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ARTICLE

Mechanism of proton transfer to coordinated thiolates: encapsulation of acid stabilizes precursor intermediate†

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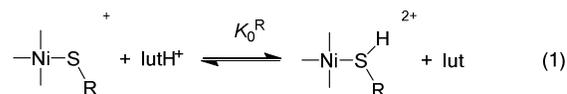
Earlier kinetic studies on the protonation of the coordinated thiolate in the square-planar $[\text{Ni}(\text{SC}_6\text{H}_4\text{R}'\text{-4})(\text{triphos})]^+$ ($\text{R}' = \text{NO}_2, \text{Cl}, \text{H}, \text{Me}$ or MeO) by lutH^+ ($\text{lut} = 2,6\text{-dimethylpyridine}$) indicate a two-step mechanism involving initial formation of a (kinetically detectable) precursor intermediate, $\{[\text{Ni}(\text{SC}_6\text{H}_4\text{R}'\text{-4})(\text{triphos})]\dots\text{Hlut}\}^{2+}$ (K_1^{R}), followed by an intramolecular proton transfer step (k_2^{R}). The analogous $[\text{Ni}(\text{SR})(\text{triphos})]\text{BPh}_4$ ($\text{R} = \text{Et}, \text{Bu}^t$ or Cy ; $\text{triphos} = \text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$) have been prepared and characterized by spectroscopy and X-ray crystallography. Similar to the aryl thiolate complexes, $[\text{Ni}(\text{SR})(\text{triphos})]^+$ are protonated by lutH^+ in an equilibrium reaction but the observed rate law is simpler. Analysis of the kinetic data for both $[\text{Ni}(\text{SR})(\text{triphos})]^+$ and $[\text{Ni}(\text{SC}_6\text{H}_4\text{R}'\text{-4})(\text{triphos})]^+$ shows that both react by the same mechanism, but that K_1^{R} is largest when the thiolate is poorly basic, or the 4-R' substituent in the aryl thiolates is electron-withdrawing. These results indicate that it is both $\text{NH}\dots\text{S}$ hydrogen bonding and encapsulation of the bound lutH^+ (by the phenyl groups on triphos) which stabilize the precursor intermediate.

Introduction

The study of simple proton transfer reactions involving metal complexes continues to be fundamental in understanding such reactions when they are part of complex multistage processes, as in the reactions of natural and synthetic catalysts. Of particular current interest is the protonation at coordinated sulfur sites, since such ligands are common in metalloenzymes.^{1,2}

Usually, the kinetics of proton transfer reactions are very simple and give little mechanistic insight.¹ However, studies on $[\text{Ni}(\text{SC}_6\text{H}_4\text{R}'\text{-4})(\text{triphos})]^+$ ($\text{R}' = \text{NO}_2, \text{Cl}, \text{H}, \text{Me}$ or MeO ; $\text{triphos} = \text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$) have shown that the reactions with mixtures of lutH^+ and lut ($\text{lut} = 2,6\text{-dimethylpyridine}$) in MeCN involve protonation of the coordinated thiolate {equation (1)}, and the kinetics of these simple protonation reactions are unusually complicated. In particular, a non-linear dependence on the concentration of lutH^+ indicates that a precursor intermediate, $\{[\text{Ni}(\text{SC}_6\text{H}_4\text{R}'\text{-4})(\text{triphos})]\dots\text{Hlut}\}^{2+}$, which presumably contains a $\text{NH}\dots\text{S}$ hydrogen bond, accumulates at high concentrations of lutH^+ .^{2e} Analysis of the kinetics allows determination of the equilibrium constant for the formation of this intermediate (K_1^{R}) and the rate constant for the subsequent intramolecular proton transfer step (k_2^{R}). The reason why the precursor intermediate accumulates is because its formation from $[\text{Ni}(\text{SC}_6\text{H}_4\text{R}'\text{-4})(\text{triphos})]^+$ and lutH^+ is rapid

but the subsequent intramolecular proton transfer step is relatively slow. However, this is not the whole story and in this paper we describe the kinetics of the reactions of the analogous $[\text{Ni}(\text{SR})(\text{triphos})]^+$ ($\text{R} = \text{Et}, \text{Bu}^t$ or Cy) with mixtures of lutH^+ and lut in MeCN . Analysis of the kinetics shows that the precursor intermediate does not accumulate for these complexes, under conditions identical to those used with $[\text{Ni}(\text{SC}_6\text{H}_4\text{R}'\text{-4})(\text{triphos})]^+$. This observation indicates that the principal factor stabilizing the precursor intermediate is not exclusively $\text{NH}\dots\text{S}$ hydrogen bonding but also the encapsulation of the bound lutH^+ by the phenyl groups on triphos.



Experimental

All preparations and manipulations were routinely performed under an atmosphere of dinitrogen using Schlenk or syringe techniques as appropriate. All solvents were dried and distilled under dinitrogen immediately prior to use. The following chemicals were purchased from Sigma-Aldrich and used as received: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, EtSH , CySH , Bu^tSH , NaBPh_4 , lut , triphos and D_2O . CD_3CN was purchased from Goss Scientific

and used as received. Toluene was used as received. Acetonitrile was distilled from calcium hydride and methanol from Mg(OMe)₂. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium. ¹H NMR spectra chemical shifts are quoted relative to TMS. ³¹P{¹H} NMR spectra chemical shifts are relative to H₃PO₄.

Preparation of compounds [lutH]BPh₄,³ NaSR (R = Et, Cy or Bu^t)⁴ and [NiCl(triphos)]BPh₄⁵ were prepared by the methods described in the literature (see ESI).

[Ni(SR)(triphos)]BPh₄ (R = Et, Bu^t or Cy) The complexes were prepared by a method analogous to that previously described for R = Et.⁵ To a suspension of [NiCl(triphos)]BPh₄ (0.5 g; 0.53 mmol) in THF (ca. 20 mL) was added a slight excess of NaSR (0.75 mmol). The colour 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 (ca. 50 mL) 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 (dichloromethane and ether were used instead for the Bu^t compound). Leaving the solution undisturbed at room temperature for 48 h produced well-formed red crystals. The 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. The identity of each product was confirmed by NMR spectroscopy and X-ray crystallography. [Ni(SEt)(triphos)]BPh₄, ¹H NMR: δ 8.24–7.39 (m, PPh, 25H), 7.33–6.75 (m, BPh, 20H), 2.1–1.9 (m, CH₂, 10H), 0.69 (t, J_{HH} = 7.3 Hz, CH₃, 3H); ³¹P{¹H} NMR: δ 105.5 (t, J_{PP} = 26.2 Hz, PPh), 54.0 (d, J_{PP} = 24.9 Hz, PPh₂); UV-visible: λ = 350 nm (ε = 3600 dm³ mol⁻¹ cm⁻¹); λ = 500 nm (ε = 600 dm³ mol⁻¹ cm⁻¹). [Ni(SBu^t)(triphos)]BPh₄, ¹H NMR: δ 8.30–7.37 (m, PPh, 25H), 7.35–6.79 (m, BPh, 20H), 2.1–1.95 (m, CH₂, 8H), 0.8 (s, CH₃, 9H); ³¹P{¹H} NMR: δ 104 (t, J_{PP} = 26.3 Hz, PPh), 53.6 (d, J_{PP} = 26.2 Hz, PPh₂); UV-visible: λ = 350 nm (ε = 3200 dm³ mol⁻¹ cm⁻¹); λ = 575 nm (ε = 360 dm³ mol⁻¹ cm⁻¹). [Ni(SCy)(triphos)]BPh₄, ¹H NMR: δ 8.26–7.45 (m, PPh, 25H), 7.35–6.79 (m, BPh, 20H), 1.87–1.76 (m, CH, 1H), 1.24–0.89 (m, CH₂, 4H), 0.99–0.79 (m, CH₂, 4H), 0.55–0.32 (m, CH₂, 2H); ³¹P{¹H} NMR: δ 104 (t, J_{PP} = 21.1 Hz, PPh), 53.6 (d, J_{PP} = 21.0 Hz, PPh₂); UV-visible: λ = 350 nm (ε = 3800 dm³ mol⁻¹ cm⁻¹); λ = 520 nm (ε = 730 dm³ mol⁻¹ cm⁻¹).

X-ray crystallography⁶ Diffraction data for the three complexes were measured at 150 K with Mo-Kα radiation (λ = 0.71073 Å) on an Agilent Technologies Gemini A Ultra diffractometer. Absorption corrections were based on repeated and symmetry-equivalent reflections. The structures were solved by direct methods and refined using all unique *F*² values. Two-fold disorder was resolved for the ethyl and some phenyl groups in the ethyl complex, and for a dichloromethane molecule with alternative positions close to an inversion centre in the *t*-butyl complex; a satisfactory model for disordered THF

in the cyclohexyl complex could not be achieved, so this was treated with the SQUEEZE procedure of PLATON (as a monosolvate). Selected crystal data are shown in Table 1.

Table 1 Crystal data

Compound	R = Et	R = Bu ^t	R = Cy
Chem formula	C ₃₆ H ₃₈ NiP ₃ S ⁺ •C ₂₄ H ₂₀ B ⁻	C ₃₈ H ₄₂ NiP ₃ S ⁺ •C ₂₄ H ₂₀ B ⁻ •0.5CH ₂ Cl ₂	C ₄₀ H ₃₄ NiP ₃ S ⁺ •C ₂₄ H ₂₀ B ⁻ •C ₄ H ₈ O
Formula mass	973.6	1044.1	1089.7
Crystal system	Triclinic	Triclinic	Triclinic
<i>a</i> /Å	11.4239(7)	12.5663(6)	11.3585(4)
<i>b</i> /Å	14.8484(7)	13.8894(6)	14.9357(5)
<i>c</i> /Å	16.8232(8)	17.6784(8)	19.0458(8)
<i>α</i> /°	96.983(4)	72.371(4)	79.270(3)
<i>β</i> /°	106.192(5)	75.534(4)	73.939(3)
<i>γ</i> /°	110.902(5)	67.285(4)	68.720(3)
<i>V</i> /Å ³	2481.2(2)	2681.4(2)	2879.9(2)
<i>T</i> /K	150(2)	150(2)	150(2)
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>Z</i>	2	2	2
Reflections measured	25830	27976	44424
Independent reflections	10547	10556	11699
Refined parameters	779	653	631
<i>R</i> _{int}	0.0369	0.0430	0.0335
<i>R</i> ₁ (<i>I</i> > 2σ)	0.0381	0.0506	0.0377
<i>wR</i> (<i>F</i> ²) (<i>I</i> > 2σ)	0.0747	0.1120	0.0873
<i>R</i> ₁ (all data)	0.0578	0.0785	0.0505
<i>wR</i> (<i>F</i> ²) (all data)	0.0834	0.1278	0.0939
GoF on <i>F</i> ²	1.033	1.021	1.021
Max, min diff el dens/eÅ ⁻¹	0.37, -0.39	0.77, -0.70	0.92, -0.57
CCDC ref	1042944	1042945	1042946

Kinetic studies All kinetic studies were performed using an Applied Photophysics SX.18 MV stopped-flow spectrophotometer, modified to handle air-sensitive solutions, connected to a RISC computer. The temperature was maintained using a Grant LTD 6G thermostat tank with combined recirculating pump. The experiments were conducted at 25.0°C. The wavelength used was λ = 350 nm. The solutions of complex and reactants were prepared under an atmosphere of dinitrogen and transferred to the stopped-flow apparatus using gas-tight, all-glass syringes. The kinetics were studied in dry MeCN under pseudo-first-order conditions, with [lutH]BPh₄ and lut present in at least a 10-fold excess over the concentration of the complex. Mixtures of [lutH]BPh₄ and lut were prepared from stock solutions of the two reagents. All solutions were used within 1 hour of preparation.

Under all conditions, the stopped-flow absorbance-time traces are a good fit to a single exponential curve (see ESI). The dependences on the concentrations of lutH⁺ and lut were determined from graphs of *k*_{obs}/[lut] versus [lutH⁺]/[lut] (where *k*_{obs} = pseudo-first-order rate constant). The type of plot obtained is shown in Fig. 1 and ESI. The analysis of the plots to obtain the rate laws is explained in the results and discussion section.

Table 2 Comparison of selected bond lengths and angles for [Ni(SR)(triphos)]BPh₄ (R = Et, Bu^t, Cy, Bn or Ph)

complex	R = Et	R = Bu ^t	R = Cy	R = Bn ^a	R = Ph ^b
<i>bond angles</i>					
P1–Ni–S	90.22(2)	100.57(3)	90.27(2)	103.95(4)	99.03(3)
P2–Ni–S	165.83(2)	173.78(4)	165.92(9)	164.01(4)	173.89(3)
P3–Ni–S	102.43(2)	88.78(3)	102.72(2)	89.66(4)	89.76(3)
P1–Ni–P2	85.24(2)	85.59(3)	84.71(2)	84.80(4)	86.41(2)
P1–Ni–P3	162.10(2)	160.01(3)	162.86(2)	161.90(4)	161.50(3)
P2–Ni–P3	85.23(2)	85.10(3)	85.04(2)	84.96(4)	85.82(2)
Ni–S–C	119.24(18)	110.57(11)	117.08(7)	115.18(13)	99.20(8)
<i>bond lengths</i>					
Ni–S	2.1600(6)	2.2384(8)	2.1663(6)	2.1689(10)	2.2456(7)
P1–Ni	2.1962(6)	2.2056(9)	2.1934(5)	2.2042(10)	2.2101(7)
P2–Ni	2.1339(6)	2.1372(8)	2.1284(5)	2.1468(10)	2.1506(6)
P3–Ni	2.1888(6)	2.1816(9)	2.1990(5)	2.1960(10)	2.1858(7)

(a) Dimensions correspond to the numbering scheme presented here, report of original structure had slightly different numbering scheme (P₂ and P₃ interchanged)^{2c}; (b) structure reported in reference 2e.

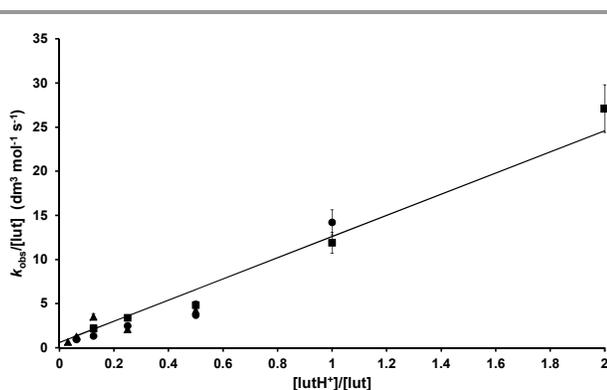


Fig. 1. Dependence of $k_{\text{obs}}/[\text{lut}]$ on $[\text{lutH}^+]/[\text{lut}]$ for the reaction of [Ni(SEt)(triphos)]⁺ with mixtures of lutH⁺ and lut in MeCN at 25.0°C. Data points correspond to: [lutH⁺] = 1.25 mmol dm⁻³, [lut] = 2.5–40 mmol dm⁻³ (▲); [lutH⁺] = 2.5 mmol dm⁻³, [lut] = 2.5–40 mmol dm⁻³ (●); [lutH⁺] = 5.0 mmol dm⁻³, [lut] = 2.5–40 mmol dm⁻³ (■). The line is that defined by Equation (2) and the parameters shown in Table 3. Error bars correspond to ± 10%.

Results and Discussion

X-ray crystal structures of [Ni(SR)(triphos)]BPh₄ (R = Et, Bu^t or Cy) The structures of [Ni(SR)(triphos)]BPh₄ (R = Et, Bu^t or Cy, the last two incorporating also disordered solvent molecules) have all been determined by X-ray crystallography (see ESI for details). The structure of the R = Bu^t cation is shown in Fig. 2 and the structures of the other cations are shown in the ESI. Selected bond lengths and angles (around Ni) for all three cations are presented in Table 2, together with the dimensions for the previously reported, structurally analogous R = Bn and R = Ph complexes.^{2c} The structure of the complexes are best described as distorted square-planar. Inspection of the

data in Table 2 shows that there are no significant systematic differences in the dimensions or geometry at Ni. It is, however, worth noting that, whilst the bond lengths and angles for [Ni(SEt)(triphos)]⁺ and [Ni(SCy)(triphos)]⁺ are very similar, there appear to be some minor differences in the [Ni(SBu^t)(triphos)]⁺ structure. Thus, the Ni–S bond in [Ni(SBu^t)(triphos)]⁺ (2.2384(8) Å) is significantly longer than those in [Ni(SEt)(triphos)]⁺ (2.1600(6) Å) and [Ni(SCy)(triphos)]⁺ (2.1663(6) Å). Furthermore, the Ni–S–C angle for [Ni(SBu^t)(triphos)]⁺ (110.57(11)°) is somewhat smaller than those in [Ni(SEt)(triphos)]⁺ (119.24(18)°) and [Ni(SCy)(triphos)]⁺ (117.08(7)°). It seems unlikely that such small differences will have a significant effect on the rates or kinetics of the protonation reactions discussed below.

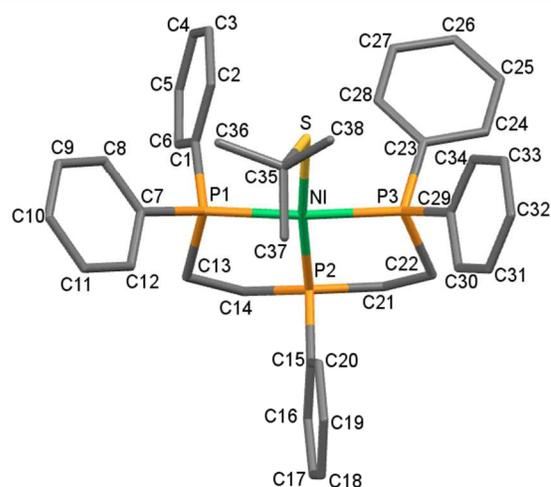


Fig. 2. Structure of the [Ni(SBu^t)(triphos)]⁺ cation, with H atoms omitted. Selected bond lengths and angles are presented in Table 2.

Table 4. Summary of the kinetic data for the reactions between [Ni(thiolate)(triphos)]⁺ and mixtures of lutH⁺ and lut in MeCN at 25.0°C

R or R'	$K_1^R / \text{dm}^3 \text{mol}^{-1}$	k_2^R / s^{-1}	$K_1^R k_2^R / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$k_{-2}^R / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$K_1^R K_2^R$	$\text{p}K_a^R$
[Ni(SR)(triphos)] ⁺						
Et	≤ 20	≥ 0.6	12.0	0.6	20.0	16.7
Cy	≤ 20	≥ 0.25	5.0	1.2	4.2	16.0
Bu ^t	≤ 20	≥ 0.65	13.0	0.7	18.6	16.7
Bn	≤ 20	≥ 0.16	3.2	2.0	1.6	15.6 ^{2e}
[Ni(SC ₆ H ₄ R'-4)(triphos)] ⁺ ^{2e}						
NO ₂	>160	7.0		1 × 10 ⁴		
Cl	>160	0.19		6		
H	200	0.10	20.0	4	5.0	14.8
Me	>160	0.05		1.5		
MeO	55.5	0.07	3.9	2.5	1.6	14.3

to [Ni(SC₆H₄R'-4)(triphos)]⁺. That the formation of **D** is favoured by the less basic arylthiolate ligands indicates that NH...S hydrogen bonding is not the principal factor stabilizing **D**. Rather, it suggests (as discussed below) that when lutH⁺ is hydrogen bonded to the complex the local environment generated by the phenyl groups on triphos which surround and encapsulate the hydrogen bonded lutH⁺ is important in stabilizing **D**. The electronic characteristics of the phenyl groups on triphos (and hence the environment surrounding the bound lutH⁺) will be modulated by the nature of the thiolate ligand.

Factors stabilizing the precursor intermediate (D). The values of K_1^R , k_2^R and k_{-2}^R for the reactions of [Ni(thiolate)(triphos)]⁺ with mixtures of lutH⁺ and lut are summarised in Table 4. Inspection of these data shows the following features. (i) Equilibrium constants for binding of lutH⁺ to all [Ni(SC₆H₄R'-4)(triphos)]⁺ (K_1^R) are significantly larger than the binding constants to [Ni(SR)(triphos)]⁺ (R = Et, Cy or Bu^t). (ii) The experimental kinetic data for the reactions of [Ni(SC₆H₄R'-4)(triphos)]⁺ with lutH⁺ do not allow K_1^R to be calculated for all complexes (only limits to K_1^R can be estimated in some cases). However, a notable feature of the data in Table 4 is that K_1^R is larger when the 4-R'-substituent is electron-withdrawing (e.g. [Ni(SC₆H₄NO₂-4)(triphos)]⁺, $K_1^{\text{NO}_2} \geq 160 \text{ dm}^3 \text{mol}^{-1}$; [Ni(SC₆H₄OMe-4)(triphos)]⁺, $K_1^{\text{MeO}} = 55.5 \text{ dm}^3 \text{mol}^{-1}$). Thus, the complexes containing the less basic thiolates (or the more electron-withdrawing 4-R'-substituents) are associated with the largest K_1^R .

That the less basic thiolates most favour the formation of **D** (i.e. highest value of K_1^R) is counter-intuitive. It seems reasonable that the precursor intermediates {[Ni(thiolate)(triphos)]...Hlut}²⁺ (**D**) involve a NH...S hydrogen bond and this proposal is consistent with earlier DFT calculations on {[Ni(SPh)(triphos)]...Hlut}²⁺.⁸ If the strength of the NH...S hydrogen bond was the principal factor in stabilizing **D**, It would be anticipated that K_1^R would increase with the basicity of the thiolate or the electron-donating

capability of the 4-R'-substituent in aryl thiolates. Clearly, the (electronic) factors which stabilize **D** are not those which result in stronger NH...S hydrogen bonds. The hydrogen bonded lutH⁺ cannot be bound to any other part of the complex in **D** and so non-bonding interactions within **D** need to be considered to understand why lutH⁺ binds most strongly to complexes containing weakly basic thiolates. In particular, we need to consider the local environment, created by the phenyl substituents on triphos that encapsulates the bound lutH⁺.

The X-ray crystal structures of [Ni(SR)(triphos)]⁺ (R = Ph,⁵ C₆H₄NO₂-4,^{2e} Bn,^{2e} Et, Cy and Bu^t) have been reported and in all structures the conformations of the two chelate rings of triphos are identical; there is a pseudo mirror plane containing P₂-Ni-S, as shown in Fig. 4. These conformations result in the two faces of the square plane being different. Thus, the side of the square plane containing the phenyl substituent on the central phosphorus (P₂) is more open (i.e. less congested), with the distance between phenyl substituents on the two terminal phosphorus atoms being *ca* 5.2 Å. In contrast, on the other side of the molecule, the distance between phenyl substituents on the two terminal phosphorus atoms is only *ca* 2.8 Å. In all the X-ray crystal structures the R group of the thiolate sits on the side of the complex with the more open face.

Formation of the precursor intermediate {[Ni(thiolate)(triphos)]...Hlut}²⁺ (**D**) necessitates that the acid binds to a lone pair of electrons on sulfur and hence the lutH⁺ sits in the closed face. Alternatively, after Ni-S bond rotation, lutH⁺ could hydrogen bond to the sulfur whilst sitting in the more open face of the complex (Fig. 4). In either case the structure of **D** is congested and in particular the phenyl substituents of the triphos ligand surround the bound lutH⁺.⁸ This observation intimates that the local environment that encapsulates the bound lutH⁺ may affect the stability of **D**.

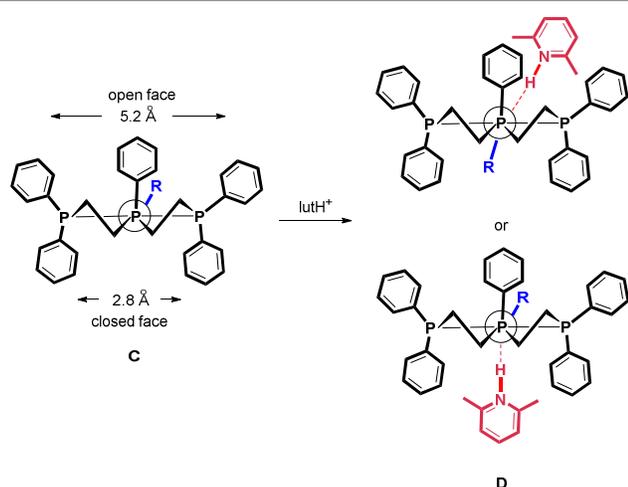


Fig. 4. Representations of the binding of lutH^+ to $[\text{Ni}(\text{SR})(\text{triphos})]^+$ (**C**) to form **D**, showing how the conformation of the triphos chelate rings differentiates the two faces of **C**. The view is along the $\text{P}_2\text{-Ni-S}$ axis (P_2 = central P of triphos; in the orientation shown, Ni and S are behind P_2).

Because of the congestion in **D** the lutH^+ binds in a cavity created by the phenyl groups of triphos and consequently the binding affinity of lutH^+ is affected by the local environment created by these phenyl groups. In $[\text{Ni}(\text{thiolate})(\text{triphos})]^+$ it seems likely that the electronic characteristics of the thiolate ligand are transmitted, through the Ni, to the phenyl groups of the triphos ligand and this modulates the local environment encapsulating the bound lutH^+ .⁹

Studies on simple organic molecules have shown that aromatics can associate (π -stack) with one another and that this association is stabilized by electron-withdrawing substituents on the aromatics.¹⁰ The same reactivity pattern is reflected in the variation of K_1^{R} with changes in the thiolate, suggesting that the binding of lutH^+ to $[\text{Ni}(\text{thiolate})(\text{triphos})]^+$ is affected by the local encapsulating environment created by the phenyl groups of triphos. The electronic characteristics of the thiolate ligand will modulate both the $\text{NH}\dots\text{S}$ hydrogen bonding and the encapsulation, but in opposite ways: hydrogen bonding is favoured by basic thiolates, or aryl thiolates with an electron-donating substituent, whilst the non-bonding interactions associated with the encapsulation is facilitated by thiolates with the opposite characteristics. The results presented in this paper indicate that modulating the local environment encapsulating the bound lutH^+ is more important in stabilizing **D** than changing the basicity of the coordinated thiolate (which would affect the $\text{NH}\dots\text{S}$ bond strength).

The proposal that it is the surroundings encapsulating lutH^+ , rather than the strength of the $\text{NH}\dots\text{S}$ hydrogen bond, which is important in stabilizing **D** also rationalizes the reactivity of other similar complexes. Thus, for the reactions of mixtures of lutH^+ and lut with $[\text{Ni}(\text{XPh})(\text{triphos})]^+$ ($\text{X} = \text{Se}$ or O)⁹ the kinetics with $\text{X} = \text{Se}$ (poorly basic) exhibit a non-linear dependence on $[\text{lutH}^+]$ {equation (5)} but the kinetics for $\text{X} = \text{O}$ (strongly basic) exhibit a linear dependence on $[\text{lutH}^+]$

{equation (6)}. Furthermore, we have previously shown that the reactions of $[\text{Ni}(\text{SC}_6\text{H}_4\text{R}'\text{-4})_2(\text{dppe})]$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) with mixtures of lutH^+ and lut follow a similar reactivity pattern to $[\text{Ni}(\text{SC}_6\text{H}_4\text{R}'\text{-4})(\text{triphos})]^+$.^{2d} Thus, for $[\text{Ni}(\text{SC}_6\text{H}_4\text{NO}_2\text{-4})_2(\text{dppe})]$, the kinetics of the protonation reactions exhibit a non-linear dependence on $[\text{lutH}^+]$ {equation (5)}. However, with $[\text{Ni}(\text{SC}_6\text{H}_4\text{R}'\text{-4})_2(\text{dppe})]$ ($\text{R}' = \text{MeO}$, Me , H or Cl) containing thiolates with more electron-releasing 4- R' -substituents, the reactions show a linear dependence on $[\text{lutH}^+]$ {equation (6)}.

It is unusual that the principal factor controlling the stability of $\{[\text{Ni}(\text{thiolate})(\text{triphos})]\dots\text{Hlut}\}^{2+}$ (**D**) is the local environment surrounding the hydrogen bonded acid rather than the $\text{NH}\dots\text{S}$ hydrogen bond strength. The reason why this behaviour is observed for **D** could, at least in part, be because the basicities (and hence presumably the $\text{NH}\dots\text{S}$ hydrogen bonding strengths) of the coordinated thiolates in $[\text{Ni}(\text{thiolate})(\text{triphos})]^+$ are very similar, as described in the next section.

Rates of proton transfer and pK_a s of $[\text{Ni}(\text{thiol})(\text{triphos})]^{2+}$.

The rate constants for protonation of $[\text{Ni}(\text{thiolate})(\text{triphos})]^+$ by lutH^+ ($K_1^{\text{R}}k_2^{\text{R}}$) and deprotonation of $[\text{Ni}(\text{thiol})(\text{triphos})]^{2+}$ by lut (k_2^{R}) are presented in Table 4. It is notable that both $K_1^{\text{R}}k_2^{\text{R}}$ and k_2^{R} show little variation with the thiolate. Furthermore, this pattern extends to $[\text{Ni}(\text{XPh})(\text{triphos})]^+$ ($\text{X} = \text{O}$, $K_1^{\text{O}}k_2^{\text{O}} = 1.65$, $k_2^{\text{O}} = 1.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $\text{X} = \text{Se}$, $K_1^{\text{Se}}k_2^{\text{Se}} = 14.9$, $k_2^{\text{Se}} = 0.4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). We have noted this feature before and suggested it is because a significant barrier to proton transfer in these systems is the sterically demanding lutH^+ and lut accessing the basic site through the phenyl substituents on the triphos ligand.⁸

The equilibrium constant (K_0^{R}) for equation (1) can be calculated from the kinetic data using equations (8). Since, for lutH^+ , $\text{pK}_a^{\text{lut}} = 14.1$ in MeCN,¹² the pK_a^{R} of the coordinated thiol can be calculated using equation (9).

$$\frac{[\text{Ni}(\text{SHR})(\text{triphos})^{2+}][\text{lut}]}{[\text{Ni}(\text{SR})(\text{triphos})^+][\text{lutH}^+]} = K_0^{\text{R}} = K_1^{\text{R}}.k_2^{\text{R}} = \frac{K_1^{\text{R}}.k_2^{\text{R}}}{k_2^{\text{R}}} \quad (8)$$

$$K_0^{\text{R}} = K_a^{\text{lut}}/K_a^{\text{R}} \quad (9)$$

Calculations show that $\text{pK}_a^{\text{R}'} = 14.5 \pm 0.3$ for $[\text{Ni}(\text{SC}_6\text{H}_4\text{R}'\text{-4})(\text{triphos})]^+$ ($\text{R}' = \text{H}$ or MeO , Table 4). This value is in good agreement with $\text{pK}_a^{\text{R}'} = 14.3 \pm 0.4$, reported earlier for the similar $[\text{Ni}(\text{SC}_6\text{H}_4\text{R}'\text{-4})_2(\text{dppe})]$.^{2d} For $[\text{Ni}(\text{SR})(\text{triphos})]^+$ ($\text{R} = \text{alkyl}$) $\text{pK}_a^{\text{R}} = 16.3 \pm 0.5$. Thus, as expected, the coordinated alkyl thiol is less acidic than coordinated aryl thiols. However, the difference is smaller than that of the free thiols ($\text{pK}_a^{\text{PhSH}} = 21.5$; $\text{pK}_a^{\text{EtSH}} = 28.6$, in MeCN).^{12,13} This 'levelling' of the pK_a s of coordinated thiols has been observed before^{2d} and also for other types of ligands.¹⁴ As we have discussed before,⁸ these pK_a s (calculated from the kinetic data) need to be treated with some caution. However, the rather small difference in the pK_a s of coordinated alkyl and aryl thiols ($\Delta\text{pK}_a \sim 2$) indicates that $\text{NH}\dots\text{S}$ hydrogen bonding in **D** would be relatively insensitive

to the nature of the coordinated thiolate and hence rather minor non-bonding interactions associated with the encapsulation of the bound lutH^+ can make a relatively significant contribution to the stability of **D**.

Conclusions

The studies described in this paper show that the different kinetics observed for the equilibrium protonation reactions of $[\text{Ni}(\text{SC}_6\text{H}_4\text{R}'\text{-4})(\text{triphos})]^+$ and $[\text{Ni}(\text{SR})(\text{triphos})]^+$ with mixtures of lutH^+ and lut are consistent with a single mechanism involving initial formation of a precursor hydrogen-bonded intermediate $\{[\text{Ni}(\text{thiolate})(\text{triphos})]\dots\text{Hlut}\}^{2+}$ (**D**) followed by intramolecular proton transfer (Figure 3). It might be expected that **D** is most stable (highest K_1^{R}) with complexes containing the most basic thiolates because this would increase the strength of the $\text{NH}\dots\text{S}$ hydrogen bonding in **D**. However, the results presented herein show that quite the opposite is true, and that changing the electronic character of the coordinated thiolate results in a reactivity pattern which is not consistent with hydrogen bonding being the only (or indeed the principal) factor stabilising **D**. Rather the electronic influences that the thiolate has on K_1^{R} indicate that an important factor stabilizing **D** is the local environment created by the phenyl groups of triphos which encapsulate the bound lutH^+ . This local environment is modulated by the electronic characteristics of the coordinated thiolate. The results and conclusions presented in this paper suggest that preparing elaborate ligands (which generate extended cavities around reaction sites) could be used to control the rates of proton transfer to coordinated molecules and ions in transition metal complexes.

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Notes and references

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† CCDC-1042944–1042946 contain the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Electronic Supplementary Information (ESI) available: synthesis and characterization of reagents; summary of kinetic data for the reactions of $[\text{Ni}(\text{SR})(\text{triphos})]^+$ ($\text{R} = \text{Et}, \text{Bu}^t$ or Cy) with mixtures of lutH^+ and lut in MeCN, crystallography results tables and pictures. See DOI: 10.1039/b000000x/

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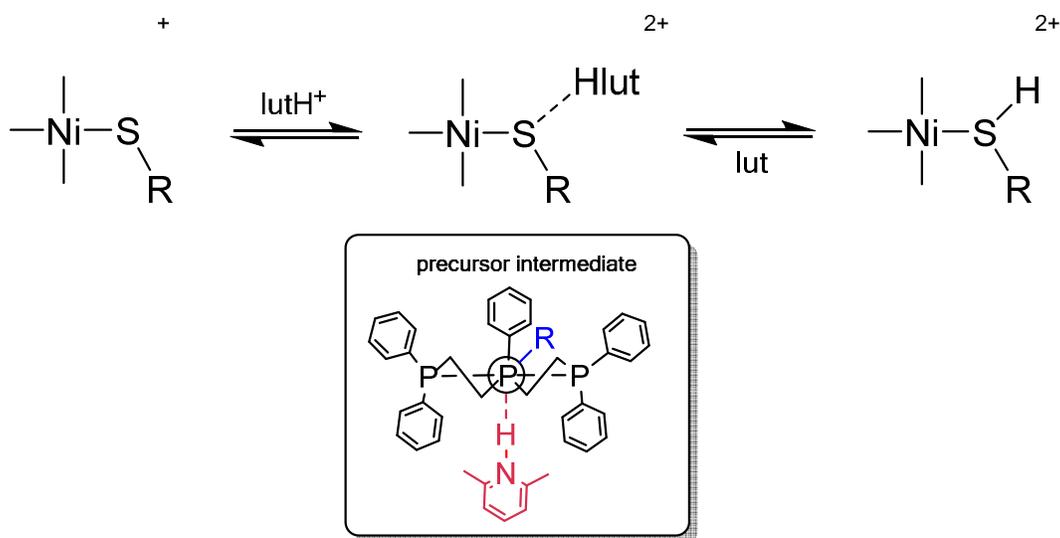
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Mechanism of proton transfer to coordinated thiolates: encapsulation of acid stabilizes precursor intermediate

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and Richard A. Henderson

ABSTRACTS

Graphical Abstract



Textual Abstract

Hydrogen bonded intermediate in protonation of [Ni(thiolate)(triphos)]⁺ by 2,6-lutidinium is stabilized by encapsulation of the acid by phenyl groups of triphos.