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# Sterics level the rates of proton transfer to [Ni(XPh){PhP(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>}]<sup>+</sup> (X = O, S or Se)

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#### **Kinetic Studies.**

#### Table S1

Kinetic data for the reaction of  $[Ni(OPh)(triphos)]^+$  (0.25 mmol dm<sup>-3</sup>) with mixtures of lutH<sup>+</sup> and lut in MeCN at 25.0 °C.<sup>a</sup>

[lutH <sup>+</sup> ] / mmol dm <sup>-3</sup>	[lut] / mmol dm <sup>-3</sup>	$k_{ m obs}$ / s <sup>-1 b</sup>	$\Delta A$	$A_{\mathrm{f}}$
10.0	1.25	0.021	0.107	0.49
	2.5	0.028	0.066	0.526
	5.0	0.031	0.087	0.528
	10.0	0.033	0.086	0.540
	20.0	0.040	0.037	0.589
20.0	1.25	0.033	0.242	0.434
	2.5	0.030	0.255	0.441
	5.0	0.055	0.183	0.460
	10.0	0.051	0.195	0.469
	20.0	0.051	0.184	0.486
40.0	2.50	0.065	0.403	0.250
	5.0	0.073	0.339	0.286
	10.0	0.075	0.243	0.310
	20.0	0.078	0.283	0.370

#### footnotes.

<sup>a</sup> These are equilibrium reactions as shown by the kinetics (see text) and the spectroscopic changes observed. {*i.e.* at constant [lutH<sup>+</sup>], increase in [lut] is associated with a decrease in the absorbance change ( $\Delta A = A_i - A_f$ ) and an increase in the final absorbance ( $A_f$ ), and, at constant [lut], increase in [lutH<sup>+</sup>] is associated with an increase in  $\Delta A$ }. The small irregularities in these patterns evident in the experimental data are presumably due to contributions to the total absorbance from lutH<sup>+</sup> and lut, and the low wavelength ( $\lambda = 350$  nm) used to study the kinetics.

We have been unable to isolate salts of the product,  $[Ni(HOPh)(triphos)]^{2+}$ . The only reasonable protonation site is the oxygen atom. The only other possible site for protonation is the nickel, but there is no precedent for Ni<sup>IV</sup> complexes of the type  $[Ni(H)(OPh)(triphos)]^{2+}$ .

<sup>b</sup> All curves fitted to the equation:  $A_t = A_f + \Delta A_e$ -kobs.t



**Fig S1**. Stopped-flow absorbance-time curve for the reaction between  $[Ni(OPh)(triphos)]^+$  (0.25 mmol dm<sup>-3</sup>) and lutH<sup>+</sup> (40 mmol dm<sup>-3</sup>) and lut (5.0 mmol dm<sup>-3</sup>) in MeCN at 25.0 °C;  $\lambda = 350$  nm. The experimental curve is shown in black and the exponential curve fit is grey. The equation of the exponential curve is A<sub>t</sub> = 0.286+0.339e<sup>-0.073t</sup>.

#### Table S2

Kinetic data for the reaction of  $[Ni(SePh)(triphos)]^+$  (0.25 mmol dm<sup>-3</sup>) with mixtures of lutH<sup>+</sup> and lut in MeCN at 25.0 °C.<sup>a</sup>

[lutH <sup>+</sup> ] / mmol dm <sup>-3</sup>	[lut] / mmol dm <sup>-3</sup>	$k_{ m obs}$ / s <sup>-1 b</sup>	ΔΑ	$\mathbf{A}_{\mathrm{f}}$
5.0	2.5	0.035	0.190	0.290
	5.0	0.034	0.140	0.290
	10.0	0.038	0.116	0.282
	20.0	0.044	0.097	0.278
	40.0	0.057	0.085	0.282
10.0	2.5	0.037	0.093	0.293
	5.0	0.036	0.085	0.290
	10.0	0.038	0.086	0.281
	20.0	0.040	0.071	0.289
	40.0	0.036	0.068	0.287
20.0	2.5	0.046	0.072	0.285
	5.0	0.042	0.070	0.280
	10.0	0.043	0.061	0.276
	20.0	0.041	0.060	0.270
	40.0	0.044	0.059	0.260

#### footnotes.

<sup>a</sup> These are equilibrium reactions as shown by the kinetics (see text) and the spectroscopic changes observed. {*i.e.* at constant [lutH<sup>+</sup>], increase in [lut] is associated with a decrease in the absorbance change ( $\Delta A = A_i - A_f$ ) and, at constant [lut], increase in [lutH<sup>+</sup>] is associated with an increase in  $\Delta A$ }. The irregularities in these patterns evident in the experimental data are due to: (i) the larger equilibrium constant for this reaction (K = 37.3), compared to that of [Ni(OPh)(triphos)]<sup>+</sup> (K = 1.1), resulting in smaller perturbations to the absorbances from changes in [lutH<sup>+</sup>] and [lut], and (ii) contributions to the total absorbance from lutH<sup>+</sup> and lut and the low wavelength ( $\lambda = 350$  nm) used to study the kinetics.

We have been unable to isolate salts of the product,  $[Ni(HSePh)(triphos)]^{2+}$ . The only reasonable protonation site is the selenium atom. The only other possible site for protonation is the nickel, but there is no precedent for Ni<sup>IV</sup> complexes of the type  $[Ni(H)(SePh)(triphos)]^{2+}$ . Attempts to use <sup>77</sup>Se NMR spectroscopy failed because  $[Ni(SePh)(triphos)]^+$  was insufficiently soluble to obtain good spectra.

<sup>b</sup> All curves fitted to the equation:  $A_t = A_f + \Delta A.e^{-kobs.t}$ 



**Fig S2**. Stopped-flow absorbance-time curve for the reaction between  $[Ni(SePh)(triphos)]^+$  (0.25 mmol dm<sup>-3</sup>) and lutH<sup>+</sup> (5.0 mmol dm<sup>-3</sup>) and lut (40.0 mmol dm<sup>-3</sup>) in MeCN at 25.0 °C;  $\lambda = 350$  nm. The experimental curve is shown in black and the exponential curve fit is grey. The equation of the exponential curve is  $A_t = 0.367+0.116e^{-0.057t}$ .

#### Calculations.

All theoretical calculations in this work were performed using the computational methods implemented in the GAUSSIAN03 package<sup>10</sup> The geometries of the compounds were optimized at the B3LYP/Lanl2dz levels of theory.

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, revision D.01; Gaussian, Inc.: Wallingford, CT*, 2004.

### Figure S3.

Pictures of the optimised structure of  $\{[Ni(OC_6H_5)(triphos)]^+--lutH^+\}$  showing the geometry of the hydrogen bonding interaction. Both pictures are of the same structure but from different orientations. Selected bond lengths and angles are shown in Table S3, and selected non-bonding H--H distances between the lutH+ and phenyl groups on triphos are shown in Table S4. Key: Ni = green; P = orange; O = red; N = blue; H = white and C = grey.



### Figure S4.

Pictures of the optimised structure of  $\{[Ni(SC_6H_5)(triphos)]^+--lutH^+\}$  showing the geometry of the hydrogen bonding interaction. Both pictures are of the same structure but from different orientations. Selected bond lengths and angles are shown in Table S3, and selected non-bonding H--H distances between the lutH+ and phenyl groups on triphos are shown in Table S4. Key: Ni = green; P = orange; S = yellow; N = blue; H = white and C = grey.





### Figure S5.

Pictures of the optimised structure of  $\{[Ni(SeC_6H_5)(triphos)]^+--lutH^+\}$  showing the geometry of the hydrogen bonding interaction. Both pictures are of the same structure but from different orientations. Selected bond lengths and angles are shown in Table S3, and selected non-bonding H--H distances between the lutH+ and phenyl groups on triphos are shown in Table S4. Key: Ni = green; P = orange; Se = dark yellow; N = blue; H = white and C = grey.





## Table S3.

Selected bond lengths and angles derived from the calculations for the hydrogen-bonded species  $\{[Ni(XPh)(triphos)]^+-lutH^+\}$  (X = O, S or Se).

parameter	complex		
bond lengths / Å	[Ni(OPh)(triphos)] <sup>+</sup>	[Ni(SPh)(triphos)] <sup>+</sup>	[Ni(SePh)(triphos)] <sup>+</sup>
Ni-P1	2.3835	2.3238	2.3215
Ni-P2	2.3067	2.2948	2.3002
Ni-P3	2.3610	2.3442	2.3409
Ni-X	1.8944	2.2839	2.3901
C-X	1.3958	1.8485	1.9716
H-X	1.6842	2.3670	2.5471
N-H	1.0609	1.0368	1.0354
bond angles / o			
P1-Ni-P2	84.2774	85.2205	85.1328
P2-Ni-P3	84.5498	85.6313	85.5031
P1-Ni-P3	151.9061	153.4338	154.4351
P1-Ni-X	101.8269	103.6225	103.5088
P2-Ni-X	171.6689	167.8539	167.5933
P3-Ni-X	92.3319	89.7014	90.0012
Ni-X-C	128.3714	117.9724	115.2255
Ni-X-H	124.1439	130.3322	123.0030
С-Х-Н	101.8936	97.3252	95.1183

## Table S4.

Closest non-bonding H--H distances derived from the calculations for the hydrogen-bonded species  $\{[Ni(XPh)(triphos)]^+-lutH^+\}$  (X = O, S or Se).



 $P_t$  = terminal phosphorus,  $P_c$  = central phosphorus

parameter	complex		
HH distances / Å	[Ni(OPh)(triphos)] <sup>+</sup>	[Ni(SPh)(triphos)] <sup>+</sup>	[Ni(SePh)(triphos)] <sup>+</sup>
H <sup>a</sup> H <sup>c</sup>	2.7280	2.9861	3.2426
H <sup>b</sup> H <sup>d</sup>	3.2301	3.1326	3.7575
H <sup>b</sup> H <sup>e</sup>	2.3823	3.0990	2.8099