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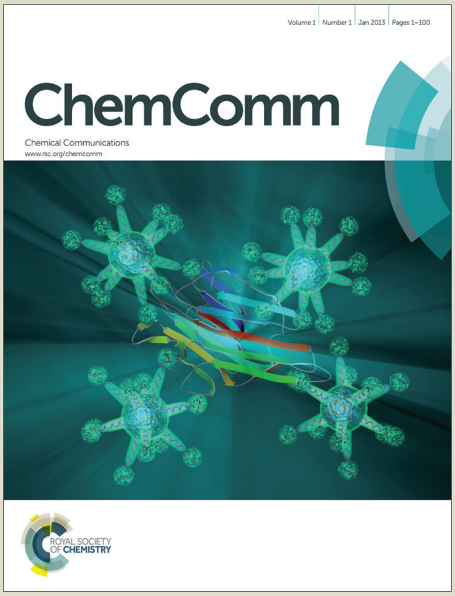
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Sterics level the rates of proton transfer to $[Ni(XPh)\{PhP(CH_2CH_2PPh_2)_2\}]^+$ (X = O, S or Se)

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Rates of proton transfers between lutH$^+$ (lut = 2,6-dimethylpyridine) and $[Ni(XPh)(PhP\{CH_2CH_2PPh_2\}_2)]^+$ (X = O, S or Se) are slow and show little variation ($k^O : k^S : k^{Se} = 1 : 12 : 9$). This unusual behaviour is a consequence of sterics affecting the optimal interaction between the reactants prior to proton transfer.

Thermodynamically-favourable proton transfer reactions occur at the diffusion-controlled rate provided: (a) both the donor and acceptor group belong to the classical hydrogen bond formers (O- or N-type) and (b) the electronic and spatial configurations of the acids and their conjugate bases are identical. Thus, proton transfer to oxygen sites are normally diffusion-controlled, whilst proton transfer to analogous sulfur sites are slower because the stronger hydrogen bonding to oxygen stabilises the transition state for proton transfer.[1] Invariably, proton transfer involving carbon and metal sites is slow.[2] In this communication we describe the kinetics of the equilibrium proton transfer reactions between lutH$^+$ (lut = 2,6-dimethylpyridine) and the square-planar $[Ni(XPh)(triphos)]^+$ (X = O, S or Se; triphos = $PhP\{CH_2CH_2PPh_2\}_2$) shown in equation (1).[3] The kinetics were monitored using stopped-flow spectrophotometry in MeCN as solvent and comparison of the rates of proton transfer within this series of complexes shows that the reactions are markedly slower than the diffusion-controlled rate ($k_{diff} = 4 \times 10^{10}$ dm^3 mol^{-1} s^{-1}),[4] and essentially invariant for the whole series. Molecular mechanics calculations indicate that the reason for this behaviour is because steric factors make it difficult for the acid to position itself correctly in preparation for proton transfer.

$$[Ni(XPh)(triphos)]^+ + lutH^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [Ni(HXPh)(triphos)]^{2+} + lut \qquad (1)$$

We have studied the kinetics of the reaction between $[Ni(SePh)(triphos)]^+$ and an excess of both lutH$^+$ and lut in MeCN. The reaction exhibits a first order dependence on the concentration of the complex, as indicated by the exponential fits to the absorbance-time curves (see ESI). Furthermore, plots of k_{obs}/[lut] versus [lutH$^+$]/[lut] are linear but only when the concentration of lutH$^+$ is constant (Fig. 1). Analysis of these data are consistent with the rate law shown in equation (2), and the values of K_1^{Se}, k_2^{Se} and k_{-2}^{Se} are presented in the Table.

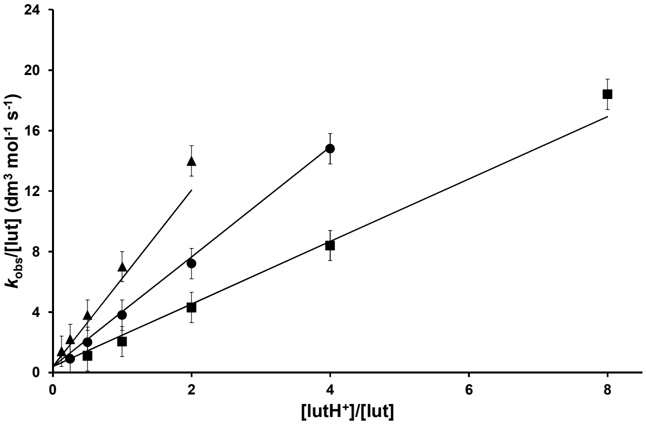

Fig. 1. Plot of k_{obs}/[lut] versus [lutH$^+$]/[lut] for the reaction of $[Ni(SePh)(triphos)]^+$ (0.25 mmol dm^{-3}) with mixtures of lutH$^+$ and lut in MeCN at 25.0 ºC. Data points correspond to [lutH$^+$] = 5 mmol dm^{-3}, [lut] = 2.5 – 40 mmol dm^{-3} (▲); [lutH$^+$] = 10 mmol dm^{-3}, [lut] = 2.5 – 40 mmol dm^{-3} (●); [lutH$^+$] = 20 mmol dm^{-3}, [lut] = 2.5 – 40 mmol dm^{-3} (■). Lines drawn are defined by equation (2) and the parameters in the Table.

$$\text{Rate} = \left\{ \frac{K_1^X k_2^X[lutH^+]}{1 + K_1^X[lutH^+]} + k_{-2}^X[lut]\right\}[Ni(XPh)(triphos)^+] \qquad (2)$$

We recently studied the similar equilibrium reaction between lutH$^+$ and $[Ni(SPh)(triphos)]^+$ in the presence of lut, under identical conditions, and the kinetics also followed the rate law in equation (2).[5] The values of K_1^S, k_2^S and k_{-2}^S are summarised in the Table. The rate law of equation (2) indicates the two step mechanism presented in Fig. 2. The mechanism comprises two coupled equilibria. The first step involves initial association of lutH$^+$ to $[Ni(XPh)(triphos)]^+$

(presumably hydrogen bonding to X). In the second step, intramolecular proton transfer between $lutH^+$ and X occurs.

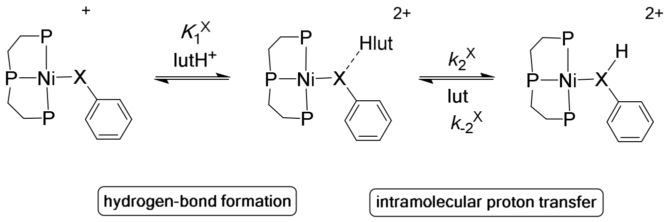

Fig. 2. Mechanism of proton transfer between $lutH^+$ and $[Ni(XPh)(triphos)]^+$ (X = O, S or Se). Phenyl substituents on triphos omitted for clarity.

Table. Rate constants for the equilibrium reactions between mixtures of $lutH^+$ and lut and $[Ni(XPh)(triphos)]^+$ (X = O, S or Se) in MeCN at 25 °C.

X	$K_1^Xk_2^X$ $dm^3\ mol^{-1}\ s^{-1}$	k_{-2}^X $dm^3\ mol^{-1}\ s^{-1}$	pK_a^{X} [c]	pK_a [d]
O	1.65±0.1	1.5±0.1	14.1	28.5
S [a]	20.0±1.0	4.0±0.2	14.8	21.5
Se [b]	14.9±1.0	0.4±0.05	15.7	18.1

footnotes: [a] rate law is that shown in eqn. (2), $K_1^S = 200\ dm^3\ mol^{-1}$, $k_2^S = 0.1\ s^{-1}$, $k_{-2}^S = 4.0\ dm^3\ mol^{-1}\ s^{-1}$;[5] [b] rate law is that shown in eqn. (2), $K_1^{Se} = 310\ dm^3\ mol^{-1}$, $k_2^{Se} = 0.048\ s^{-1}$, $k_{-2}^{Se} = 0.4\ dm^3\ mol^{-1}\ s^{-1}$. [c] Calculated using $K_1^Xk_2^X/k_{-2}^X = K_a^{lutH}/K_a^X$; $pK_a^{lutH} = 14.1$[6]. [d] pK_a (in MeCN) of uncoordinated PhXH (X = O is experimental,[7] others are calculated[8]).

The kinetics of the reaction between $[Ni(OPh)(triphos)]^+$ and an excess of both $lutH^+$ and lut have also been studied in MeCN. The reaction exhibits a first order dependence on the concentration of the complex. However, in contrast to the studies with the sulfur and selenium analogues, a plot of k_{obs}/[lut] versus $[lutH^+]$/[lut] is a single straight line (for all data) with a positive intercept, as shown in Fig. 3. The associated rate law is shown in equation (3) where k_f = forward rate constant for protonation = 1.65±0.1 $dm^3\ mol^{-1}\ s^{-1}$ and k_b = rate constant for deprotonation = 1.5±0.1 $dm^3\ mol^{-1}\ s^{-1}$.

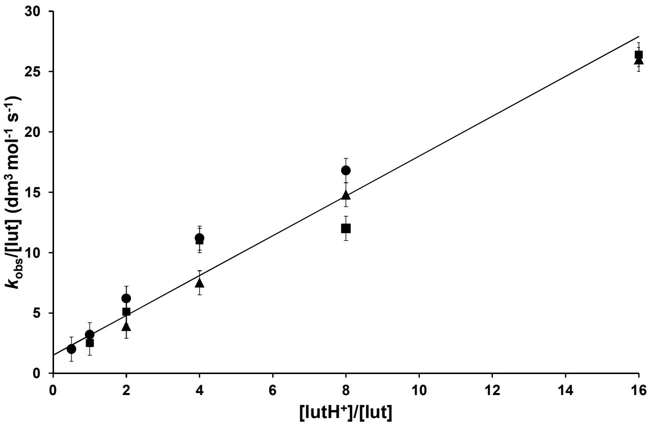

Fig. 3. Plot of k_{obs}/[lut] versus $[lutH^+]$/[lut] for the reaction of $[Ni(OPh)(triphos)]^+$ (2 mmol dm^{-3}) with mixtures of $lutH^+$ and lut in MeCN at 25.0 °C. Data points correspond to $[lutH^+]$ = 10 mmol dm^{-3}, [lut] = 1.25 – 20 mmol dm^{-3} (●); $[lutH^+]$ = 20 mmol dm^{-3}, [lut] = 1.25 – 20 mmol dm^{-3} (■); $[lutH^+]$ = 40 mmol dm^{-3}, [lut] = 1.25 – 20 mmol dm^{-3} (▲). Line drawn is defined by equation (3) and the values reported in the text.

$$\text{Rate} = \{k_f[lutH^+] + k_b[lut]\}[Ni(OPh)(triphos)^+] \qquad (3)$$

It is reasonable that the reaction between $lutH^+$ and $[Ni(OPh)(triphos)]^+$ occurs by the same mechanism as for the sulfur and selenium analogues, shown in Fig. 2. Equation (3) is consistent with this mechanism and the general rate law shown in equation (2). If $K_1^O[lutH^+] < 1$, then equation (2) simplifies to equation (3), where $k_f = K_1^Ok_2^O$ and $k_b = k_{-2}^O$. The values of these constants are presented in the Table.

A notable feature about the data in the Table is that the rates of proton transfer to $[Ni(XPh)(triphos)]^+$ and from $[Ni(HXPh)(triphos)]^{2+}$ are much slower than the diffusion-controlled limit and, more unexpectedly, are essentially all the same ($K_1^Ok_2^O : K_1^Sk_2^S : K_1^{Se}k_2^{Se} = 1 : 12 : 9$; $k_{-2}^O : k_{-2}^S : k_{-2}^{Se} = 3.8 : 10 : 1$). This behaviour is unprecedented. The rates of proton transfer to oxygen sites are usually diffusion-controlled with transfer to analogous sulfur sites being slightly slower.[1] We are unaware of any previous study comparing the rates of proton transfer to analogous oxygen, sulfur and selenium sites.

Typically, in proton transfer reactions, the acid and base can approach one another essentially unhindered to achieve the optimal hydrogen bonding configuration, prior to proton transfer.[1,9] However, in systems where both the acid and base contain sterically demanding substituents (in our case, methyl groups on $lutH^+$ and phenyl groups on triphos), such an optimal geometry may be difficult to achieve, resulting in a decrease in the rate.

Using molecular mechanics calculations (GAUSSIAN03 package,[10] geometries optimized at the B3LYP/Lanl2dz levels of theory, see ESI) we have investigated the interactions between $[Ni(XPh)(triphos)]^+$ and $lutH^+$ in search for the origins of these slow proton transfer rates. The calculations show that the interaction between $lutH^+$ and $[Ni(XPh)(triphos)]^+$ involves hydrogen bonding of the acid to X as shown in Fig. 4 (dimensions and angles for the optimised structures are summarised in ESI).

Our calculations on the $\{[Ni(XPh)(triphos)]^+\text{--}lutH^+\}$ adducts show that the N--X distances (R_{NX}) are: N--O, R_{NO} = 2.75 Å; N--S, R_{NS} = 3.41 Å; N--Se, R_{NSe} = 3.59 Å (see Fig 4 and ESI). Earlier theoretical studies on systems of the type $\{H_nX\text{--}H\text{--}YH_m\}^+$ have calculated the proton transfer potentials for a series of H-bond lengths and shown that the energy barrier to proton transfer increases dramatically as the bond is elongated.[11] The optimal N--X distances are markedly different (X = O, R_{NO} ~ 2.9 Å; X = S, R_{NS} ~ 3.3 Å).[11,12] Our calculations on the $\{[Ni(XPh)(triphos)]^+\text{--}lutH^+\}$ adducts indicate that the N--X distances are in good agreement with the earlier calculated optimal distances necessary for rapid proton transfer.

Other calculations for $\{H_nX\text{--}H\text{--}YH_m\}^+$ have indicated that deviations of the N--X angle from the optimal (pointing directly at the lone pair) also result in an increase to the barrier for proton transfer. However, distortions of less than 20° make only a small increase in the barrier to proton transfer.[11,13] Our calculated geometries for the $\{[Ni(XPh)(triphos)]^+\text{--}lutH^+\}$ adducts {Fig. 4 (bottom)} show that the associated $lutH^+$ is orientated away from the bulky triphos substituents (angles: Ni-O-H = 133.6°; Ni-S-H = 148°; Ni-Se-H = 123°; see ESI), presumably because of steric issues between the triphos ligand and $lutH^+$. This enforced orientation of the associated $lutH^+$ compromises the optimal angle for proton transfer. However, the angular deviation from the optimal is, in all cases, less than 10°.

Our calculations indicate that the $lutH^+$ and $[Ni(XPh)(triphos)]^+$ can associate in a manner which essentially achieves both the optimal hydrogen bonding distance and the correct angle for rapid proton transfer. It appears that the reason for slow proton transfer is not the geometry of the hydrogen-bonded precursor but, rather, an issue with the trajectory that $lutH^+$ must follow to achieve this optimal hydrogen-bonded geometry. The calculations show that the optimal geometries for $\{[Ni(XPh)(triphos)]^+\text{--}lutH^+\}$ involve inserting the $lutH^+$ between the phenyl substituents of the triphos ligand, and this is a tight fit (Fig 4). Thus, the closest non-bonding H--H distance (R_{HH}) between the methyl group (on $lutH^+$) and the phenyl substituent (on triphos) {left hand side of Fig. 4 (top)} are: X = O, R_{HH} = 2.73 Å; X = S, R_{HH} = 2.99 Å; X = Se, R_{HH} = 3.76 Å. Consequently, the associated $lutH^+$ has little oscillatory freedom: average oscillation angles, $\theta_{av} \sim \pm 10^o$ (X = O); $\theta_{av} \sim \pm 11.3^o$ (X = S); $\theta_{av} \sim \pm 18.3^o$ (X = Se). Furthermore, the non-bonding H--H distance between the methyl group (top of $lutH^+$ in Fig. 4) and the phenyl substituent on the central phosphorus of triphos is short (X = O, R_{HH} = 2.38 Å; X = S, R_{HH} = 3.10 Å; X = Se, R_{HH} = 2.81 Å); see ESI. These non-bonding interactions must reduce the degrees of rotational freedom of the $lutH^+$ on its trajectory to forming the hydrogen bond and hence impedes proton transfer.

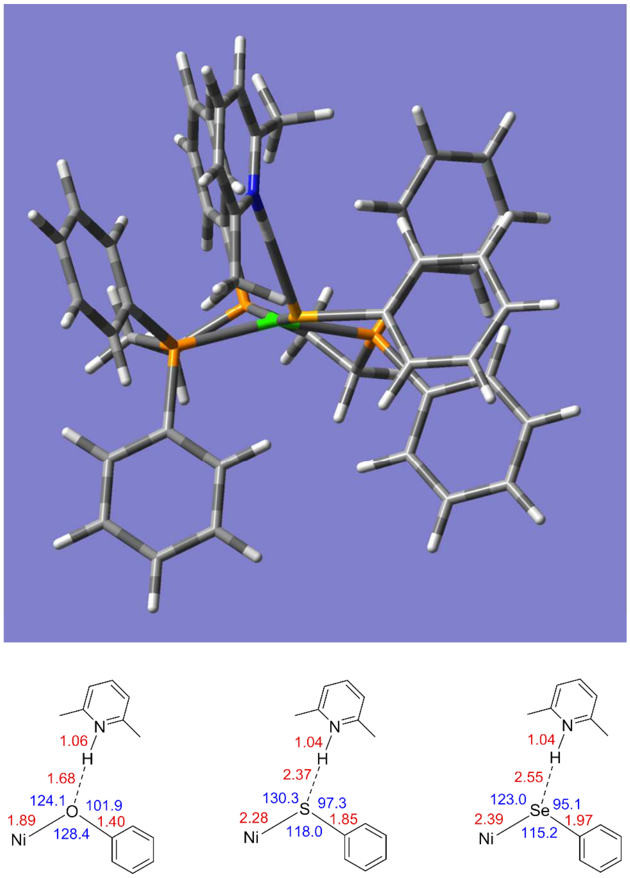

Fig. 4. Calculated optimised geometries for the association between $lutH^+$ and $[Ni(XPh)(triphos)]^+$ (X = O, S or Se). Top picture shows the interaction for X = Se (key: Ni = green; P = orange; Se = dark yellow; N = blue; H = white and C = grey). Bottom picture compares the optimal angles (in blue) and distances (in red) for the adducts with X = O, S and Se.

It is intuitively reasonable that the rates of proton transfer involving the reaction of the sterically-demanding $lutH^+$ with the sterically-demanding $[Ni(XPh)(triphos)]^+$ are slow because of steric factors. However, calculations indicate that the optimal geometries for proton transfer can be achieved in the hydrogen-bonded adducts, $\{[Ni(XPh)(triphos)]^+\text{--}lutH^+\}$. Therefore, the reason for the slow reactions is because the rate of formation of this optimal interaction is slow; the bulky reactants restrict the approach of the $lutH^+$ towards the complex. Furthermore it could be that the trajectory to form the optimal geometries shown in Fig. 4 is so difficult (slow) to achieve that proton transfer actually occurs through an association which is geometrically non-optimal, involving proton transfer over long distances at non-optimal angles.

Finally, we have calculated the apparent pK_a^X values of $[Ni(XHPh)(triphos)]^+$ using the kinetic data reported herein and presented in the Table. It is to be noted that the values of these apparent pK_a^Xs follow a trend diametrically opposite to that of the free PhXH, with coordinated PhOH being most acidic and PhSeH least acidic (see Table). This is because the equilibrium constants (K) for equation (1), calculated from the kinetic data ($K = k_f/k_b = K_1^X k_2^X / k_{-2}^X$), reflect the rates of proton transfer to and from the XPh ligand and not the acidity of this ligand, and hence are not true pK_a^Xs.

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Notes and references

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Electronic Supplementary Information (ESI) available: [summary of kinetic data for the reactions of $[Ni(XPh)(triphos)]^+$ (X = O or Se); selected bond lengths and angles for calculated structures of $\{[Ni(XPh)(triphos)]^+\text{--}lutH^+\}$]. See DOI: 10.1039/c000000x/

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