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Kinetic Evidence for Intramolecular Proton Transfer Between Nickel and Coordinated Thiolate

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The complexes [Ni(YR)(triphos)]BPh_4 {Y = S, R = Ph or Et or Y = Se, R = Ph; triphos = $(Ph_2PCH_2CH_2)_2PPh$} have been prepared and characterized, and the X-ray crystal structure of [Ni(SPh)(triphos)]BPh_4 has been solved. In MeCN, [Ni(YR)(triphos)]$^+$ are protonated by [lutH]$^+$ (lut = 2,6-dimethylpyridine) to give [Ni(YHR)(triphos)]$^{2+}$. Studies on the kinetics of these equilibrium reactions reveal an unexpected difference in the reactivities of [Ni(SPh)(triphos)]$^+$ and [Ni(SEt)(triphos)]$^+$. In both cases, the reactions exhibit a first-order dependence on the concentration of complex. When R = Ph, the dependence on the concentrations of [lutH$^+$] and lut is given by $k_{obs} = k_1^{Ph}[lutH^+] + k_{-1}^{Ph}[lut]$, which is typical of an equilibrium reaction where k_1^{Ph} and k_{-1}^{Ph} correspond to the forward and back reactions, respectively. Analogous behavior is observed for [Ni(SePh)(triphos)]$^+$. However, for [Ni(SEt)(triphos)]$^+$, the kinetics are more complicated , and $k_{obs} = \{k_1k_2[lutH^+] + (k_{-2} + k_2)\}/(k_1[lutH^+] + k_{-1}[lut])$, which is indicative of a mechanism involving two coupled equilibria in which the initial protonation of the thiolate is followed by a unimolecular equilibrium reaction that is assumed to involve the formation of an η^2-EtS–H ligand. The difference in reactivity between the complexes with alkyl and aryl thiolate ligands is a consequence of the {Ni(triphos)}$^{2+}$ site "leveling" the basicities of these ligands. The pK_a's of the PhSH and EtSH constituents coordinated to the {Ni(triphos)}$^{2+}$ are 16.0 and 14.6, respectively, whereas the difference in pK_a's of free PhSH and EtSH differ by ca. 4 units. The pK_a of [Ni(SeHPh)(triphos)]$^+$ is 14.4. The more strongly σ-donating EtS ligand makes the {Ni(triphos)}$^{2+}$ core sufficiently electron-rich that the basicities of the sulfur and nickel in [Ni(SEt)(triphos)]$^+$ are very similar; therefore, the proton serves as a bridge between the two sites. The relevance of these observations to the proposed mechanisms of nickel-based hydrogenases is discussed.

Introduction

The discovery of several diverse biological roles for nickel[1] has led to a resurgence in interest in nickel thiolate complexes.[2,3] While much attention has been devoted to synthesizing complexes that model the structure of nickel centers in metalloenzymes, there are few studies mimicking the proposed reactivity of these biological sites. One elementary reaction of particular interest is the migration of protons between sulfur and metal atoms that have been proposed to play key roles in the action of the nickel-based hydrogenases (Figure 1).

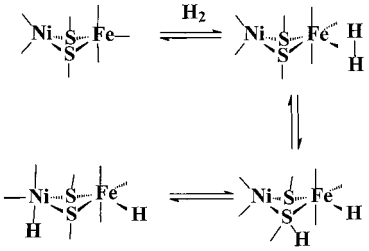

Figure 1. Intramolecular transfer of hydrogen from sulfur to metal as proposed by the action of hydrogenase from theoretical studies.[4,5]

The movement of protons between metal and sulfur ligands has been proposed in the actions of other metalloenzymes.[4−6] Thus, both the nitrogenases[7] and hydrogenases[8] catalyze the

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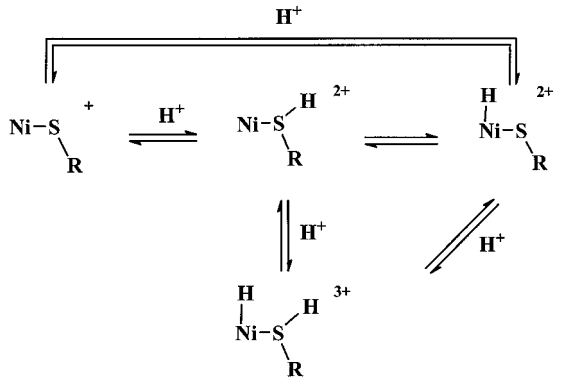

Figure 2. Possible intramolecular and acid−base-catalyzed pathways for the transfer of a proton between sulfur and metal.

reduction of protons to dihydrogen. The structures of the active sites of these enzymes have been determined, and for the Mo-based nitrogenase, this active site is a cluster comprising seven Fe, nine S, and a single Mo (FeMoco). The active site of the Ni-based hydrogenase is a binuclear species in which the Ni and Fe are bridged by cysteinate ligands. These structures give little indication of how protons are reduced to dihydrogen, but the predominant sulfur ligation at both sites has led to proposals that sulfur plays a key role in the process (Figure 2).

Possible pathways for dihydrogen oxidation by hydrogenase have been investigated in quantum mechanical calculations, and a common feature in all of the studies is the heterolytic cleavage of coordinated dihydrogen, followed by proton transfer to a cysteinate sulfur. Specifically, in the Ni-based hydrogenases, the proposed mechanism involves binding of dihydrogen to iron with H^- transfer to iron and H^+ transfer to the cysteinate ligand and subsequent proton transfer to nickel, as shown in Figure 1. Although thiol and hydride/thiolate complexes are known, there are few studies that show that the hydrogen can move between metal and sulfur.[11−14] In those studies where there is evidence for such transfer, no kinetic studies have been performed; consequently, we have no basic understanding of the electronic factors that facilitate this transfer nor any direct evidence that the reaction is truly intramolecular. While the intramolecular migration of protons between metal and ligand is a reaction that is widespread among carbon-based ligands,[9] this pathway is less evident with more electronegative donor atoms, where acid−base-catalyzed mechanisms may be energetically more favorable.[10]

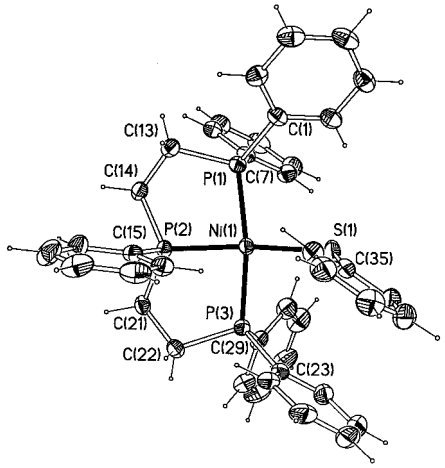

Figure 3. X-ray crystal structure of $[Ni(SPh)(triphos)]^+$ with 50% probability ellipsoids. Important dimensions associated with this cation are listed in the text.

In this contribution, we report studies on the protonation of $[Ni(YR)(triphos)]^+$ (Figure 3 {Y = S, R = Ph or Et or Y = Se, R = Ph; triphos = $(Ph_2PCH_2CH_2)_2PPh$} by $[lutH]^+$ (lut = 2,6-dimethylpyridine) as shown in eq 1, which shows that the $\{Ni(triphos)\}^{2+}$ site effectively levels the basicities of alkyl and aryl thiolates. With the more electron-releasing EtS ligand, this process has the effect that in $[Ni(SEt)(triphos)]^+$, initial protonation at the sulfur is followed by intramolecular equilibration. Evidence is presented that this process involves the formation of an η^2-EtS−H complex.

$$[Ni(YR)(triphos)]^+ + [lutH^+] \rightleftharpoons [Ni(YHR)(triphos)]^{2+} + [lut] \quad (1)$$

Experimental Section

All manipulations were performed under an atmosphere of dinitrogen using Schlenk and vacuum lines or syringe techniques, as appropriate. Lithium, sodium, triphos, lutidine, Me_3SiCl, $NaBPh_4$, PhSH, EtSH, and $NiCl_2{\cdot}6H_2O$ were purchased from Aldrich and used as received.

All solvents were dried and distilled under dinitrogen immediately prior to use. MeCN was distilled from CaH_2, THF, from Na/benzophenone, and diethyl ether, from Na.

The compounds $[lutH]BPh_4$ and $[lutD]BPh_4$ were prepared by the methods reported in the literature.[15] ^1H NMR studies on $[lutD]BPh_4$ demonstrated that the material was only 70% D-labeled.

Preparation of Complexes. [NiCl(triphos)]BPh_4. To a solution of $NiCl_2{\cdot}6H_2O$ (1.6 g; 6.7 mmol) in MeOH (ca. 20 mL) was added a solution of triphos (3.5 g; 6.7 mmol) in a 50:50 toluene/MeOH mixture, and the resulting red solution was stirred for 0.5 h. After allowing all the solid to dissolve (ca. 1 h), the solvent was removed in vacuo until a yellow solid started to precipitate from solution. The solid was removed by filtration, washed with diethyl ether, and then dried in vacuo.

The solid ([NiCl(triphos)]Cl) was weighed and then dissolved in the minimum amount of MeOH. A solution containing 1 mol equiv of $Na[BPh_4]$ in MeOH was added to the MeOH solution dropwise to produce a bright yellow solid of $[NiCl(triphos)]BPh_4$.

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Table 1. Elemental Analysis and Spectroscopic Characterization of Nickel Complexes

formula	elemental analysis[a]		^{1}H NMR[b]	^{31}P NMR[c]
	C	H		
[Ni(SPh)(triphos)]BPh_4	76.4	5.7	7.3−8.4 (m, triphos and PhS *Ph*)	107.5 (t, J_{PP} = 36.5 Hz; mid P)
	(76.0)	(5.7)	6.5−7.2 (m, B*Ph*$_4$)	54.2 (d, J_{PP} = 36.5 Hz; end P)
			3.0, 3.25 (br, −CH_2−)	
[Ni(SePh)(triphos)]BPh_4	73.0	5.5	7.3−8.4 (m, triphos and PhSe *Ph*)	117.5 (t, J_{PP} = 36.5 Hz; mid P)
	(76.0)	(5.7)	6.5−7.2 (m, B*Ph*$_4$)	50.0 (d, J_{PP} = 36.5 Hz; end P)
			3.0, 3.25 (br, −CH_2−)	
[Ni(SEt)(triphos)]BPh_4	74.8	5.6	7.3−7.9 (m, triphos *Ph*)	113.1 (t, J_{PP} = 36.5 Hz; mid P)
	(76.0)	(5.7)	6.6−7.0 (m, B*Ph*$_4$)	64.7 (d, J_{PP} = 36.5 Hz; end P
			2.6, 2.8 (br, −CH_2−)	
			0.7 (t, J_{HH} = 7.3 Hz, CH_3)	
			1.9 (q, J_{HH} = 7.3 Hz, CH_2CH$_3$)	

[a] Calculated values shown in parentheses. [b] Shifts relative to TMS. [c] Shifts relative to TMP.

[Ni(YR)(triphos)]BPh_4 (Y = S, R = Et or Ph; Y = Se, R = Ph). These complexes were all prepared by essentially the same route. LiYR was prepared by the reaction between Li and RYH in THF and isolated as a white solid. To a suspension of [NiCl(triphos)]BPh_4 (0.5 g; 0.53 mmol) in THF (ca. 20 mL) was added LiYR (0.35 g; 3.0 mmol). The color changed rapidly from bright yellow to dark red, and the mixture became homogeneous. After the solution was stirred for ca. 0.5 h, it was concentrated in vacuo to ca. 10 mL. Addition of an excess of MeOH produced a dark red microcrystalline solid. The solid was removed by filtration, washed with MeOH, and then dried in vacuo.

Recrystallization of the complex was accomplished by dissolving the solid in the minimum amount of THF and then adding a large excess of MeOH. Leaving the solution undisturbed at room temperature for 48 h produced well-formed crystalline needles. These crystals were removed by filtration, washed with MeOH, and dried in vacuo. Crystals grown in such a manner were suitable for X-ray crystallographic analysis (vide infra).

Results from microanalysis and spectroscopic characterization of the complexes are presented in Table 1.

Characterization of the Products of the Protonation Reactions. We have been unable to isolate the products [Ni(SHPh)(triphos)]{BPh_4}$_2$ and [Ni(SHEt)(triphos)]{BPh_4}$_2$ from the reactions with [lutH]BPh_4. This problem is, in part, due to the large excess of [lutH]$^+$ necessary to drive the equilibrium protonation to completion. Using stronger acids such as anhydrous HCl and HBF_4·OEt_2 resulted in the dissociation of thiol because of either multiple protonation of the complex or attack by the nucleophilic conjugate base. Thus, in the reaction of [Ni(SPh)(triphos)]$^+$ with HCl, [NiCl(triphos)]BPh_4 was isolated and identified by elemental analysis and ^{31}P{^{1}H} NMR spectroscopy: δ 113.1 (t, J_{PP} = 35.0 Hz; mid P), 64.7 (d, J_{PP} = 35.0 Hz; terminal P). This product was shown to be identical to an authentic sample of [NiCl(triphos)]BPh_4.

We have characterized the product in solution using ^{1}H NMR spectroscopy. Solutions containing mixtures of [Ni(SEt)(triphos)]$^+$ and a 20-fold excess of [lutH]$^+$ in CD_3CN exhibited a broad peak at δ 3.8, which we tentatively attribute to the S−H group.[16] In addition, the resonances of the ethyl group (δ 0.74 (t, J_{HH} = 7.4 Hz, CH_3), 1.34 (q, J_{HH} = 7.4 Hz, CH_2)) are significantly shifted from those of [Ni(SEt)(triphos)]$^+$ (Table 1). The ^{31}P NMR spectrum of the protonated species (δ 115 (t, J_{PP} = 36.5 Hz, mid P), 66 (d, J_{PP} = 36.5 Hz, end P) is little different from that of [Ni(SEt)(triphos)]$^+$.

Kinetic Studies. The kinetic studies on the compounds described in this contribution were performed on an Applied Photophysics stopped-flow SX.18V spectrophotometer, which was modified to handle air-sensitive solutions. All studies were conducted at 25.0 °C, a temperature that was maintained using a Grant LTD6G recirculating thermostat tank.

The kinetics were studied in dry MeCN under pseudo-first-order conditions, with [lutH$^+$] and lut present in at least a 10-fold excess over the concentration of complex. Mixtures of [lutH]BPh_4 and lut were prepared from stock solutions of the two reagents. All solutions were used within 1 h of preparation.

Under all the conditions described herein, the absorbance−time curves were of the form of a single exponential, with an initial absorbance corresponding to that of [Ni(SR)(triphos)]$^{2+}$ and a final absorbance corresponding to that of the equilibrium mixture of [Ni(SR)(triphos)]$^+$ and [Ni(SHR)(triphos)]$^{2+}$. Typical absorbance−time curves are shown in Figure 4. The associated rate constants (k_{obs}) were determined by a computer fit to the exponential absorbance−time curve. In all cases, the curve was an exponential for more than four half-lives. The dependence of k_{obs} on [lutH]$^+$ and [lut] were determined graphically, as illustrated in Figures 5 and 6.

X-ray Crystal Structure Determination of [Ni(SPh)(triphos)]BPh_4. Crystal data for $C_{64}H_{58}BNiP_3S$ (formula weight 1021.59, burgundy crystals, triclinic, space group $P\bar{1}$): a = 14.6807(11) Å, b = 18.6897(14) Å, c = 20.9971(16) Å; α = 111.050(2)°, β = 101.407(2)°, γ = 96.042(2)°. V = 5171.7(7) Å^3, T = 160 K, Z = 4, $R(F, F^2 > 2\sigma)$ = 0.0431, $R_w(F^2$, all data) = 0.1044, GOF = 1.007. The data collection and structure determination followed standard procedures using a Bruker AXS SMART CCD diffractometer and Mo Kα radiation (θ_{max} = 28.6°, 44882 reflections measured, 23463 unique, semiempirical absorption corrections were based on symmetry-equivalents), direct methods, and full-matrix least-squares refinement on all unique F^2 values. The programs used were Bruker SMART (data collection), SAINT (integration), and SHELXTL (structure solution).

Results and Discussion

The transfer of a proton between nickel and sulfur could, in principle, occur by any of the three mechanisms shown in Figure 2. In addition to the intramolecular pathway, there is the direct route involving competitive protonation of nickel and sulfur and an acid−base-catalyzed pathway involving an intermediate in which both nickel and sulfur are protonated. Analogous pathways have been discussed for nitrogen-based ligands.[7] Currently, there are no studies that allow us to establish the relative merits of these pathways.

A major problem in investigating the mechanism of protonation of metal thiolates and establishing the way in which the proton moves about the complex is that S−H bonds are sufficiently acidic that they undergo rapid exchange

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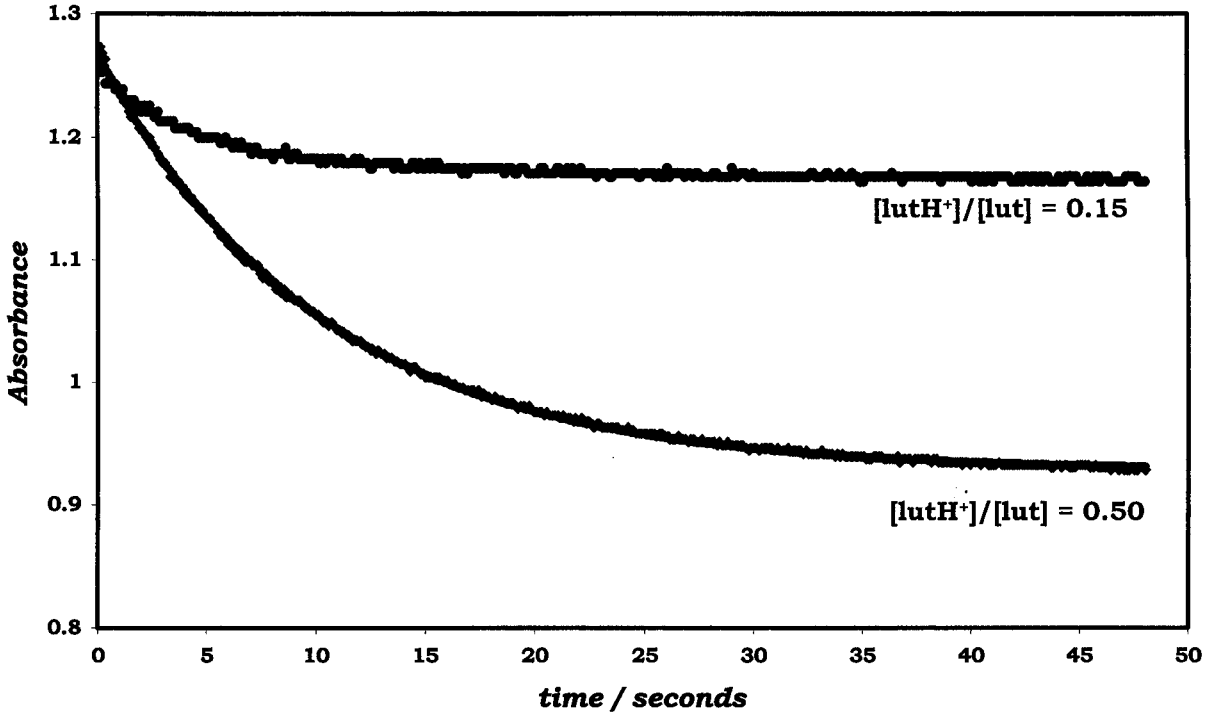

Figure 4. Typical absorbance−time curves for the reaction of $[Ni(SPh)(triphos)]^+$ with $[lutH]^+$ in MeCN at 25.0 °C, showing the effect of increasing $[lutH^+]/[lut]$. Curves were recorded at $\lambda = 350$ nm and $[lutH^+] = 5.0$ mmol dm^{-3}. Analysis of the magnitude of the absorbance changes from such curves allows determination of K_1SPh using the molar extinction coefficients of $[Ni(SPh)(triphos)]^+$ ($\epsilon = 5.2 \times 10^3$ dm^3 mol^{-1} cm^{-1}) and $[Ni(SHPh)(triphos)]^{2+}$ ($\epsilon = 1.8 \times 10^3$ dm^3 mol^{-1} cm^{-1}) at $\lambda = 350$ nm.

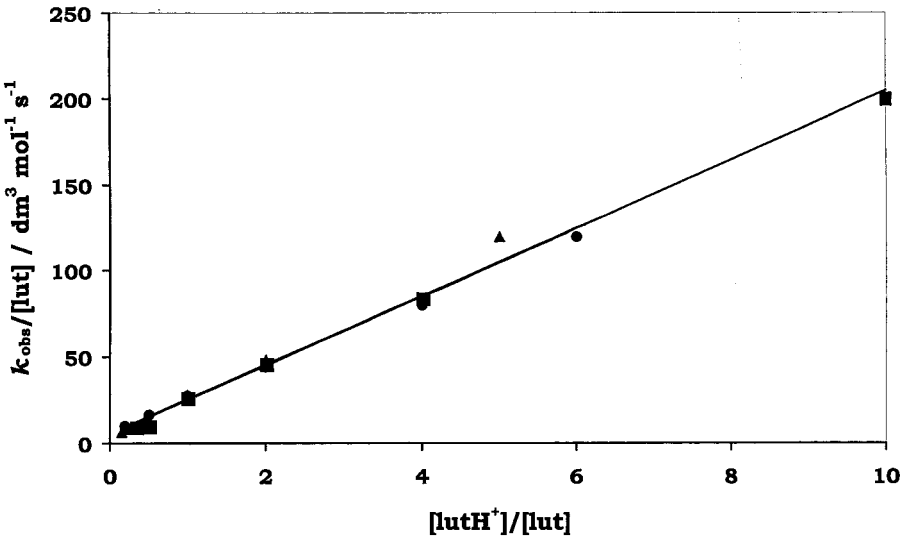

Figure 5. Graph of k_{obs}/[lut] versus $[lutH^+]/[lut]$ for the reaction of $[Ni(SPh)(triphos)]^+$ with $[lutH]^+$ in MeCN at 25.0 °C. The data points correspond to $[lutH^+] = 5.0$ mmol dm^{-3}, [lut] = 1.0−30.0 mmol dm^{-3} (▲); $[lutH^+] = 10.0$ mmol dm^{-3}, [lut] = 1.0−30.0 mmol dm^{-3} (■); and $[lutH^+] = 1.0-40.0$ mmol dm^{-3}, [lut] = 5.0 mmol dm^{-3} (●). The line drawn is that defined by eq 2.

with protons in solution. Consequently, isotopic labeling cannot be used to follow the course of the reaction, which necessitates relying on kinetics to distinguish between the pathways shown in Figure 2.

In this work, we have prepared structurally simple complexes of the type $[Ni(YR)(triphos)]^+$ and have shown they are mononuclear species. We have also studied the kinetics of reversible protonation of these complexes in MeCN. Only the sulfur atoms in $[Ni(SPh)(triphos)]^+$ and $[Ni(SEt)(triphos)]^+$ contain lone pairs of electrons that can be protonated, yet these complexes show surprisingly different kinetic behavior. We attribute this difference to $[Ni(SHEt)(triphos)]^{2+}$ undergoing intramolecular proton transfer between sulfur and nickel.

The Structure of [Ni(SPh)(triphos)]BPh$_4$. One of the major requirements of these studies is to keep the system as uncomplicated as possible to simplify the interpretation of the kinetics. To this end, it is clearly advantageous if the complexes are mononuclear. The triphos ligand, with the sterically demanding phenyl groups, has been employed to discourage the thiolates from acting as bridging ligands and thus aiding the formation of dimeric species. Confirmation

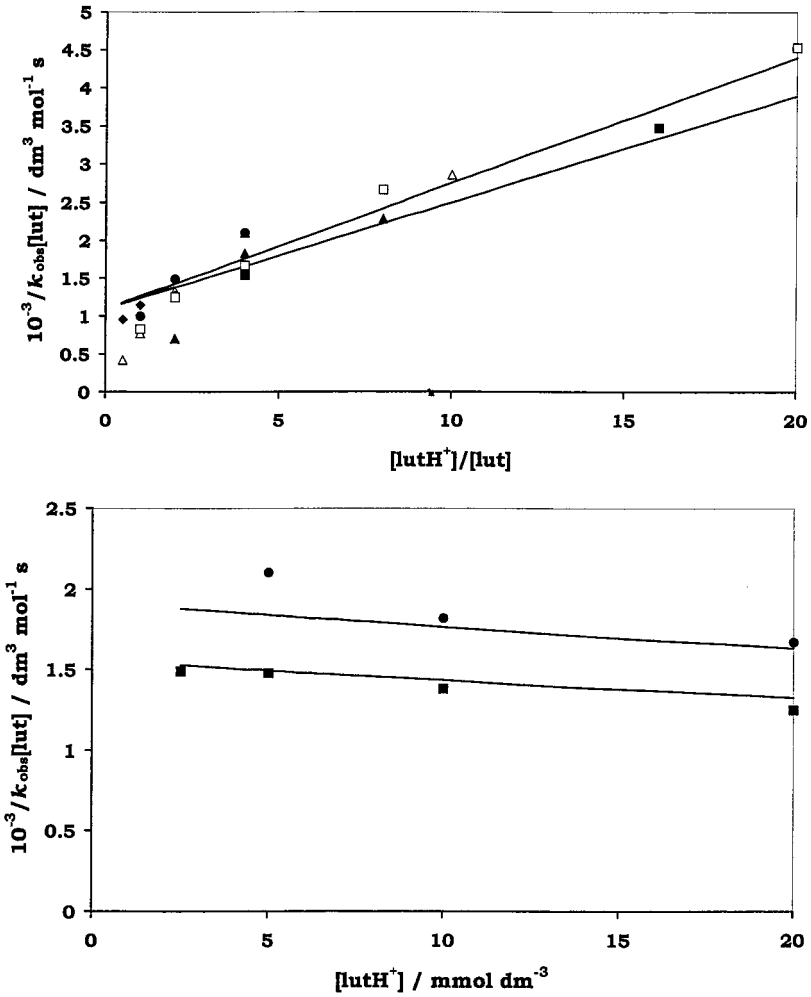

Figure 6. (Top) Graph of $1/k_{obs}$[lut] versus [lutH$^+$]/[lut], at constant [lutH$^+$], for the reaction of [Ni(SEt)(triphos)]$^+$ with [lutH]$^+$ in MeCN at 25.0 °C. The data points correspond to [lutH$^+$] = 10.0 mmol dm^{-3}, [lut] = 1.0−20.0 mmol dm^{-3} (△); [lutH$^+$] = 20.0 mmol dm^{-3}, [lut] = 1.0−20.0 mmol dm^{-3} (□); [lutH$^+$] = 2.5 mmol dm^{-3}, [lut] = 1.25−5.0 mmol dm^{-3} (◆); [lutH$^+$] = 5.0 mmol dm^{-3}, [lut] = 1.25−5.0 mmol dm^{-3} (●); [lutH$^+$] = 10.0 mmol dm^{-3}, [lut] = 1.25−5.0 mmol dm^{-3} (▲); and [lutH$^+$] = 20.0 mmol dm^{-3}, [lut] = 1.25−5.0 mmol dm^{-3} (■). (Bottom) Graph of $1/k_{obs}$[lut] versus [lutH$^+$] at constant [lutH$^+$]/[lut] for the same reaction. Data points correspond to [lutH$^+$]/[lut] = 2.0 (■) and [lutH$^+$]/[lut] = 4.0 (●). All lines drawn are those defined by eq 4.

that the complexes are indeed mononuclear was established by the X-ray crystal structure of [Ni(SPh)(triphos)]BPh_4. The structure of the cation is shown in Figure 3. Although there are few mononuclear Ni complexes with which to compare this structure, there is nothing exceptional about the structural parameters of this complex compared to those of other thiophenolate complexes.

The Ni center has a slightly distorted square-planar geometry with P(1)−Ni−P(2) = 86.41(2)°; P(2)−Ni−P(3) = 85.82(2)°; P(3)−Ni−S(1) = 89.76(3)°; P(1)−Ni−S(1) = 99.03(3)°; P(1)−Ni−P(3) = 161.50(3)°, and P(2)−Ni-S(1) = 173.89(3)°. The Ni−P(2) bond distance (2.1506(6) Å), where the trans atom is sulfur, is shorter than the Ni−P(1) (2.2101(7) Å) and Ni−P(3) (2.1858(7) Å) bond distances. This effect has been observed before.[17] Finally, the Ni−S(1)−C(35) angle is 99.20(8)°, a value that also fits into the generally observed pattern that the M−S−C angle is equal to or less than the ideal sp^2 hybridized angle.[17] Only when steric hindrance becomes a problem is this angle greater than 120°.

Reaction of [lutH]$^+$ with [Ni(SPh)(triphos)]$^+$. When studied on a stopped-flow spectrophotometer, the reaction between [Ni(SPh)(triphos)]$^+$ and an excess of [lutH]$^+$ and [lut] in MeCN exhibits a single-exponential absorbance−time curve. The magnitude of the absorbance change increases with [lutH$^+$]/[lut] (up to a maximum value), which is typical of an equilibrium reaction (Figure 4). This behavior is observed in all the reactions with [lutH]$^+$ described in this contribution.

The exponential shape of the absorbance−time curves indicates that the reaction exhibits a first-order dependence on the concentration of [Ni(SPh)(triphos)]$^+$. Consistent with this interpretation, experiments were performed in which the concentration of the complex was varied ([Ni] = 0.05−0.25 mmol dm^{-3}) and the concentrations of [lutH]$^+$ (10.0 mmol dm^{-3}) and lut (5.0 mol dm^{-3}) were constant, but there was no effect on k_{obs} (0.22 ± 0.01s^{-1}).

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The dependence of k_{obs} on the concentrations of $[lutH]^+$ and lut is shown in Figure 5, and analysis of the data yields the rate law shown in eq 2.

$$\frac{-d[Ni(SPh)(triphos)^+]}{dt} = \{k_1^{PhS}[lutH^+] + k_{-1}^{PhS}[lut]\}[Ni(SPh)(triphos)^+] \quad (2)$$

This rate law is consistent with a single-step equilibrium reaction[18] involving proton transfer to and from the complex, as shown in eq 3. Protonation is presumed to occur at one of the lone pairs of electrons on the sulfur. Graphical analysis of the data gives $k_1^{PhS} = 20 \pm 2$ dm^3 mol^{-1} s^{-1} and $k_{-1}^{PhS} = 5 \pm 0.7$ dm^3 mol^{-1} s^{-1}.

The equilibrium constant (K_1^{PhS}) for this protonation reaction can be calculated from the kinetic data: $K_1^{PhS} = k_1^{PhS}/k_{-1}^{PhS} = 4.0 \pm 1.0$. This value is in excellent agreement with the value determined from spectrophotometric analysis of the effect of $[lutH^+]/[lut]$ on the magnitude of the absorbance change (Figure 4), $K_1^{PhS} = 3.6$.

Because the acid strength of $[lutH]^+$ is known in MeCN ($pK_a^{lut} = 15.4$),[19] pK_a^{SPh}(= 16.0) of $[Ni(SHPh)(triphos)]^{2+}$ can be calculated. Earlier work[20] has shown that for free PhSH in MeCN, $pK_a \geq 19.3$. Thus, coordination of PhSH to $\{Ni(triphos)\}^{2+}$ renders it at least 4000 times more acidic.

The reaction of $[Ni(SePh)(triphos)]^+$ with mixtures of $[lutH]^+$ and lut in MeCN exhibits analogous kinetics to that of $[Ni(SPh)(triphos)]^+$. $k_1^{SePh} = 40 \pm 3$ dm^3 mol^{-1} s^{-1} and $k_{-1}^{SePh} = (4.2 \pm 0.3) \times 10^2$ dm^3 mol^{-1} s^{-1}; hence, $K_1^{SePh} = 9.5 \times 10^{-2}$. Spectrophotometric analysis gives $K_1^{SePh} = (8.9 \pm 1.2) \times 10^{-2}$, which is in good agreement with the value calculated from the rate constants. Therefore, we calculate $pK_a^{SePh} = 14.4$ for $[Ni(SeHPh)(triphos)]^{2+}$. That the coordinated PhSeH is more acidic than the coordinated PhSH is consistent with the difference in acidities of the free molecules; however, coordinated PhSeH is only 2.5 times more acidic than coordinated PhSH. The difference in acidities of coordinated PhSH and PhSeH is markedly less than the 1000-fold (at least) difference observed for the free molecules[21], indicating that the $\{Ni(triphos)\}^{2+}$ core effectively levels the acidities of coordinated thiols. Studies of the kinetics of protonation of $[Ni(SEt)(triphos)]^+$ show that this effect extends to alkanethiolates.

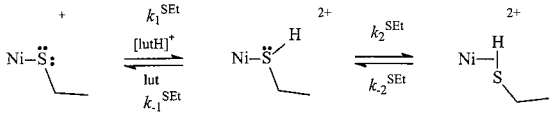
Reaction of $[lutH]^+$ with $[Ni(SEt)(triphos)]^+$. When studied using stopped-flow spectrophotometry, the reaction between $[Ni(SEt)(triphos)]^+$ and mixtures of $[lutH\}^+$ and $\{lut\}$ is characterized by exponential absorbance−time curves, the magnitude of which varies with $[lutH^+]/[lut]$ in the same manner as does that in the studies with $[Ni(SPh)(triphos)]^+$. The exponential shape of the absorbance−time curves indicates a first-order dependence on the concentration of $[Ni(SEt)(triphos)]^+$, and consistent with this behavior, the value of k_{obs} did not change in experiments in which the concentration of $[Ni(SEt)(triphos)]^+$ was varied from 0.05 to 0.25 mmol dm^{-3} at constant concentrations of $[lutH]^+$ (10.0 mmol dm^{-3}) and lut (5.0 mmol dm^{-3}).

The dependence of the rate constant on the concentrations of $[lutH]^+$ and [lut] is more complicated than that observed with $[Ni(SPh)(triphos)]^+$. In particular, increasing $[lutH^+]/[lut]$ results in a decrease in the rate. To analyze the data, it is necessary to consider two conditions: (i) the variation of the rate with $[lutH^+]/[lut]$ at constant $[lutH^+]$, for which the top graph in Figure 6 shows a linear relationship between $1/k_{obs}$[lut] and $[lutH^+]/[lut]$ and (ii) the variation of the rate with $[lutH^+]$ at constant $[lutH^+]/[lut]$, for which the bottom graph in Figure 6 shows the variation of $1/k_{obs}$[lut] with $[lutH^+]$.

Analysis of these data shows that the rate law is described by eq 4.

$$\frac{-d[Ni(SEt)(triphos)^+]}{dt} = \frac{\{(8.8 \pm 1.0)[lutH^+] + (1.0 \pm 0.2)\}[Ni(SEt)(triphos)^+]}{(1.8 \pm 0.3) \times 10^2[lutH^+] + (1.2 \pm 0.2) \times 10^3[lut]} \quad (4)$$

This rate law is consistent with a mechanism comprising two coupled equilibria, in which the initial protonation of $[Ni(SEt)(triphos)]^+$ is followed by a second equilibrium which comprises unimolecular steps.[22] The mechanism shown in eq 5 is consistent with this behavior. In line with the studies on $[Ni(SPh)(triphos)]^+$, we propose that the initial protonation occurs at the ethyl thiolate ligand, which is followed by the intramolecular equilibrium involving an η^2-EtS−H ligand. Effectively, this process is a partial proton transfer to the nickel. The rate law associated with this mechanism when $k_2^{SEt} < k_{-2}^{SEt}$ is shown in eq 6, and comparison with eq 4 gives $k_1^{SEt} = (1.8 \pm 0.3) \times 10^2$ dm^3 mol^{-1} s^{-1}, $k_{-1}^{SEt} = (1.2 \pm 0.2) \times 10^3$ dm^3 mol^{-1} s^{-1}, $k_2^{SEt} = (0.05 \pm 0.01)$ s^{-1}, and $k_{-2}^{SEt} = (0.95 \pm 0.01)$ s^{-1}.



(5)

$$\frac{-d[\{Ni(SEt)(triphos)^+\}]}{dt} = \frac{\{k_1^{SEt}k_2^{SEt}[lutH^+] + (k_2^{SEt} + k_{-2}^{SEt})\}[Ni(SEt)(triphos)^+]}{k_1^{SEt}[lutH^+] + k_{-1}^{SEt}[lut]} \quad (6)$$

We have been able to characterize the product $[Ni(SHEt)(triphos)]^{2+}$ only in solution (see Experimental Section). We have no direct evidence for the existence of $[Ni(\eta^2\text{-EtSH})(triphos)]^{2+}$, which is not surprising when the kinetic data are considered. The product distribution between [Ni(SHEt)-

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(triphos)]$^{2+}$ and [Ni(η^2-EtSH)(triphos)]$^{2+}$ is independent of the concentration of acid, with the η^2-EtS−H species representing only 5% of the mixture. Because of this insurmountable problem in establishing an unambiguous product-analysis technique, we will now consider in more detail alternative interpretations of the kinetics of the reaction between [Ni(SEt)(triphos)]$^+$ and [lutH]$^+$.

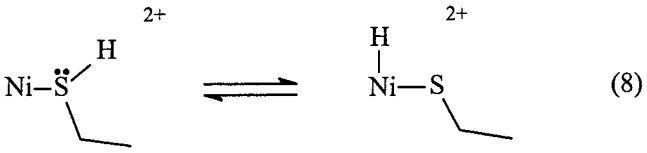
While the rate law shown in eq 6 is consistent with the mechanism shown in eq 5, it does not unambiguously identify the k_2^{SEt} and k_{-2}^{SEt} steps as being associated with the formation of an η^2-EtS−H species. Certainly, the structural simplicity of [Ni(SEt)(triphos)]$^+$ limits the number of alternatives, but one possible explanation for the observed behavior is that the initial protonation of the thiolate is followed by an isomerization of the square-planar [Ni(SEt)(triphos)]$^+$ to the tetrahedral [Ni(SHEt)(triphos)]$^{2+}$. Although isomerizations between square-planar and tetrahedral forms are well-known in Ni^{II}−phosphine complexes,[23] we are unaware of such reactions being catalyzed by protonation. In addition, it is difficult to reconcile why [Ni(SHEt)(triphos)]$^{2+}$ would undergo such an isomerization while [Ni(SHPh)(triphos)]$^{2+}$ would not.

Our proposal that the k_2^{SEt} and k_{-2}^{SEt} steps are associated with movement of the proton is consistent with the results from studies using [lutD]$^+$ (70% D-labeled) that show k_1^{SEt}, k_{-1}^{SEt}, and k_2^{SEt} are all associated with appreciable primary isotope effects. Analysis of the data from the reaction between [Ni(SEt)(triphos)]$^+$ and [lutD]$^+$ yields the rate law given in eq 7.

$$\frac{-\mathrm{d[Ni(SEt)(triphos)^+]}}{\mathrm{d}t} = \frac{\{(3 \pm 0.2)[\mathrm{lutD^+}] + (1.0 \pm 0.2)\}[\mathrm{Ni(SEt)(triphos)^+}]}{(1 \pm 0.2) \times 10^2[\mathrm{lutD^+}] + (7 \pm 0.5) \times 10^2[\mathrm{lut}]} \quad (7)$$

Comparison of eqs 6 and 7 gives $(k_1^{SEt})^D = (1 \pm 0.2) \times 10^2$ dm^3 mol^{-1} s^{-1}, $(k_{-1}^{SEt})^D = (7 \pm 0.5) \times 10^2$ dm^3 mol^{-1} s^{-1}, $(k_2^{SEt})^D = (0.03 \pm 0.01)$ s^{-1}, and $(k_{-2}^{SEt})^D = (0.97 \pm 0.01)$ s^{-1}. Comparison with the results using [lutH]$^+$ gives $(k_1^{SEt})^H/(k_1^{SEt})^D = 1.8$, $(k_{-1}^{SEt})^H/(k_{-1}^{SEt})^D = 1.7$, $(k_2^{SEt})^H/(k_2^{SEt})^D = 1.7$, and $(k_{-2}^{SEt})^H/(k_{-2}^{SEt})^D = 0.98$. The primary isotope effects observed for k_1^{SEt} and k_{-1}^{SEt} are consistent with proton transfer between [Ni(SEt)(triphos)]$^+$ and [lutH]$^+$ but do not, of course, define the site of protonation. However, a key result is that k_2^{SEt} is associated with an appreciable isotope effect, which indicates that k_2^{SEt} is involved with proton movement. This result is consistent with the proposed pathway shown in eq 5.[24] The small value of $(k_{-2}^{SEt})^H/(k_{-2}^{SEt})^D$ means that we cannot be confident that this effect is a true inverse isotope effect. Inverse isotope effects are expected to play a role in the transfer of a proton from metal (low υ_{M-H}; ca. 1900 cm^{-1}) to sulfur (high υ_{S-H}; ca. 2600 cm^{-1}).[25] However, there is no precedent for the movement described in the mechanism shown in eq 5, where the proton is always bound to sulfur and merely switches the interaction with nickel on and off.

Although the results are consistent with movement of the proton, it seems unlikely that they correspond to complete proton transfer as shown in eq 8. Complete proton transfer would result in a five-coordinate d^6 Ni^{IV} species, which is unprecedented. However, η^2-thiol ligands have been observed before. In complexes of the type [Fe(SR)(CO)$_3$L] {L = PEt$_3$ or P(OEt)$_3$}[26], the site of protonation is sensitive to both L and R, and with [Fe(SMe)(CO)$_3$(PEt$_3$)], an η^2-MeS−H species is formed.



(8)

Electronic Factors Controlling Migration. The effect that the {Ni(triphos)}$^{2+}$ core has on the acidities of coordinated thiols is fundamental to understanding why the proton in [Ni(SHEt)(triphos)]$^{2+}$ interacts with nickel but not with [Ni(SHPh)(triphos)]$^{2+}$. Earlier in the discussion, we calculated pK_a^{SPh} = 16.0 for [Ni(SHPh)(triphos)]$^{2+}$ and commented on how similar this value is to that of [Ni(SeHPh)(triphos)]$^{2+}$ (pK_a = 14.4). From the kinetic analysis of the [Ni(SEt)(triphos)]$^+$ system, we calculate $K_1^{SEt} = k_1^{SEt}/k_{-1}^{SEt} = 0.15$, and hence p$K_a^{SEt}$ = 14.6 for [Ni(SHEt)(triphos)]$^{2+}$. It is surprising that free PhSH is a 10^4 times stronger acid[27] than free EtSH, but when PhSH and EtSH are coordinated to {Ni(triphos)}$^{2+}$, the acid strengths are similar. If we consider [Ni(SeHPh)(triphos)]$^{2+}$, the effect of coordination on acidity is even more marked. While free PhSeH is a 10^7 times stronger acid than free EtSH, when coordinated to {Ni(triphos)}$^{2+}$, it is only 1.6 times more acidic!

Coordination to the {Ni(triphos)}$^{2+}$ site effectively levels the acidities of the PhSH, EtSH, and PhSeH ligands. This leveling must have its origins in the bonding between nickel and thiols.

Thiolate ligands are good σ-donors, and the better electron-releasing capability of alkyl groups over aryl groups makes EtS a better σ-donor ligand than PhS. It seems likely that the electron density imparted to the {Ni(triphos)}$^{2+}$ site by the thiolate is dissipated by π-back-bonding to the phosphorus atoms, leading to the effective leveling of acidities of coordinated thiols and resulting in the acidities of coordinated PhSeH, PhSH, and EtSH varying by less than a factor of 40. The {Ni(triphos)}$^{2+}$ core's leveling of the acidities of the thiols must have a complementary effect on the electron-richness of the {Ni(triphos)}$^{2+}$ site. It seems reasonable that the electron-releasing EtS ligand must make the {Ni(triphos)}$^{2+}$ site in [Ni(SEt)(triphos)]$^+$ more electron-rich than it does in [Ni(SPh)(triphos)]$^+$. Thus, the basicities of

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the nickel and sulfur sites are sufficiently similar so that in $[Ni(SHEt)(triphos)]^{2+}$ the proton effectively bridges the two sites.

The transfer of a proton from sulfur to metal has been proposed before. In addition to the $[Fe(\eta^2\text{-}MeS{-}H)(CO)_3(PEt_3)]$ complexes discussed above,[26] the so-called oxidative addition of RSH to $[IrCl(CO)(PPh_3)_2]$ has been proposed to involve a three-center Ir−H−SR transition state in which the lengthening of the S−H bond is synchronous with the binding of these two atoms to iridium.[28] More recently, a so-called agostic Os−H−S interaction has been proposed for the reaction of thiols[29] with $[Os_3(CO)_{11}(NCMe)]$, and proton transfer between sulfur and hydride[30] has been observed in $[Os(\eta^2\text{-}H_2)(CO)(quS)(PPh_3)_2]^+$ (quS = quinoline-8-thiolate).

Rates of Protonation of Sulfur in $[Ni(SR)(triphos)]^+$. The studies reported in this contribution have resulted in the determination of the rate constants for proton transfer to $[Ni(YR)(triphos)]^+$ by $[lutH]^+$ and from $[Ni(YHR)(triphos)]^{2+}$ to [lut]. In all cases, the rate of proton transfer is appreciably slower than the diffusion-controlled limit ($k_{diff} = 1 \times 10^{10}$ $dm^3\ mol^{-1}\ s^{-1}$), even though stereochemical lone pairs of electrons are available on the sulfur.[31] The most likely reason these proton-transfer reactions are so slow is that unfavorable steric interactions occur upon approach of $[lutH]^+$ (or lut) to $[Ni(YR)(triphos)]^+$ (or its conjugate acid). The steric problems arise from the methyl groups on {lut} and the phenyl groups on the triphos ligand. Although detailed discussion of the rate constants is premature at this stage, two features indicate that steric factors are important in defining the rates of these reactions. First, the size of Y appears to be important in defining the rate constant. Thus, although protonation of $[Ni(SePh)(triphos)]^+$ is thermodynamically less favorable than protonation of $[Ni(SPh)(triphos)]^+$, the rate constant for protonation of the former by $[lutH]^+$ is twice that of the latter. Presumably, this result is a consequence of less congestion in the transition state of $[Ni(SePh)(triphos)]^+$ upon proton transfer with the larger Se atom. Second, the rate of proton transfer to $[Ni(SEt)(triphos)]^+$ is ca. 10 times faster than the rate of proton transfer to $[Ni(SPh)(triphos)]^+$, which, in part, is probably because the EtS ligand is sterically less demanding than the PhS ligand. Therefore, EtS presents less hindrance to the approaching $[lutH]^+$ than does PhS.

Relevance to the Action of Hydrogenases. Recent mechanistic proposals concerning the action of the Ni-based hydrogenases[4,5,8] have involved intramolecular proton transfers between cysteinate sulfur and metal atoms (Ni or Fe), as outlined in Figure 1. In this contribution, we have reported kinetic studies on some simple Ni−thiolate complexes that are pertinent to these discussions. In particular, we have shown that the initial protonation of $[Ni(SR)(triphos)]^+$ occurs at a lone pair of electrons on the sulfur (most basic site). This result is in line with the observation that protonation at the metal is usually kinetically slower than protonation of a lone pair of electrons.[32,33] With $[Ni(SPh)(triphos)]^+$, no further reaction occurs, but with $[Ni(SEt)(triphos)]^+$, the more electron-releasing alkanethiolate ligand increases the basicity of the nickel, and it is proposed that the proton interacts with both the nickel and sulfur sites.

The studies in this contribution were performed in MeCN, and the reported pK_a's correpond to this solvent. The question is what behavior would be expected in water? Using the relationship shown in eq 9,[34] it can be estimated that the pK_a's of $[Ni(YHR)(triphos)]^{2+}$ in water would fall in the range 7−8, indicating that the reactions discussed herein would be physiologcally relevant.

$$pK_a(H_2O) = pK_a(MeCN) - 7.5 \qquad (9)$$

Thus, under physiological conditions, a thiolate sulfur is always the initial site of protonation, but in the presence of coordinated alkanethiolates (e.g., cysteinate), partial proton transfer (i.e., formation of η^2-RS−H) to the nickel could ensue.

Supporting Information Available: Listings of kinetic data and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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