives. Exploiting this greater stability, we characterised examples of chloride and bromide derivatives. Related fluorides could be prepared by F^- abstraction from BF_4^-. Spectroscopic evidence is presented for the hydroperoxide $[(diphosphine)Ni(dithiolate)(OOH)Fe(CO)_2L]^+$, which was prepared by oxidation of a model for Ni-SU and Ni-SI$_r$ states.

Introduction

Hydrogen processing in Nature is mediated by the hydrogenases (H$_2$ases), a class of enzyme prevalent in anaerobic bacteria.[1] A major subclass of these enzymes, the nickel-iron hydrogenases, is expressed to catalyse the redox reaction $2H^+ + 2e^-$ H$_2$, which is central to the metabolism of certain bacteria and archaea.[2] The [NiFe]-H$_2$ase active site features a Ni(cysteinato)$_4$ centre, two thiolate ligands of which bridge to a Fe(CN)$_2$(CO) fragment (Figure 1). The states of the enzyme are classified according to the identity (or absence) of the bridging ligand X, the oxidation states of the metal centres, and the protonation of two of the four thiolate ligands. Of relevance to this paper, aerobic deactivation of the enzyme affords states in which oxygenic ligands bridge the two metal ions.[3] For example, a Ni(II)(OH)Fe(II) core is observed for (Ni-SI$_r$)$_I$,[4] whereas in the Ni-SU state the divalent metal ions are thought to be bridged by a hydroperoxo ligand.[5] Our attention was thus drawn to the rarity of model compounds featuring Fe(μ-SR)$_2$(μ-X)Ni cores.[6]

Much recent work has focused on synthetic modelling of the [NiFe]-H$_2$ase active sites,[7] no doubt motivated by the increased understanding of the natural systems and hydrogen processing catalysts that such work promises.[8] The Ni(I)Fe(I) models of type (diphosphine)Ni(dithiolate)Fe(CO)$_3$ are of particular interest,[9] as their conjugate acids, the

Correspondence to: Thomas B. Rauchfuss, rauchfuz@illinois.edu.

only synthetic nickel-iron dithiolate hydrides, represent structural and functional models for Ni-R.[10] We have reported a promising procedure for the neutral complexes from the precursors (diphosphine)Ni(dithiolate) and *cis*-[FeI$_2$(CO)$_4$].[11] The Ni(II)Fe(II) intermediate thus generated, tentatively formulated as [(diphosphine)Ni(dithiolate)IFe(CO)$_3$]I, is reduced with CoCp$_2$ to afford the targeted Ni(I)Fe(I) complex. Attempts to isolate the metastable intermediate have been unfruitful, as exemplified by the crystallization of the CO-free species (dcpe)Ni(2,2-dimethyl-1,3-propanedithiolate)FeI$_2$ (dcpe = 1,2-bis(dicyclohexylphosphino)ethane), thought to arise from nucleophilic attack of I$^-$ and concomitant decarbonylation.[11] According to IR spectroscopic data, solutions of the putative iodide salt can also be prepared by treatment of (diphosphine)Ni(dithiolate)Fe(CO)$_3$ with I$_2$, the ensuing heterolysis resulting in the bridging iodo species as its iodide salt. Presented here are syntheses and characterization of bridging halide complexes of type [(diphosphine)Ni(pdt)XFe(CO)$_3$]$^+$ (pdt^{2-} = 1,3-propanedithiolate) as well as substituted derivatives [(diphosphine)Ni(pdt)XFe(CO)$_2$(monophosphine)]$^+$. The work illustrates the radical character of [(diphosphine)Ni(pdt)Fe(CO)$_3$]$^+$ and its participation in atom transfer reactions.

Results

Tricarbonyl Halides [(diphosphine)Ni(pdt)XFe(CO)$_3$]$^+$

As mentioned in the Introduction, halide salts of type [(diphosphine)Ni(pdt)XFe(CO)$_3$]X are unstable towards decarbonylation. In CH$_2$Cl$_2$ solution, the tricarbonyls [(dppe)Ni(pdt)IFe(CO)$_3$]Br([**1I**]I, dppe = 1,2- bis(diphenylphosphino)ethane) and [(dppe)Ni(pdt)BrFe(CO)$_3$]Br [**1Br**]Br were found to convert to (dppe)Ni(pdt)FeI$_2$ and (dppe)Ni(pdt)FeBr$_2$, respectively. IR analysis of these paramagnetic materials indicated the absence of $_{CO}$ bands, with elemental analyses also being consistent with these formulations (see Experimental section). Consequently, our focus shifted to salts of [(diphosphine)Ni(pdt)XFe(CO)$_3$]$^+$ with non-nucleophilic anions. Oxidation of (diphosphine)Ni(pdt)Fe(CO)$_3$ with ferrocenium tetrafluoroborate (FcBF$_4$) furnishes the paramagnetic Ni(II)Fe(I) derivatives [(diphosphine)Ni(pdt)Fe(CO)$_3$]BF$_4$.[12] The salt [(dppe)Ni(pdt)Fe(CO)$_3$]BF$_4$ ([**1**]BF$_4$) reacts with I$_2$ (0.5 equiv.) in CH$_2$Cl$_2$, resulting in a colour change from dark brown to red. The solutions thus formed have $_{CO}$ bands identical to those of [(diphosphine)Ni(dithiolate)Fe(CO)$_3$]/I$_2$ mixtures. Notably, the stretching frequencies ($_{CO}$ = 2097, 2055, 2026 cm^{-1}) are higher than those for the hydride [**1H**]BF$_4$ ($_{CO}$ = 2082, 2024 cm^{-1}), reflecting the poorer -donating ability of the iodo ligand vs the hydride ligand (Figure 2). Furthermore, three $_{CO}$ bands are easily resolved in the IR spectra for these halides, whereas the hydrides exhibit an A-E pattern in the $_{CO}$ region typical of a more symmetrical coordination environment.

The new compound was obtained as an orange powder, analytical data for which were consistent with its formulation as the diamagnetic salt [(dppe)Ni(pdt)IFe(CO)$_3$]BF$_4$ ([**1I**]BF$_4$). The complex cation could be identified by ESI-MS (*m/z* 828.9) and ^{31}P NMR spectroscopy (49.2), the latter confirming its high symmetry. Analogously, iodination of the dcpe-containing species [(dcpe)Ni(pdt)Fe(CO)$_3$]BF$_4$ ([**2**]BF$_4$)[13] afforded the salt [(dcpe)Ni(pdt)IFe(CO)$_3$]BF$_4$ ([**2I**]BF$_4$). The transformations are summarised in Scheme 1.

Structure of (diphosphine)Ni(pdt)IFe(CO)$_3$]$^+$

The solid state structure of [**1I**]BF$_4$ was determined by X-ray crystallography; an ORTEP of the cation is presented in Figure 3. As expected, the complex features Fe and Ni centres bridged by dithiolate and iodo ligands. The intermetallic separation (3.018 Å) is consistent with the absence of metal-metal bonding, which is expected for a Ni(II)Fe(II) system. The Fe coordination environment is approximately octahedral, with the Ni centre being best

described as square-pyramidal, although the long Ni···I distance (2.931 Å) suggests that this apical ligand interacts only weakly with Ni. The iodo ligand is indeed nearer to the Fe centre (2.682 Å) and the situation is similar in the hydride [**1H**]$^+$ (Fe–H, 1.460 Å; Ni–H, 1.637 Å), with which [**1I**]$^+$ is almost isostructural. The related chloro complex [(dppe)Ni(pdt)ClFe(CO)(dppe)]$^+$ has a similar Ni–Fe distance (3.076 Å), with the Cl$^-$ ligand being much closer to the metal centres (Fe–Cl, 2.362 Å; Ni–Cl, 2.668Å) than I$^-$ is in [**1I**]$^{+.10}$ Notably, [(dppe)Ni(pdt)ClFe(CO)(dppe)]$^+$ is prepared from the divalent metal precursors (dppe)NiCl$_2$ and (pdt)Fe(CO)$_2$(dppe), whereas [**1I**]$^+$ is formed by a pathway probably involving I$_2$ homolysis.

Reactivity of [(diphosphine)Ni(pdt)XFe(CO)$_3$]$^+$

Solid [**1I**]BF$_4$ is air-stable, although in CH$_2$Cl$_2$ solution it decomposes over the course of hours even in the absence of air. The $_{CO}$ bands for [**1I**]BF$_4$ rapidly disappear when CH$_2$Cl$_2$ solutions of the compound are treated with NBu$_4$I (1 equiv.), consistent with the formation of the CO-free product (dppe)Ni(pdt)FeI$_2$. This halide-induced decarbonylation is consistent with the instability of the iodide salt [**1I**]I (*vide supra*) and is depicted in Scheme 2. Bromination of [**1**]BF$_4$ using Br$_2$ (0.5 equiv.) or *N*-bromosuccinimide (1 equiv.) affords the bromide derivative [(dppe)Ni(pdt)BrFe(CO)$_3$]BF$_4$ ([**1Br**]BF$_4$). However, in comparison to the iodide complex, the bromide is less stable, decomposition to insoluble CO-free materials being apparent within minutes in CH$_2$Cl$_2$. Also unstable is the chloro species [(dppe)Ni(pdt)ClFe(CO)$_3$]BF$_4$ ([**1Cl**]BF$_4$), which was prepared from [**1**]BF$_4$ and PhICl$_2$ (0.5 equiv.). This trend in the stability of the halide complexes mirrors that observed for the FeX$_2$(CO)$_4$ compounds (X = I, Br, Cl).[14]

Conversion of [**1Br**]BF$_4$ to [**1I**]BF$_4$ (as well as the decomposition product) proceeds in the presence of I$_2$, reflecting the better donor ability of I$^-$ versus Br$^-$. Similarly, the hydride [**1H**]BF$_4$ is completely consumed upon treatment with excess I$_2$, [**1I**]BF$_4$ being the only CO-containing product. A CO-free byproduct is also likely given the lower intensity of the CO bands and the detection of free CO in the headspace. Like [(dppe)Ni(pdt)ClFe(CO)(dppe)]$^+$, [**1Br**]$^+$ and [**1I**]$^+$ are unreactive toward Ag$^+$ salts, behaviour that is often characteristic of bridging halide ligands.[15] The bromo complex [**1Br**]$^+$ also forms from [**1**]$^+$ upon abstraction of Br$^.$ from benzyl bromide.

Dicarbonyl-Phosphine Iodides [(diphosphine)Ni(pdt)IFe(CO)$_2$(PR$_3$)]$^+$

Given the Fe(CN)$_2$(CO) fragment present in the enzyme, it was of interest to prepare derivatives in which of one or more of the carbonyl ligands was replaced by stronger -donor ligands. Similar approaches were previously used by us to obtain the mixed-valence species [(diphosphine)Ni(pdt)Fe(CO)$_2$(PR$_3$)]$^+$, and the hydrides [(diphosphine)Ni(pdt)HFe(CO)$_2$(PR$_3$)]$^+$, models for the Ni-L[12] and Ni-R states,[16] respectively. The tricarbonyl iodide [**1I**]$^+$ reacts only slowly with tertiary phosphines. A more efficient route to the derivatives [(diphosphine)Ni(pdt)IFe(CO)$_2$(PR$_3$)]$^+$ involves radical iodination of the substituted Ni-L models. For example, treatment of [(dppe)Ni(pdt)Fe(CO)$_2$(PPh$_3$)]BF$_4$ (**1a**]BF$_4$)[12] with I$_2$ (0.5 equiv.) in CH$_2$Cl$_2$ afforded [(dppe)Ni(pdt)IFe(CO)$_2$(PPh$_3$)]BF$_4$ ([**1aI**]BF$_4$). The phosphine-substituted iodide exhibits enhanced stability relative to its unsubstituted parent [**1I**]BF$_4$. The product was characterised according to FT-IR, NMR, ESI-MS and analytical data. In particular, ^{31}P NMR spectra of [**1aI**]BF$_4$ in CD$_2$Cl$_2$ feature three resonances, consistent with a basal orientation of the PPh$_3$ ligand. This stereochemistry is also found in the hydride [**1aH**]BF$_4$,[16] but it contrasts that of the precursor [**1a**]BF$_4$, in which the monophosphine is apical.[12] The PCy$_3$-iodo complex salt [(dppe)Ni(pdt)IFe(CO)$_2$(PCy$_3$)]BF$_4$ ([**1bI**]BF$_4$) could be prepared in a similar fashion; selected data for new compounds are presented below (Table 1). Cationic diiron dithiolato halides, exemplified by [Fe$_2$(pdt)Cl(CO)$_6$]$^+$,[15] are also stabilised by phosphine ligands.[17]

The well-resolved ^{31}P NMR spectrum indicates that [**1aI**]BF$_4$ is stereochemically rigid. In contrast, the corresponding hydride is dynamic, resulting from rotation at the Ni(diphosphine) centre. This difference is consistent with Fe-*I* forming a stronger bond to Ni than does Fe-*H*.

Cyclic Voltammetry Studies

The salts [**1I**]BF$_4$, [**1bI**]BF$_4$ and [**2I**]BF$_4$ were studied by cyclic voltammetry. Whereas the oxidation waves for the compounds are complicated, the reductions are more obvious. In the case of [**1I**]BF$_4$, irreversible reduction occurs at −0.99 V, whereas for [**2I**]BF$_4$ the process is partially reversible and occurs at −0.86 V. The hydride analogues [**1H**]BF$_4$ and [**2H**]BF$_4$ are irreversibly reduced at −1.34 and −1.56 V, respectively.[11] Overall, trends in reduction potentials are consistent with the stronger donor ability of H$^-$ versus I$^-$. The ease of reduction of the tricarbonyls [**1I**]$^+$ and [**2I**]$^+$ is consistent with their reduction by cobaltocene (CoCp$_2$), exploited by our group to prepare the neutral species **1** and **2** (Scheme 2).

The PCy$_3$-substituted derivative [**1bI**]BF$_4$ is reduced at −1.43 V, considerably more cathodic that the tricarbonyl parent [**1I**]BF$_4$. Similar shifts (~ −0.4 V) are observed for the mixed-valence salt [**1b**]BF$_4$ relative to [**1**]BF$_4$.[13] As evidenced by ^{31}P NMR spectroscopy, chemical reduction of [**1I**]BF$_4$ and [**2I**]BF$_4$ with CoCp$_2$ (2 equiv.) affords the expected crude mixtures containing the neutral species **1** (63.0) and **2** (80.9 ppm) respectively.

Dicarbonyl-Phosphine Fluorides [(diphosphine)Ni(pdt)FFe(CO)$_2$(PR$_3$)]$^+$

Attempts were made to oxidise the substituted mixed-valence derivatives [**1a**]$^+$ and [**1b**]$^+$ to the 32e$^-$ clusters [**1a**]$^{2+}$ and [**1b**]$^{2+}$, these latter species representing models for the highly electrophilic Ni-SI$_a$ state responsible for H$_2$ heterolysis. However, treatment of [**1a**]BF$_4$ with FcBF$_4$ in CH$_2$Cl$_2$ instead afforded the μ-fluorido species [(dppe)Ni(pdt)FFe(CO)$_2$(PPh$_3$)]BF$_4$ ([**1aF**]BF$_4$), presumably from the abstraction of F$^-$ from BF$_4$$^-$. FT-IR analysis revealed two sets of overlapping $_{CO}$ bands (2063, 2040, 1984, 1977 cm^{-1}), consistent with the presence of two isomers (not uncommon for such pdt^{2-}-bridged systems).[12] The mean $_{CO}$ frequency (2016 cm^{-1}) is slightly higher than that for [**1aCl**]BF$_4$ (2011 cm^{-1}), which is in line with the poorer donor ability of the lighter halido ligands. The identity of [**1aF**]BF$_4$ was further confirmed by ESI-MS (*m*/*z* 955.3) and analytical data. The PCy$_3$ congener [**1bF**]BF$_4$ could be prepared in a similar fashion from [**1b**]BF$_4$.

Attempted Synthesis of Hydroxo- and Hydroperoxo-Bridged Complexes

Several sets of experiments were conducted in an effort to install bridging oxygenic ligands, as seen in the Ni-SI and Ni-SU states of the enzyme. The mixed-valence Ni(II)Fe(I) complexes, e.g. [**1**]$^+$ react with water but not in a rationalizable manner, and no hydroxides could be detected. Thus treatment of a CH$_2$Cl$_2$ solution of [**1**]BF$_4$ with water afforded **1** in ~50% yield according to IR analysis. Sensitive qualitative tests failed to indicate the formation of hydrogen peroxide in the reaction solutions.

Attempts were also made to install peroxo bridging groups. Treatment of a CH$_2$Cl$_2$ solution of the hydride [**1aH**]BF$_4$ with aqueous H$_2$O$_2$ resulting in a colour change from brown to red. The proposed stoichiometry is shown in Scheme 3.

Although we were unable to purify the product, ESI-MS analysis of the red solution allowed for the detection of [(dppe)Ni(pdt)(OOH)Fe(CO)$_2$PPh$_3$]BF$_4$ ([**1aOOH**]$^+$, *m*/*z* 971.3). The IR spectrum exhibited two $_{CO}$ bands (2042, 1981 cm^{-1}) at energies similar to those of the iodo salt [**1aI**]BF$_4$ (2031, 1978 cm^{-1}).

Discussion

Complexes of the type (diphosphine)Ni(dithiolate)Fe(CO)$_2$L represent the most versatile models for the active site of the [NiFe]-hydrogenases, despite their abiological terminal ligation. In previous reports, we have described models for the hydride-containing state Ni-R[9] and the $S = \frac{1}{2}$ state Ni-L.[12] This paper summarises efforts to prepare synthetic models for the Ni-SU and Ni-SI$_r$ states. These enzyme states feature Ni(II)Fe(II) centres bridged by hydroxide and hydroperoxide.[18]

As for other complexes in this series of models, substitution of one CO ligand on Fe by a phosphine ligand enhances the stability of these compounds considerably. The halide-bridged species are not only important precursors to functional models[19] but also represent the closest approach to synthetic analogues of these inactive states. Halide complexes incorporating NiFe nuclei have also been prepared by Bouwman and co-workers.[20] Our attempts to purify hydroxide-, hydroperoxide- and alkoxide-bridged NiFe models have been unsuccessful, although we did detect a hydroperoxide derivative in one case. Derivatives incorporating Ni(II)(OR)(OH)Fe(II), Ni(II)(O)$_2$Fe(II)[21] and Ni(II)(OH)Fe(II) cores[22] have been reported by the Driess and Holm groups, respectively. Metal carbonyl complexes containing hydroperoxide ligands are rare, probably owing to the facility of intramolecular reactions involving CO and the peroxide. As highlighted by Stiebritz and Reiher,[23] the importance of studying O$_2$-induced hydrogenase inhibition cannot be understated, as robust enzyme variants (and their models) represent promising catalysts for hydrogen processing.

Experimental

Unless otherwise stated, all chemicals were purchased from commercial sources and used as received. *N*-Bromosuccinimide was recrystallized from H$_2$O. CD$_2$Cl$_2$ was distilled from CaH$_2$. PhICl$_2$,[24] **1**[25] and **2**[11] were prepared according to the literature methods. All reactions were conducted in an MBraun glovebox equipped with a solvent purification system; the concentrations of O$_2$ and H$_2$O in the N$_2$ atmosphere were typically 1 and 0.2 ppm, respectively. IR spectra of complexes (in CH$_2$Cl$_2$) were recorded on a Perkin-Elmer Spectrum 100 FTIR spectrometer. A Micromass Quattro II spectrometer was used to acquire ESI-MS data for analytes as dilute CH$_2$Cl$_2$ solutions. Analytical data were acquired using an Exeter Analytical CE-440 elemental analyser. NMR spectra were recorded at room temperature on a Varian Unity 500 spectrometer. ^{1}H and ^{31}P{^{1}H} spectra were collected at 500 and 202 MHz, respectively, and chemical shifts are referenced to residual CHDCl$_2$ (5.32 ppm vs TMS for ^{1}H) and external 85% H$_3$PO$_4$ (for 31P). Cyclic voltammetry experiments were carried out in a single compartment glass cell using a CH Instruments CHI630D electrochemical analyser. The working, counter and pseudo-reference electrodes were glassy carbon, platinum and silver, respectively. The analyte (1 mM) and NBu$_4$PF$_6$ (100 mM) were dissolved in CH$_2$Cl$_2$, and potentials (reported here relative to internal Fc/Fc$^+$) were swept at 0.1 Vs^{-1}. Crystallographic data were collected using a Bruker X8 diffractometer equipped with a Cu K source (= 1.54178 Å) and an Apex II detector.

(dppe)Ni(pdt)FeI$_2$

Compound **1** (21.1 mg, 30 μmol) was partially dissolved in CH$_2$Cl$_2$ (0.5 mL) and treated with I$_2$ (3.8 mg, 15 μmol) in CH$_2$Cl$_2$ (1 mL). The solution was stirred for a further 3 days, after which IR analysis indicated complete decarbonylation. Pentane (−28 °C, 15 mL) was added and the mixture allowed to stand at −28 °C for 1 h. The solids were isolated by filtration, washed with pentane (−28 °C, 2 × 2 mL) and dried briefly to afford the title compound as a red-brown powder (24.6 mg, 28 μmol, 94%).

Anal. calcd for $C_{29}H_{30}FeI_2NiP_2S_2$: C, 39.90; H, 3.46; N, 0.00. Found: C, 40.11; H, 3.47; N, 0.50.

(dppe)Ni(pdt)FeBr$_2$

This compound was prepared analogously to the iodo derivative, using Br_2 in place of I_2. Yield: 91%, red-brown powder.

Anal. calcd for $C_{29}H_{30}FeBr_2NiP_2S_2$: C, 44.71; H, 3.88; N, 0.00. Found: C, 44.68; H, 3.98; N, 0.49.

[(dppe)Ni(pdt)IFe(CO)$_3$]BF$_4$ ([1I]BF$_4$)

Compound **1** (21.1 mg, 30 μmol) and FcBF$_4$ (8.2 mg, 30 μmol) were dissolved in CH_2Cl_2 (1 mL) with rapid stirring. After 1 min the solution was treated with I_2 (3.8 mg, 15 μmol) in CH_2Cl_2 (1 mL). The solution was stirred for a further 0.5 min and pentane (−28 °C, 15 mL) was added and the mixture allowed to stand at −28 °C for 1 h. The solids were isolated by filtration, washed with pentane (−28 °C, 2 × 2 mL) and dried briefly to afford the title compound as an orange powder (26.9 mg, 29 μmol, 98%). ^{31}P NMR (CD_2Cl_2, 202 MHz): 49.2. Anal. calcd for $C_{32}H_{30}O_3S_2P_2NiFeIBF_4 \cdot CH_2Cl_2$: C, 39.56; H, 3.22; N, 0.00. Found: C, 39.71; H, 3.09; N, 0.00. ESI-MS: m/z 828.9 [M − BF$_4^-$]$^+$. Orange prismatic single crystals of [**1I**]BF$_4 \cdot 2CH_2Cl_2$ formed upon slow diffusion of pentane vapour into a concentrated CH_2Cl_2 solution of the title compound at −28 °C. One crystal (0.366 × 0.102 × 0.098 mm[3]) was subjected to X-ray diffraction at 193 K. Its space group was determined to be monoclinic *C2/c* with cell parameters: *a* 22.916Å, *b* 17.958 Å, *c* 21.500 Å,   90.00°, 107.87°,   90.00°. Integration of 5113 reflections and solution by direct methods using SHELXTL V6.12[26] afforded a model with R1 = 0.0548 and wR2 = 0.0920.

[(dppe)Ni(pdt)BrFe(CO)$_3$]BF$_4$ ([1Br]BF$_4$)

This compound was prepared analogously to [**1I**]BF$_4$, using Br_2 in place of I_2. Yield: 98%, orange powder. 31P{1H} NMR (CD_2Cl_2, 202 MHz): 59.6 (~18% impurity), 53.4. Anal. calcd for $C_{32}H_{30}O_3S_2P_2NiFeBrBF_4$: C, 44.18; H, 3.48; N, 0.00. Found: C, 44.45; H, 3.40; N, 0.00. ESI-MS: m/z 782.8 [M − BF$_4^-$]$^+$. *N*-Bromosuccinimide (5.3 mg, 30 μmol) can be used in place of Br_2. Treatment with CoCp$_2$ (2 equiv.) in CH_2Cl_2 gave a green solution and IR bands at 2028 and 1952 cm^{-1}, consistent with formation of the neutral species.

[(dppe)Ni(pdt)ClFe(CO)$_3$]BF$_4$ ([1Cl]BF$_4$)

This compound was prepared analogously to [**1I**]BF$_4$, using PhICl$_2$ in place of I_2. Yield: 93%, orange powder.

^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz):   54.5. Anal. calcd for $C_{32}H_{30}O_3S_2P_2NiFeClBF_4$: C, 46.56; H, 3.66; N, 0.00. Found: C, 46.81; H, 3.52; N, 0.00. ESI-MS: m/z 736.8 [M − BF$_4^-$]$^+$.

[(dppe)Ni(pdt)IFe(CO)$_2$(PR$_3$)]BF$_4$

Compound **1** (14.1 mg, 20 μmol) and FcBF$_4$ (5.5 mg, 20 μmol) were dissolved in CH_2Cl_2 (1 mL) with rapid stirring. After 1 min the solution was added dropwise to PR$_3$ (25 μmol) in CH_2Cl_2 (0.5 mL). The solution was stirred for a further 5 min before being treated with I_2 (2.5 mg, 10 μmol) in CH_2Cl_2 (1 mL) with rapid stirring. After 5 min, pentane (−28 °C, 15 mL) was added and the mixture allowed to stand at −28 °C for 1 h. The solids were isolated by filtration, washed with pentane (−28 °C, 2 × 2 mL) and dried briefly to afford the product.

[(dppe)Ni(pdt)IFe(CO)$_2$(PPh$_3$)]BF$_4$ ([1aI]BF$_4$)

Yield: 72%, orange powder. ^{31}P NMR (CD$_2$Cl$_2$, 202 MHz):   48.6 (dd, J_{PP} = 36, 30 Hz), 45.1 (d, J_{PP} = 36 Hz), 42.6 (d, J_{PP} = 30 Hz). Anal. calcd for C$_{49}$H$_{45}$BF$_4$FeINiO$_2$P$_3$S$_2$·0.3CH$_2$Cl$_2$: C, 50.32; H, 3.91; N, 0.00. Found: C, 50.22; H, 3.91; N, 0.00. ESI-MS: m/z 1063.0 [M − BF$_4^-$]$^+$.

[(dppe)Ni(pdt)IFe(CO)$_2$(PCy$_3$)]BF$_4$ ([1bI]BF$_4$)

Yield: 68%, orange powder. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202 MHz):   44.9 (dd, J_{PP} = 36, 24 Hz), 44.2 (d, J_{PP} = 36 Hz), 42.8 (d, J_{PP} = 24Hz). Anal. calcd for C$_{49}$H$_{63}$BF$_4$FeINiO$_2$P$_3$S$_2$: C, 50.33; H, 5.43; N, 0.00. Found: C, 50.09; H, 5.54; N, 0.00. ESI-MS: m/z 1081.2 [M − BF$_4^-$]$^+$.

[(dppe)Ni(pdt)ClFe(CO)$_2$(PR$_3$)]BF$_4$

Compound **1** (14.1 mg, 20 µmol) and FcBF$_4$ (5.5 mg, 20 µmol) were dissolved in CH$_2$Cl$_2$ (1 mL) with rapid stirring. After 1 min the solution was added dropwise to PR$_3$ (25 µmol) in CH$_2$Cl$_2$ (0.5 mL). The solution was stirred for a further 5 min before being treated with PhICl$_2$ (4.1 mg, 15 µmol) in CH$_2$Cl$_2$ (1 mL) with rapid stirring. After 20 min, pentane (−28 °C, 15 mL) was added and the mixture allowed to stand at −28 °C for 1 h. The solids were isolated by filtration, washed with pentane (−28 °C, 2 × 2 mL) and dried briefly to afford the products.

[(dppe)Ni(pdt)ClFe(CO)$_2$(PPh$_3$)]BF$_4$ ([1aCl]BF$_4$)

Yield: 95%, orange powder. ^{31}P NMR (CD$_2$Cl$_2$, 202 MHz):   53.1 (m), 44.7 (m) ppm. Anal. calcd for C$_{49}$H$_{45}$BF$_4$FeClNiO$_2$P$_3$S$_2$: C, 55.54; H, 4.34; N, 0.00. Found: C, 55.59; H, 4.49; N, 0.00. ESI-MS: m/z 1054.9 [M + CH$_2$Cl$_2$ −BF$_4^-$]$^+$, 970.9 [M − BF$_4^-$]$^+$.

[(dppe)Ni(pdt)ClFe(CO)$_2$(PCy$_3$)]BF$_4$ ([1bCl]BF$_4$)

Yield: 92%, orange powder. ^{31}P NMR (CD$_2$Cl$_2$, 202 MHz):   53.7 (m), 51.6 (m) ppm. Anal. calcd for C$_{49}$H$_{63}$BF$_4$FeClNiO$_2$P$_3$S$_2$: C, 54.60; H, 5.89; N, 0.00. Found: C, 54.48; H, 5.99; N, 0.00. ESI-MS: m/z 989.2 [M − BF$_4^-$]$^+$.

[(dppe)Ni(pdt)FFe(CO)$_2$(PPh$_3$)]BF$_4$ ([1aF]BF$_4$)

[**1a**]BF$_4$ (21.2 mg, 20 µmol) in CH$_2$Cl$_2$ (1 mL) was treated with FcBF$_4$ (5.5 mg, 20 µmol) in CH$_2$Cl$_2$ (1 mL) with stirring. After 5 min, pentane (−28 °C, 15 mL) was added and the mixture allowed to stand at −28 °C for 1 h. The solids were isolated by filtration, washed with pentane (2 × 2 mL) and dried briefly to afford the title compound as an orange powder (18.9 mg, 18 µmol, 90%). FT-IR: $_{CO}$ = 2063, 2040, 1984, 1977 cm^{-1}. Anal. calcd for C$_{49}$H$_{45}$BF$_5$FeNiO$_2$P$_3$S$_2$·CH$_2$Cl$_2$: C, 53.23; H, 4.20; N, 0.00. Found: C, 53.27; H, 4.20; N, 0.09. ESI-MS: m/z 955.3 [M −BF$_4^-$]$^+$.

[(dppe)Ni(pdt)FFe(CO)$_2$(PCy$_3$)]BF$_4$ ([1bF]BF$_4$)

This compound was prepared analogously to [**1aF**]BF$_4$, instead using the precursor [**1b**]BF$_4$. Yield = 86%, orange powder. FT-IR: $_{CO}$ = 2051, 2030, 1975, 1961 cm^{-1}. Anal. calcd for C$_{49}$H$_{63}$BF$_5$FeNiO$_2$P$_3$S$_2$·1.2CH$_2$Cl$_2$: C, 51.83; H, 5.67; N, 0.00. Found: C, 51.90; H, 5.76; N, 0.09. ESI-MS: m/z 972.6 [M −BF$_4^-$]$^+$.

Generation of [(dppe)Ni(pdt)OOHFe(CO)$_2$(PPh$_3$)]BF$_4$ ([1aOOH]BF$_4$)

[**1aH**]BF$_4$ (20.5 mg, 20 µmol) in CH$_2$Cl$_2$ (2 mL) was treated with H$_2$O$_2$ (30% aqueous solution, 100 µL, ~900 µmol) and stirred in the absence of light. The dark brown solution

became pale red, with ESI-MS and IR analyses indicating conversion to the new salt. ESI-MS: m/z 971.3 $[M - BF_4^-]^+$.

[(dcpe)Ni(pdt)IFe(CO)$_3$]BF$_4$ ([2I]BF$_4$)

This compound was prepared analogously to [**1**I]BF$_4$, instead using **2** as the precursor. Yield: 72%, orange powder. ^{31}P NMR (CD$_2$Cl$_2$, 202 MHz) : 63.6. Anal. calcd for C$_{32}$H$_{54}$O$_3$S$_2$P$_2$NiFeIBF$_4$: C, 40.84; H, 5.78; N, 0.00. Found: C, p40.78; H, 5.96; N, 0.00. ESI-MS: m/z 853.0 $[M - BF_4^-]^+$.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

References

1. Frey M. ChemBioChem. 2002; 3:153–60. [PubMed: 11921392]

2. Hatchikian EC, Bruschi M, Le Gall J. Biochem Biophys Res Commun. 1978; 82:451–61. [PubMed: 208565]

3. Lacey ALD, Fernández VM, Rousset M, Cammack R. Chem Rev. 2007; 107:4304–30. [PubMed: 17715982]

4. Pandelia ME, Ogata H, Lubitz W. Chem Phys Chem. 2010; 11:1127–40. [PubMed: 20301175]

5. Ogata H, Lübitz W, Higuchi Y. Dalton Trans. 2009:7577–87. [PubMed: 19759926]

6. Ohki Y, Yasumura K, Ando M, Shimokata S, Tatsumi K. Proc Natl Acad Sci. 2010; 107:3994–97. [PubMed: 20147622]

7. Tard C, Pickett CJ. Chem Rev. 2009; 109:2245–74. [PubMed: 19438209] Ohki Y, Tatsumi K. Eur J Inorg Chem. 2011:973–85.Ichikawa K, Matsumoto T, Ogo S. Dalton Trans. 2009:4304–09. [PubMed: 19662307]

8. Lewis NS, Nocera DG. Proc Natl Acad Sci USA. 2006; 103:15729–35. [PubMed: 17043226] Helm ML, Stewart MP, Bullock RM, Rakowski DuBois M, DuBois DL. Science. 2011; 333:863–66. [PubMed: 21836012]

9. Zhu W, Marr AC, Wang Q, Neese F, Spencer DJE, Blake AJ, Cooke PA, Wilson C, Schröder M. Proc Natl Acad Sci. 2005; 102:18280–85. [PubMed: 16352727]

10. Barton BE, Whaley CM, Rauchfuss TB, Gray DL. J Am Chem Soc. 2009; 131:6942–43. [PubMed: 19413314]

11. Carroll ME, Barton BE, Gray DL, Mack AE, Rauchfuss TB. Inorg Chem. 2011; 50:9554–63. [PubMed: 21866886]

12. Schilter D, Nilges MJ, Chakrabarti M, Lindahl PA, Rauchfuss TB, Stein M. Inorg Chem. 2012; 51:2338–48. [PubMed: 22304696]

13. Schilter D, Rauchfuss TB, Stein M. Inorg Chem. 2012; 51:0000.

14. King, RB. Organometallic Syntheses: Transition-Metal Compounds. Academic Press; New York: 1965.

15. Matthews SL, Heinekey DM. Inorg Chem. 2011; 50:7925–27. [PubMed: 21793493]

16. Barton BE, Rauchfuss TB. J Am Chem Soc. 2010; 132:14877–85. [PubMed: 20925337]

17. Haines RJ, de Beer JA, Greatrex R. J Chem Soc, Dalton Trans. 1976:1749–57.

18. Fontecilla-Camps JC, Volbeda A, Cavazza C, Nicolet Y. Chem Rev. 2007; 107:4273–303. [PubMed: 17850165]

19. Carroll ME, Barton BE, Gray DL, Mack AE, Rauchfuss TB. Inorg Chem. 2011; 50:9554–63. [PubMed: 21866886]

20. Verhagen JAW, Lutz M, Spek AL, Bouwman E. Eur J Inorg Chem. 2003; 2003:3968–74.

21. Yao S, Driess M. Acc Chem Res. 2012; 45:276–87. [PubMed: 21875073]

22. Huang D, Holm RH. J Am Chem Soc. 2010; 132:4693–701. [PubMed: 20218565]

23. Stiebritz MT, Reiher M. Chem Sci. 2012; 3:1739.

24. Zhao XF, Zhang C. Synthesis. 2007; 4:551–57.

25. Barton BE, Rauchfuss TB. J Am Chem Soc. 2010; 132:14877–85. [PubMed: 20925337]

26. Sheldrick GM. Acta Cryst. 2008; A64:112–22.
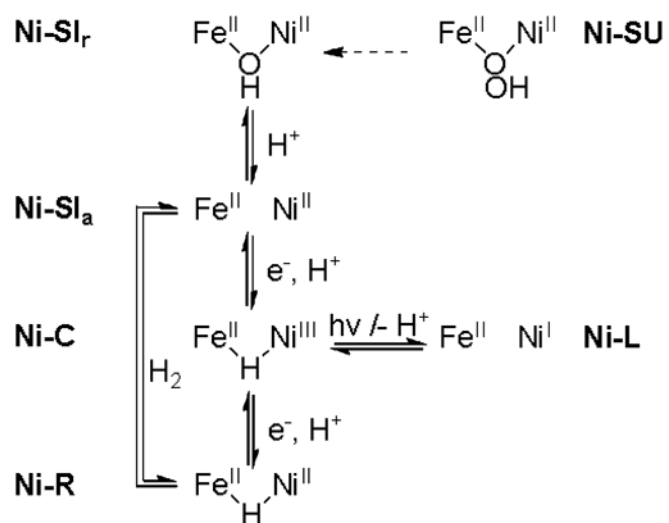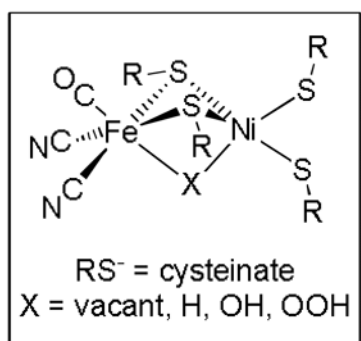
Figure 1.
Schematic of the [NiFe]-H_2ase active site (left) and some of the enzyme states (right).
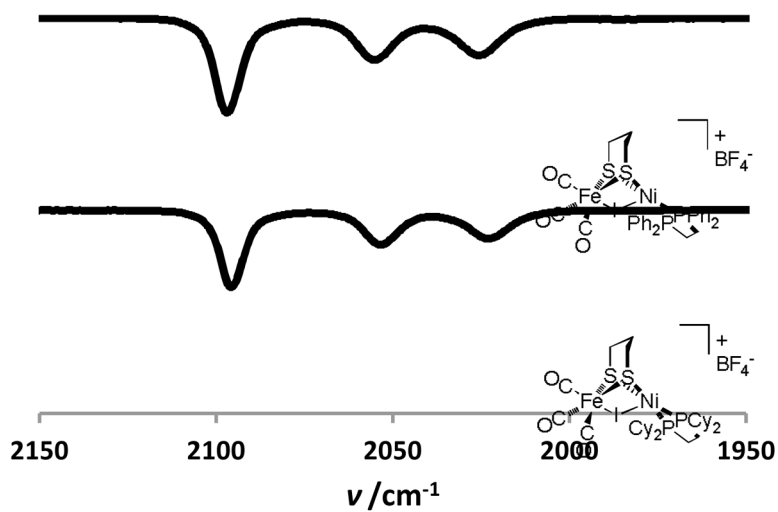
Figure 2.
FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**1I**]BF_4 (top) and [**2I**]BF_4 (bottom).
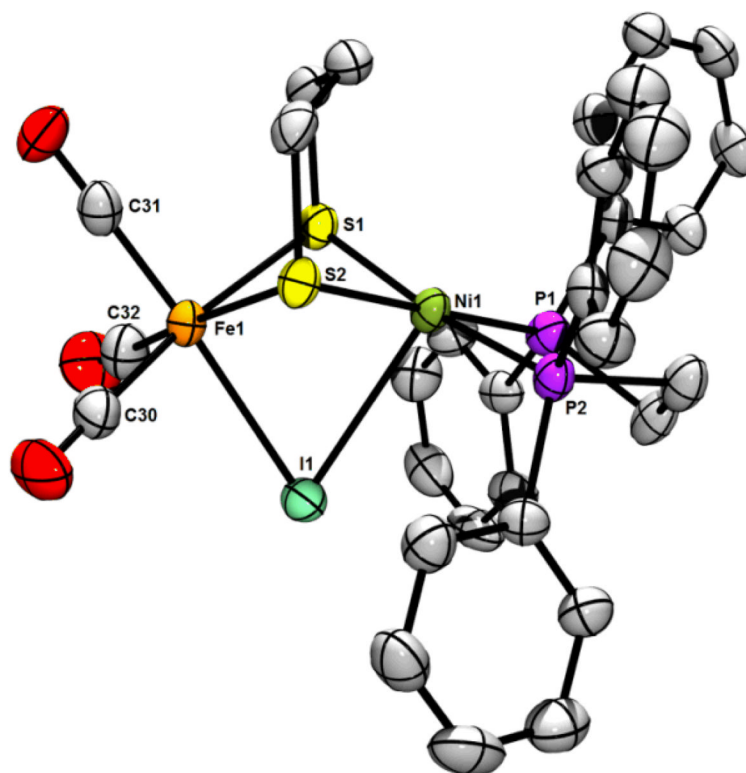
Figure 3.
ORTEP of [**1I**]BF$_4$·2CH$_2$Cl$_2$ with ellipsoids drawn at the 50% probability level. The H
atoms, disordered CH$_2$Cl$_2$ solvate molecules and BF$_4^-$ anion are omitted for clarity.
Selected distances (Å): Ni1–Fe1, 3.018; Ni1–P1, 2.189; Ni1–P2, 2.187; Ni1–S1, 2.240;
Ni1–S2, 2.227; Ni1–I1, 2.931; Fe1–S1, 2.318; Fe1–S2, 2.311; Fe1–I1, 2.682; Fe1–C30,
1.815; Fe1–C31, 1.775; Fe1–C32, 1.836. Selected angles (°): Ni1–I1–Fe1, 64.9.
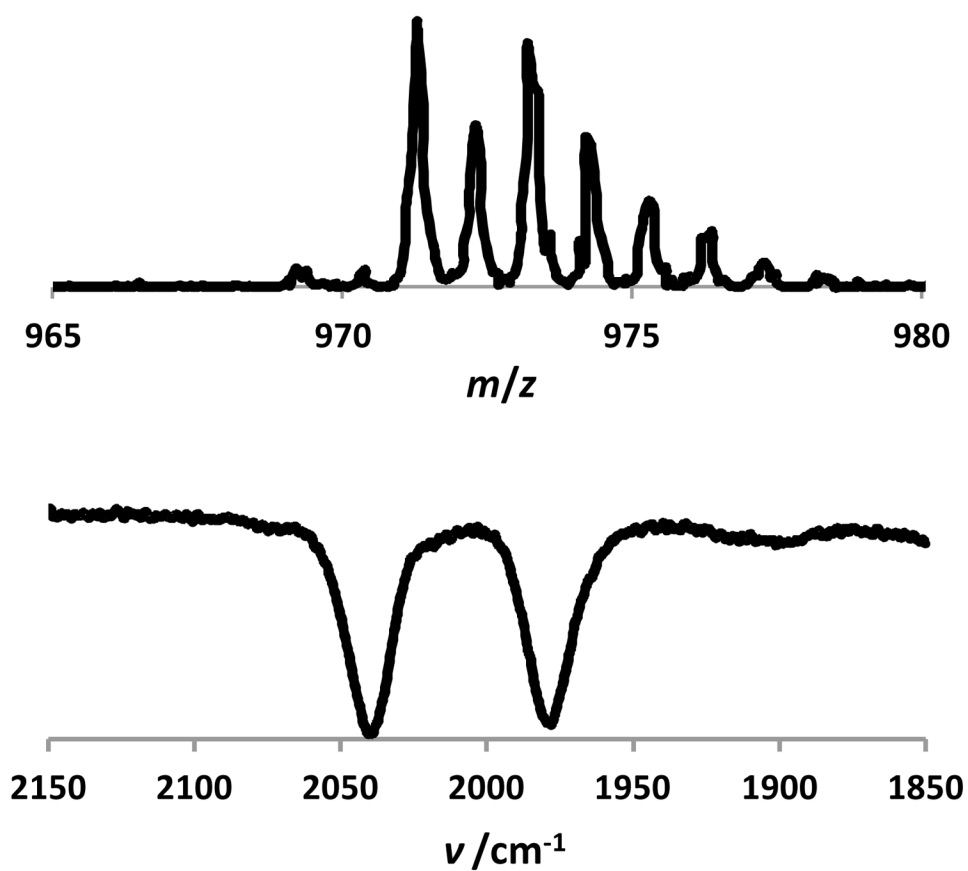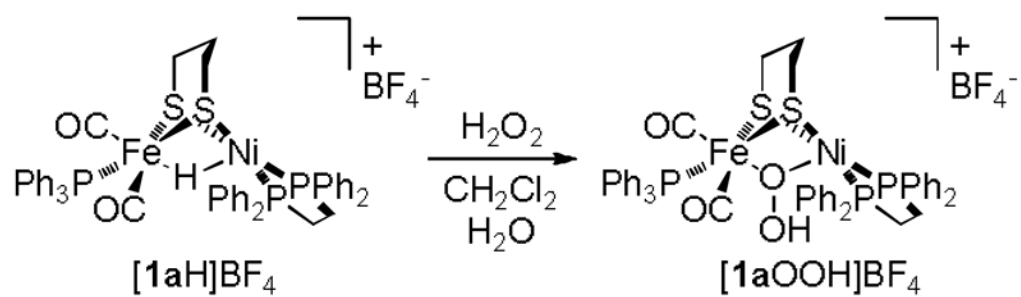
Figure 4.
Positive ion ESI mass spectrum (top) and FT-IR spectrum (ν_{CO} region, CH$_2$Cl$_2$) of [**1**aOOH]BF$_4$ (bottom).
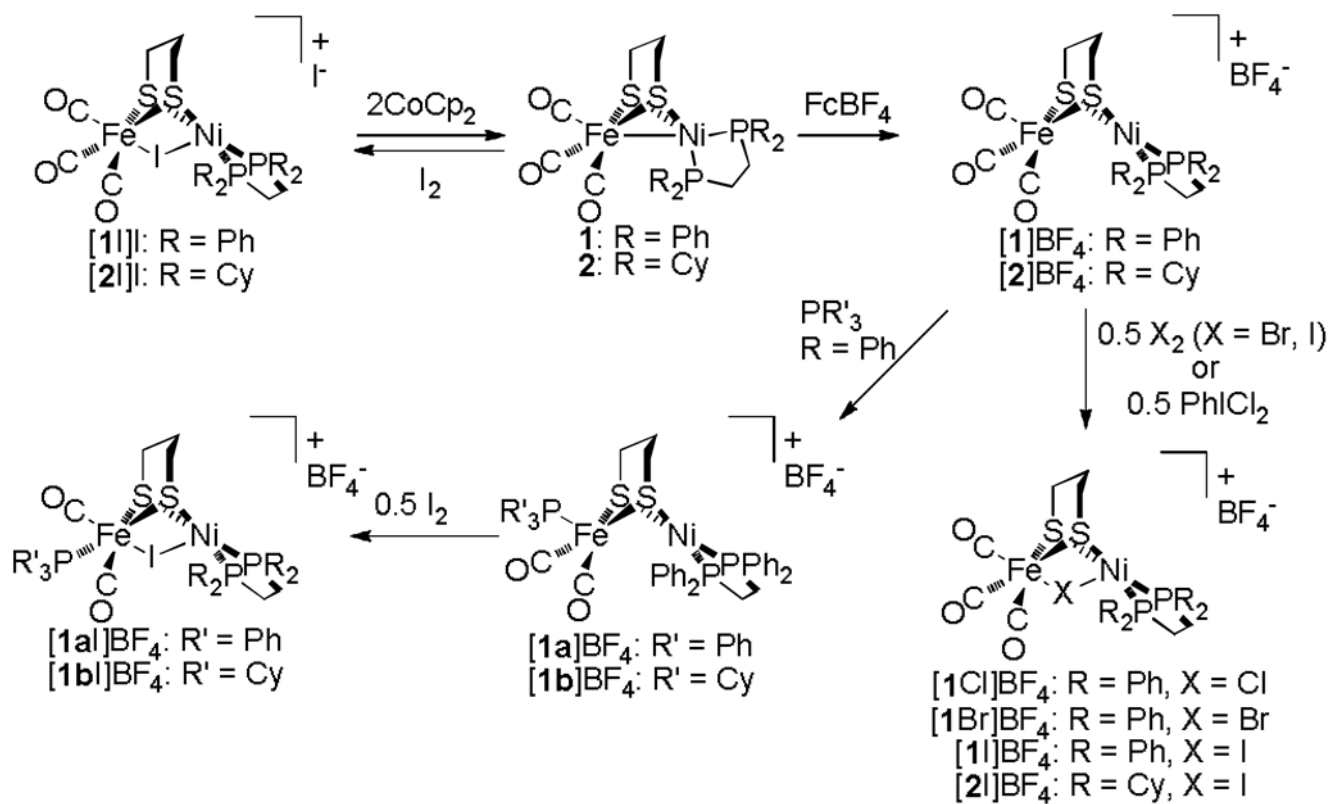
Scheme 1.
Reactions of Ni(I)Fe(I), Ni(II)Fe(I) and Ni(II)XFe(II) complexes.
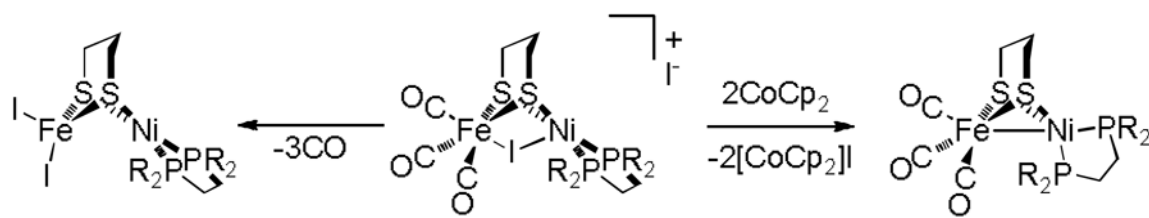
Scheme 2.
Reactions of the μ-iodo cation [**1I**]⁺.

Scheme 3.
Formation of a hydroperoxo complex from a hydride precursor.

Table 1

IR data for complexes of type [(dxpe)Ni(pdt)XFe(CO)$_2$L]BF$_4$ in CH$_2$Cl$_2$ solution.

Species	dxpe	X	L	co/cm^{-1}	E_{red}
[1I]BF$_4$	dppe	I	CO	2097, 2055, 2026	−0.99 (irrev.)
[1Br]BF$_4$	dppe	Br	CO	2106, 2065, 2028	
[1Cl]BF$_4$	dppe	Cl	CO	2111, 2072, 2031	−1.00 (irrev.)
[1aI]BF$_4$	dppe	I	PPh$_3$	2031, 1978	
[1bI]BF$_4$	dppe	I	PCy$_3$	2024, 1965	−1.43 (irrev.)
[1aCl]BF$_4$	dppe	Cl	PPh$_3$	2042, 1981	−1.34 (irrev.)
[1bCl]BF$_4$	dppe	Cl	Pcy$_3$	2033, 2068	−1.44 (irrev.)
[2I]BF$_4$	dcpe	I	CO	2096, 2054, 2023	−0.86 (i_{pc}/i_{pa} = 1.87)