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Mechanisms and rates of proton transfer to coordinated carboxydithioates: studies on $[Ni(S_2CR)\{PhP(CH_2CH_2PPh_2)_2\}]^+$ (R = Me, Et, Bu^n or Ph)

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1. KINETIC DATA

Table S1

Kinetic data for the reaction of $[Ni(S_2CMe)(triphos)]^+$ (0.5 mmol dm^{-3}) with HCl and Cl^- in MeCN at 25.0 °C (λ = 420 nm)

$[HCl]_0$ / mmol dm^{-3}	$[Cl^-]_0$ / mmol dm^{-3}	$[HCl]_e$ / mmol dm^{-3}	$[Cl^-]_e$ / mmol dm^{-3}	k_{obs} / s^{-1}	ΔA	A_f
2.5				6.1	0.023	0.502
5.0				13.3	0.033	0.505
10.0				23.7	0.034	0.505
20.0				45.4	0.044	0.505
30.0				53.5	0.042	0.507
50.0				89.9	0.038	0.508
5.0[a]				17.1	0.043	0.434
10.0[a]				22.4	0.045	0.439
20.0[a]				35.4	0.045	0.442
30.0[a]				32.2	0.040	0.443
40.0[a]				31.6	0.043	0.439
60.0[a]				37.8	0.040	0.444
80.0[a]				43.0	0.035	0.449
100.0[a]				45.5	0.032	0.443

Table S1 continued…

$[HCl]_0$ / mmol dm^{-3}	$[Cl^-]_0$ / mmol dm^{-3}	$[HCl]_e$ / mmol dm^{-3}	$[Cl^-]_e$ / mmol dm^{-3}	k_{obs} / s^{-1}	ΔA	A_f
50.0	2.5	47.8	0.29	72.3	0.038	0.506
	5.0	45.6	0.61	64.2	0.033	0.505
	10.0	41.3	1.32	58.7	0.034	0.506
	20.0	33.2	3.2	54.4	0.038	0.524
	30.0	25.9	5.9	38.9	0.039	0.539
	50.0	14.9	14.9	26.8	0.043	0.550
100.0	2.5	97.6	0.06	77.1	0.028	0.526
	5.0	95.3	0.32	65.0	0.026	0.532
	10.0	90.7	0.66	57.9	0.025	0.533
	20.0	81.4	1.44	56.6	0.024	0.537
	30.0	72.4	2.41	42.6	0.027	0.543
	50.0	55.0	5.0	40.7	0.036	0.562

footnotes.

[a] studies with DCl

Table S2

Kinetic data for the reaction of $[Ni(S_2CEt)(triphos)]^+$ (0.5 mmol dm^{-3}) with HCl and Cl^- in MeCN at 25.0 °C (λ = 420 nm)

$[HCl]_0$ / mmol dm^{-3}	$[Cl^-]_0$ / mmol dm^{-3}	$[HCl]_e$ / mmol dm^{-3}	$[Cl^-]_e$ / mmol dm^{-3}	k_{obs} / s^{-1}	− ΔA	A_f
2.5				0.10	0.013	0.266
5.0				0.14	0.015	0.305
10.0				0.22	0.024	0.310
20.0				0.27	0.032	0.316
30.0				0.33	0.040	0.324
40.0				0.35	0.042	0.325
50.0				0.40	0.045	0.346
60.0				0.37	0.046	0.341
80.0				0.38	0.049	0.348
100.0				0.46	0.050	0.346
2.5[a]				0.088	0.015	0.301
5.0[a]				0.12	0.018	0.312
10.0[a]				0.13	0.022	0.323
20.0[a]				0.16	0.026	0.330
30.0[a]				0.17	0.028	0.329
40.0[a]				0.23	0.031	0.342
50.0[a]				0.25	0.033	0.342

Table S2 continued…

$[HCl]_0$ / mmol dm^{-3}	$[Cl^-]_0$ / mmol dm^{-3}	$[HCl]_e$ / mmol dm^{-3}	$[Cl^-]_e$ / mmol dm^{-3}	k_{obs} / s^{-1}	$-\Delta A$	A_f
25.0	1.0	24.2	0.20	0.37	0.037	0.254
	2.5	23.0	0.53	0.40	0.032	0.257
	5.0	21.2	1.15	0.69	0.026	0.260
	10.0	17.6	2.64	1.34	0.013	0.275
50.0	2.5	47.8	0.29	0.50	0.044	0.290
	5.0	45.6	0.61	0.50	0.028	0.292
	10.0	41.3	1.32	0.59	0.026	0.292
	20.0	33.2	3.2	1.40	0.019	0.290
	30.0	25.9	5.9	2.75	0.018	0.394
100.0	2.5	97.6	0.06	0.39	0.050	0.305
	5.0	95.3	0.32	0.60	0.048	0.305
	10.0	90.7	0.66	0.85	0.041	0.309
	20.0	81.4	1.44	1.08	0.032	0.320
	30.0	72.4	2.41	1.24	0.021	0.322

footnotes.

[a] studies with DCl

Table S3

Kinetic data for the reaction of $[Ni(S_2CBu^n)(triphos)]^+$ (0.25 mmol dm^{-3}) with HCl and Cl^- in MeCN at 25.0 °C (λ = 420 nm)

$[HCl]_0$ / mmol dm^{-3}	$[Cl^-]_0$ / mmol dm^{-3}	$[HCl]_e$ / mmol dm^{-3}	$[Cl^-]_e$ / mmol dm^{-3}	k_{obs} / s^{-1}	$-\Delta A$	A_f
2.5				0.05	0.002	0.269
5.0				0.08	0.006	0.274
10.0				0.12	0.014	0.280
20.0				0.17	0.022	0.290
30.0				0.19	0.024	0.284
40.0				0.22	0.026	0.288
60.0				0.24	0.036	0.292
80.0				0.25	0.036	0.296
100.0				0.25	0.038	0.296
5.0[a]				0.05	0.002	0.254
10.0[a]				0.10	0.003	0.255
20.0[a]				0.13	0.005	0.260
30.0[a]				0.15	0.010	0.268
40.0[a]				0.17	0.012	0.261
60.0[a]				0.18	0.015	0.267
80.0[a]				0.18	0.016	0.267
100.0[a]				0.19	0.019	0.272

Table S3 continued…

$[HCl]_0$ / mmol dm^{-3}	$[Cl^-]_0$ / mmol dm^{-3}	$[HCl]_e$ / mmol dm^{-3}	$[Cl^-]_e$ / mmol dm^{-3}	k_{obs} / s^{-1}	$-\Delta A$	A_f
50.0	2.5	47.8	0.29	0.21	0.019	0.260
	5.0	45.6	0.61	0.24	0.016	0.272
	10.0	41.3	1.32	0.30	0.015	0.252
	20.0	33.2	3.2	0.43	0.014	0.263
	30.0	25.9	5.9	0.59	0.012	0.255
	50.0	14.9	14.9	1.24	0.008	0.243
100.0	2.5	97.6	0.06	0.21	0.018	0.270
	5.0	95.3	0.32	0.26	0.012	0.258
	10.0	90.7	0.66	0.40	0.011	0.264
	20.0	81.4	1.44	0.40	0.008	0.255

footnotes.

[a] studies with DCl

Table S4

Kinetic data for the reaction of $[Ni(S_2CPh)(triphos)]^+$ (0.5 mmol dm^{-3}) with HCl and Cl^- in MeCN at 25.0 °C (λ = 450 nm)

$[HCl]_0$ / mmol dm^{-3}	$[Cl^-]_0$ / mmol dm^{-3}	$[HCl]_e$ / mmol dm^{-3}	$[Cl^-]_e$ / mmol dm^{-3}	k_{obs} / s^{-1}	$-\Delta A$	A_f
100.0	1.0	99.0	0.03	0.23	0.008	0.262
	2.5	97.6	0.06	0.22	0.008	0.263
	5.0	95.3	0.32	0.28	0.007	0.269
	10.0	90.7	0.66	0.33	0.006	0.279
	15.0	86.0	1.0	0.38	0.004	0.290
150	2.5	147.6	0.08	0.34	0.009	0.273
	5.0	145.2	0.18	0.35	0.009	0.281
	10.0	140.5	0.50	0.40	0.008	0.287
	15.0	135.6	0.60	0.41	0.007	0.280

2. CRYSTALLOGRAPHY

Table S5. X-ray crystallographic data for $[Ni(S_2CR)(triphos)]BPh_4$ (R = Et, unsolvated; Ph, THF solvate; C_6H_4Me-4, THF and chloroform solvates; C_6H_4OMe-4, THF solvate; and C_6H_4Cl-4, THF solvate)

$[Ni(S_2CR)(triphos)]BPh_4$	R = Et unsolvated	R = C_6H_5 THF solvate	R = C_6H_4Me-4 THF solvate	R = C_6H_4Me-4 $CHCl_3$ solvate	R = C_6H_4OMe-4 THF solvate	R = C_6H_4Cl-4 THF solvate
CCDC reference	1033172	1033173	1033174	1033175	1033176	1033177
Formula	$C_{61}H_{58}BNiP_3S_2$	$C_{69}H_{66}BNiOP_3S_2$	$C_{70}H_{68}BNiOP_3S_2$	$C_{67}H_{61}BCl_3NiP_3S_2$	$C_{70}H_{68}BNiO_2P_3S_2$	$C_{69}H_{65}BClNiOP_3S_2$
M_r / g mol^{-1}	1017.6	1137.8	1151.8	1199.1	1167.8	1172.2
Crystal system	monoclinic	orthorhombic	triclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	$Pbcn$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a / Å	17.685(4)	38.8301(16)	13.850(4)	13.9329(3)	13.9067(9)	13.8395(3)
b / Å	13.749(3)	16.6153(5)	14.817(4)	14.4258(3)	14.4762(9)	14.8535(4)
c / Å	22.807(5)	18.1236(5)	15.464(4)	15.6129(3)	15.5552(10)	15.4286(4)
α / °	90	90	98.073(3)	93.5320(17)	93.2523(19)	98.071(2)
β / °	110.150(2)	90	106.188(3)	106.7120(17)	106.7604(19)	106.232(2)
γ / °	90	90	97.124(3)	98.1580(17)	98.3313(19)	97.210(2)
V / Å^3	5206(2)	11692.9(7)	2972.7(14)	2957.72(11)	2950.8(3)	2969.37(13)
Z	4	8	2	2	2	2
D_{calc} / g cm^{-3}	1.298	1.293	1.287	1.346	1.314	1.311
μ /mm^{-1}	0.510	0.529	0.452	0.657	0.528	0.567
Crystal size / mm^3	0.08×0.08×0.01	0.27×0.21×0.11	0.09×0.08×0.04	0.36×0.25×0.11	0.30×0.15×0.12	0.25×0.22×0.14
X-ray wavelength / Å	0.6889	0.71073	0.6889	0.71073	0.71073	0.71073
Temperature / K	100	150	100	150	120	150
Reflections measured	66315	52089	30189	94253	40258	98379
Unique reflections, R_{int}	9261, 0.1269	11747, 0.0487	13997, 0.0458	13375, 0.0487	13545, 0.0403	14473, 0.0484

Refined parameters	615	694	705	722	728	719
Restraints	0	642	0	694	169	681
R (F, $F^2 > 2\sigma$)	0.0530	0.0486	0.0447	0.0377	0.0434	0.0404
R_w (F^2, all data)	0.1169	0.1000	0.1259	0.0937	0.1103	0.1011
Goodness of fit on F^2	1.061	1.070	1.079	1.043	1.020	1.026
Max., min. electron density / e Å^{-3}	0.45, –0.39	0.52, –0.38	0.58, –0.59	0.67, –0.51	0.82, –0.39	0.46, –0.40

Table S6. Selected bond lengths and angles in $[Ni(S_2CR)(triphos)]^+$ (R = Et, Ph, C_6H_4Me-4, C_6H_4OMe-4 and C_6H_4Cl-4)

$[Ni(S_2CR)(triphos)]BPh_4$	R = Et	R = Ph	R = C_6H_4Me-4 THF solvate	R = C_6H_4Me-4 $CHCl_3$ solvate	R = C_6H_4OMe-4	R = C_6H_4Cl-4
Bond lengths / Å						
Ni–P1	2.1733(10)	2.2227(7)	2.2204(8)	2.2146(6)	2.2367(6)	2.2315(5)
Ni–P2	2.1516(11)	2.1484(7)	2.1757(8)	2.1743(5)	2.1712(6)	2.1739(5)
Ni–P3	2.2174(11)	2.2066(7)	2.2315(8)	2.2361(5)	2.2074(6)	2.2144(6)
Ni–S1	2.2342(11)	2.2321(7)	2.2327(8)	2.2276(5)	2.2206(6)	2.2296(5)
Ni–S2	2.3448(10)	2.3179(7)	2.2599(8)	2.2574(5)	2.2683(6)	2.2559(5)
Bond angles / °						
P1–Ni–P2	85.88(4)	87.70(3)	87.12(2)	86.90(2)	87.72(2)	87.936(19)
P2–Ni–P3	87.06(4)	87.39(3)	88.01(3)	88.06(2)	86.82(2)	87.08(2)
P1–Ni–P3	131.15(4)	130.66(3)	116.66(3)	117.47(2)	118.98(2)	115.87(2)
S1–Ni–S2	75.60(4)	76.16(2)	76.21(3)	76.248(19)	76.25(2)	76.211(18)
P1–Ni–S1	95.75(4)	92.70(3)	96.26(3)	95.67(2)	96.86(2)	96.86(2)
P1–Ni–S2	125.86(4)	107.41(3)	128.40(3)	128.46(2)	112.90(2)	114.67(2)
P2–Ni–S1	176.27(4)	176.60(3)	172.48(3)	172.29(2)	173.69(2)	172.38(2)
P2–Ni–S2	100.73(4)	100.50(3)	96.43(3)	96.461(19)	97.99(2)	96.423(19)
P3–Ni–S1	94.35(4)	94.90(3)	96.40(3)	97.15(2)	94.70(2)	96.08(2)
P3–Ni–S2	102.95(4)	121.76(3)	114.91(3)	114.05(2)	128.05(2)	129.42(2)

S1–C–S2	113.7(2)	111.88(15)	109.85(12)	109.52(11)	109.71(11)	109.78(11)

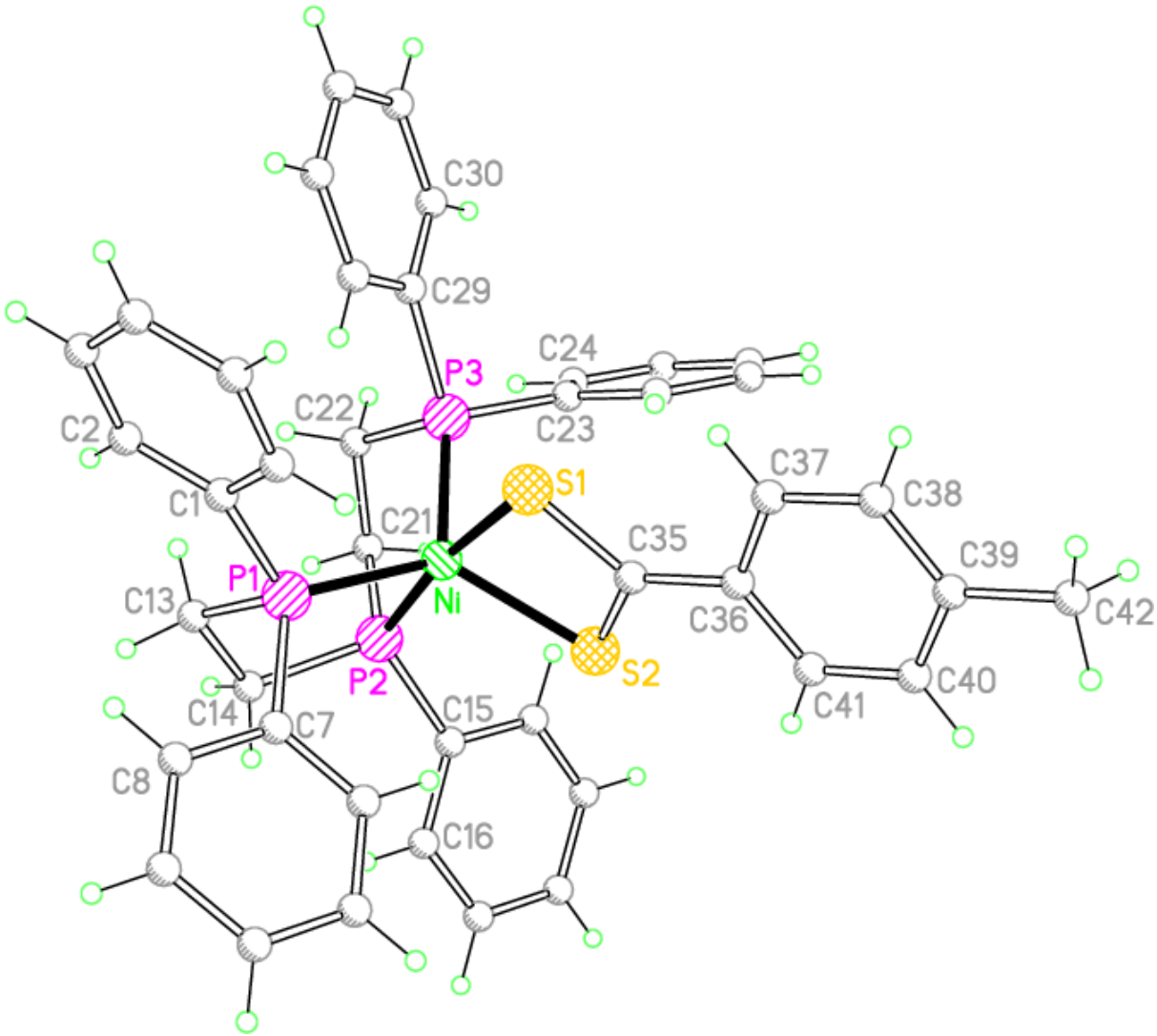

Fig. S1. Structure of the cation in $[Ni(S_2CC_6H_4Me\text{-}4)(triphos)]BPh_4 \cdot THF$

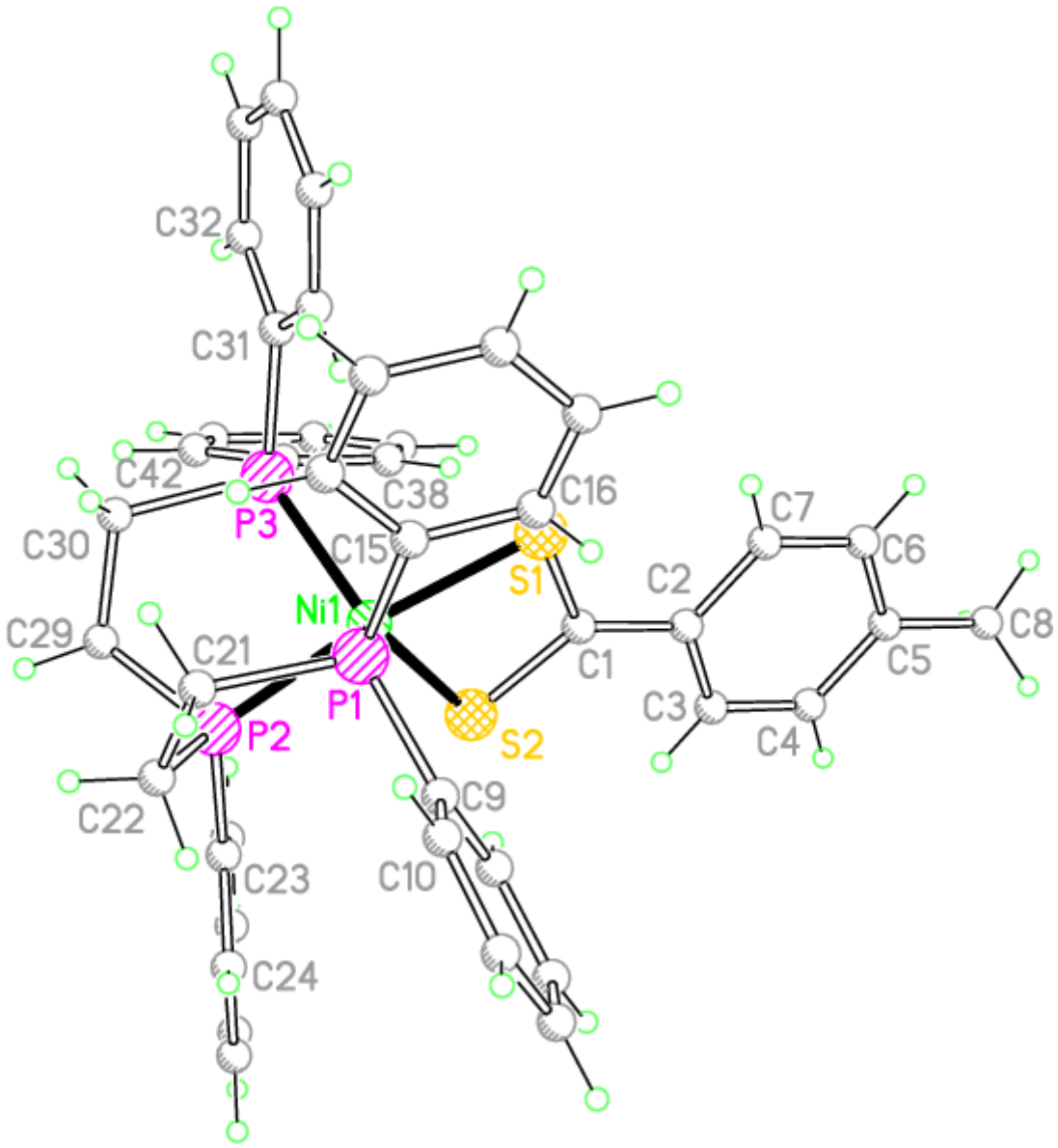

Fig. S2. Structure of the cation in $[Ni(S_2CC_6H_4Me\text{-}4)(triphos)]BPh_4 \cdot CHCl_3$

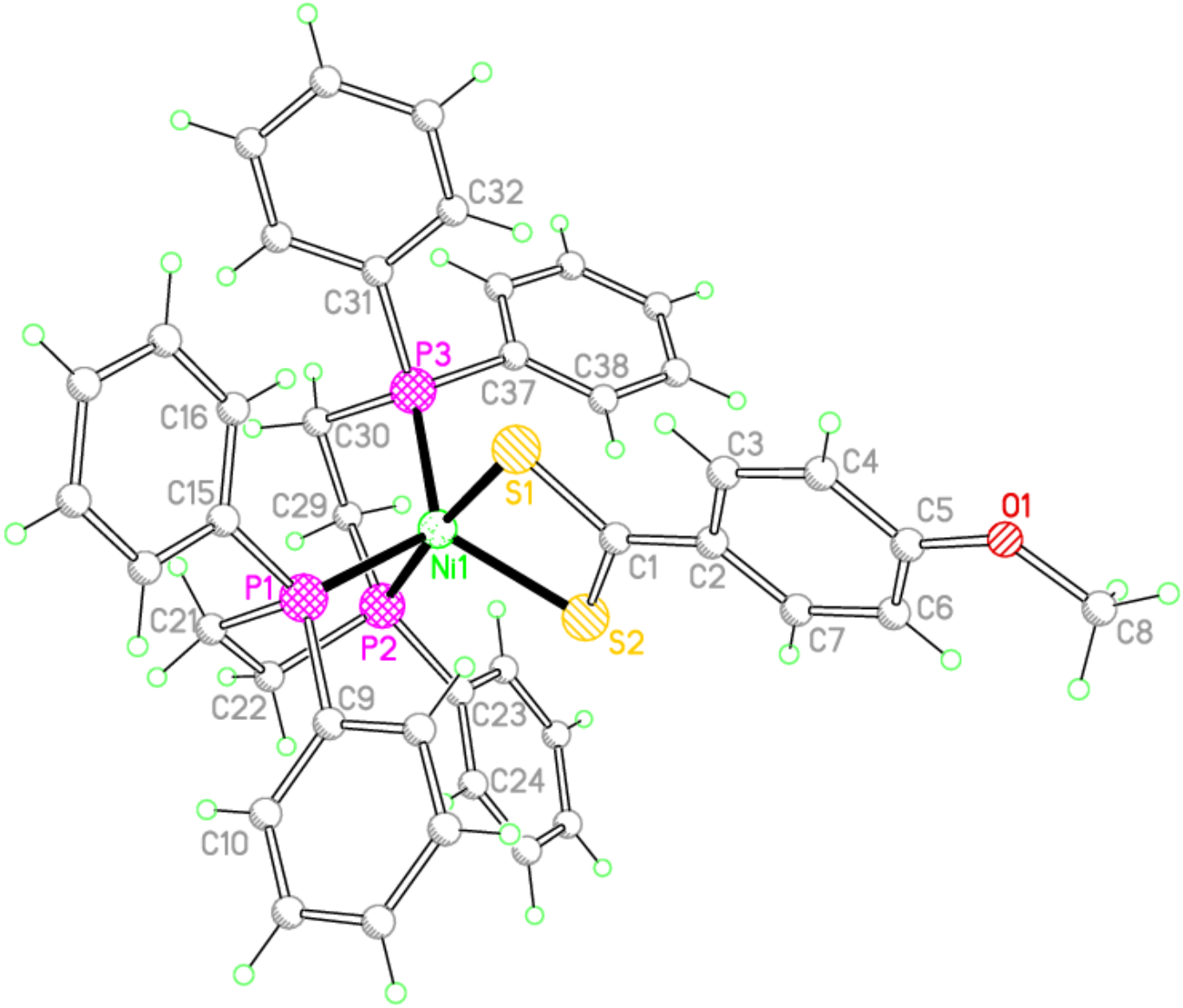

Fig. S3. Structure of the cation in $[Ni(S_2CC_6H_4OMe\text{-}4)(triphos)]BPh_4 \cdot THF$

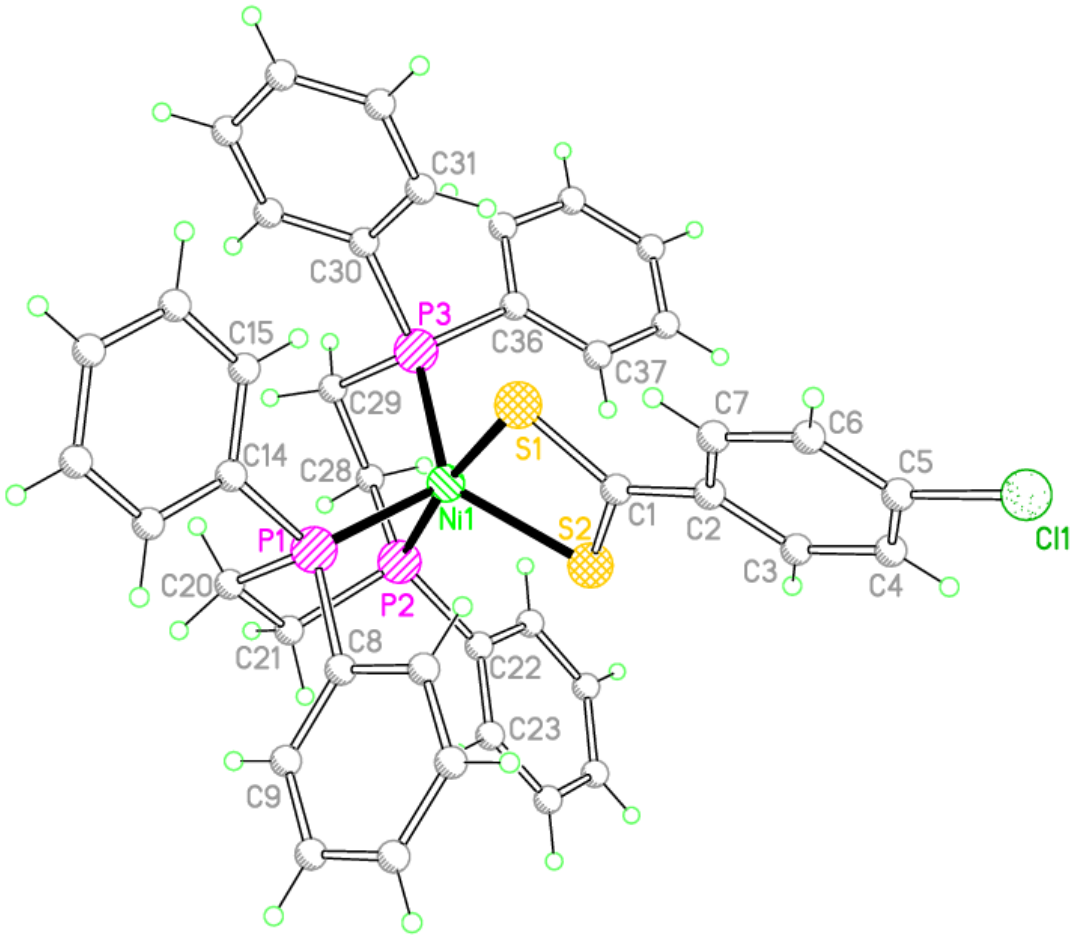

Fig. S4. Structure of the cation in $[Ni(S_2CC_6H_4Cl\text{-}4)(triphos)]BPh_4 \cdot THF$

3. DFT CALCULATIONS

All theoretical calculations in this work were performed using the computational methods implemented in the GAUSSIAN03 package[15] The geometries of the compounds were optimized at the B3LYP/Lanl2dz levels of theory.

15. 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.

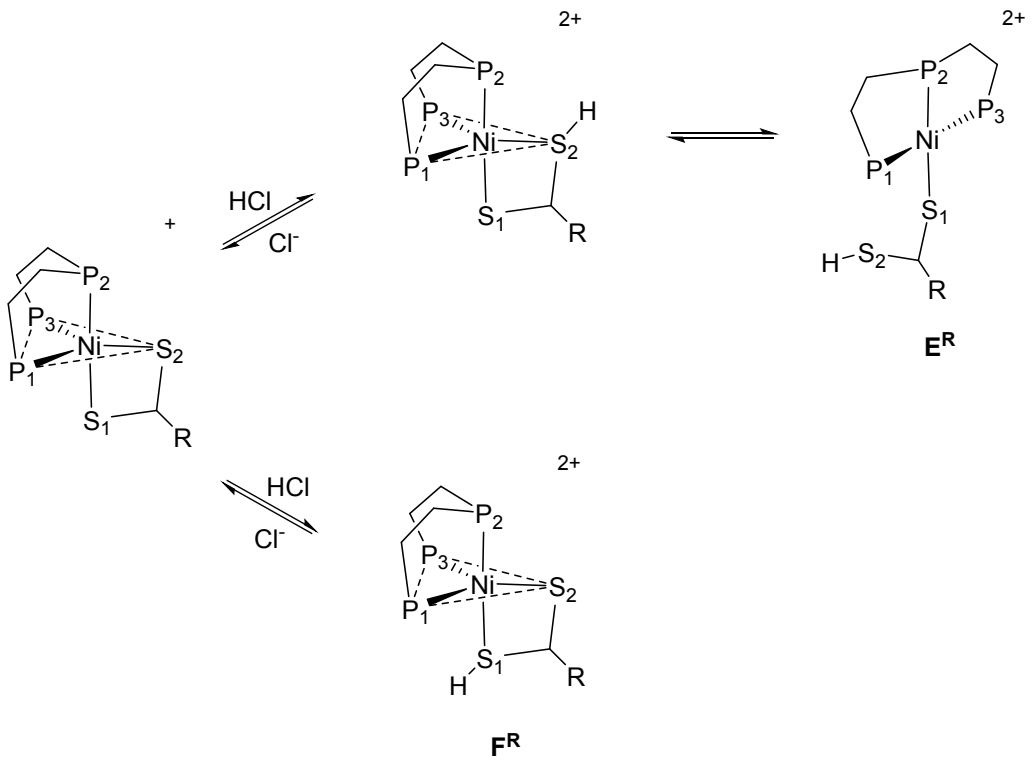

Fig. S5. Summary of the results of DFT calculations showing the different structural consequences of protonation at axial and equatorial sulfur sites in $[Ni(S_2CR)(triphos)]^+$. Selected bond lengths and bond angles of $\mathbf{E^R}$ and $\mathbf{F^R}$ (R = Me or Ph) are presented in Tables S7 and S8, respectively, and pictures of the corresponding $\mathbf{E^R}$ are shown in Figs. S6 and S7, respectively.

Table S7. Selected bond lengths and angles of $Ni(HS_2CMe)(triphos)]^{2+}$ from DFT calculations

	Complex $\mathbf{E^{Me}}$	Complex $\mathbf{F^{Me}}$
bond lengths		
$Ni–P_1$	2.3369	2.2971
$Ni–P_2$	2.3034	2.2110
$Ni–P_3$	2.3295	2.2519
$Ni–S_1$	2.3187	2.2988
$Ni–S_2$	3.4270	2.5345
bond angles		
$P_1–Ni–P_2$	85.085	87.13
$P_1–Ni–P_3$	152.052	127.98
$P_1–Ni–S_1$	94.845	95.98
$P_1–Ni–S_2$		100.92
$P_2–Ni–P_3$	85.785	86.92
$P_2–Ni–S_1$	179.017	173.19
$P_2–Ni–S_2$		119.82
$P_3–Ni–S_1$	93.840	95.83
$P_3–Ni–S_2$		106.54

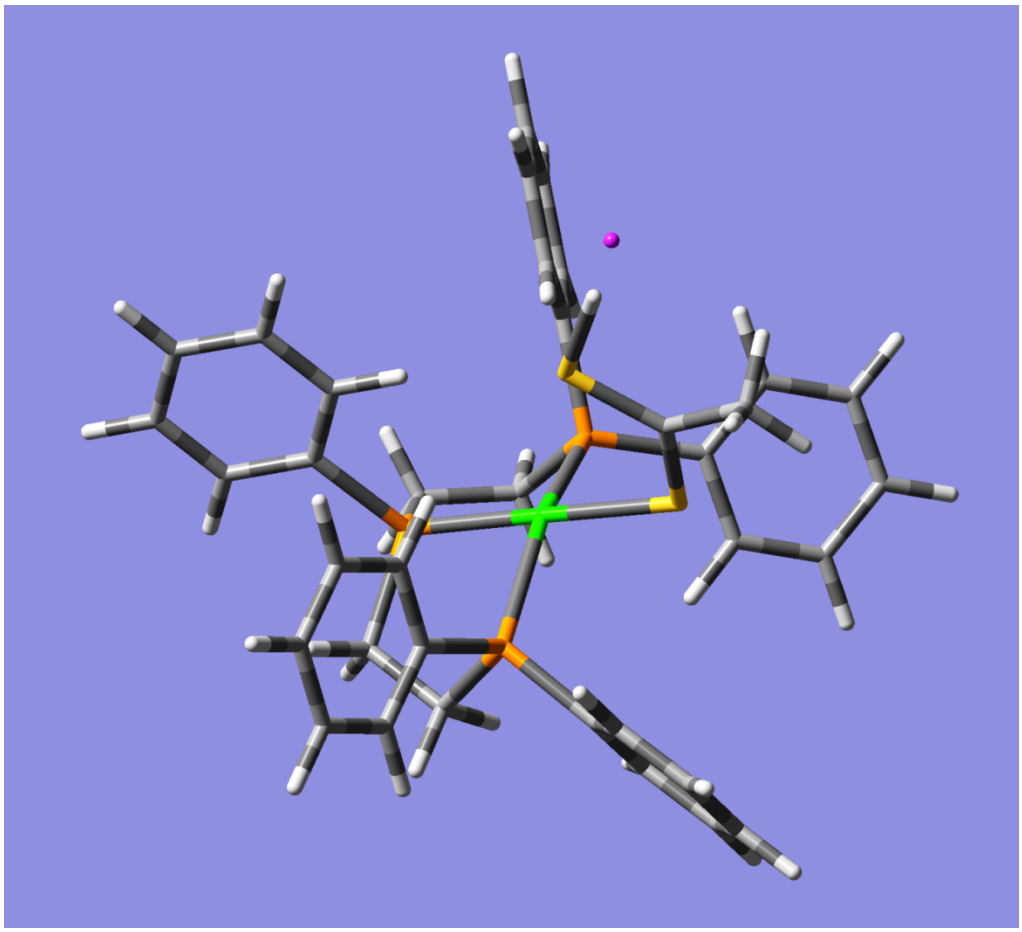

Fig. S6. Picture of the optimised structure of $[Ni(HS_2CMe)(triphos)]^{2+}$ ($\mathbf{E^{Me}}$) showing the protonated carboxydithioate ligand has undergone chelate ring opening. Key: Ni = green; P = orange; S = yellow; H = white, C = grey and Cl = magenta.

Table S8. Selected bond lengths and angles of $Ni(HS_2CPh)(triphos)]^{2+}$ from DFT calculations

	Complex E^{Ph}	Complex F^{Ph}
bond lengths		
$Ni–P_1$	2.2665	2.2665
$Ni–P_2$	2.2176	2.2630
$Ni–P_3$	2.2630	2.2176
$Ni–S_1$	2.2865	2.0423
$Ni–S_2$	3.5122	2.4400
bond angles		
$P_1–Ni–P_2$	85.90	85.90
$P_1–Ni–P_3$	152.31	152.31
$P_1–Ni–S_1$	94.17	90.91
$P_1–Ni–S_2$		104.47
$P_2–Ni–P_3$	85.25	85.25
$P_2–Ni–S_1$	179.93	167.33
$P_2–Ni–S_2$		123.24
$P_3–Ni–S_1$	94.69	92.04
$P_3–Ni–S_2$		102.33

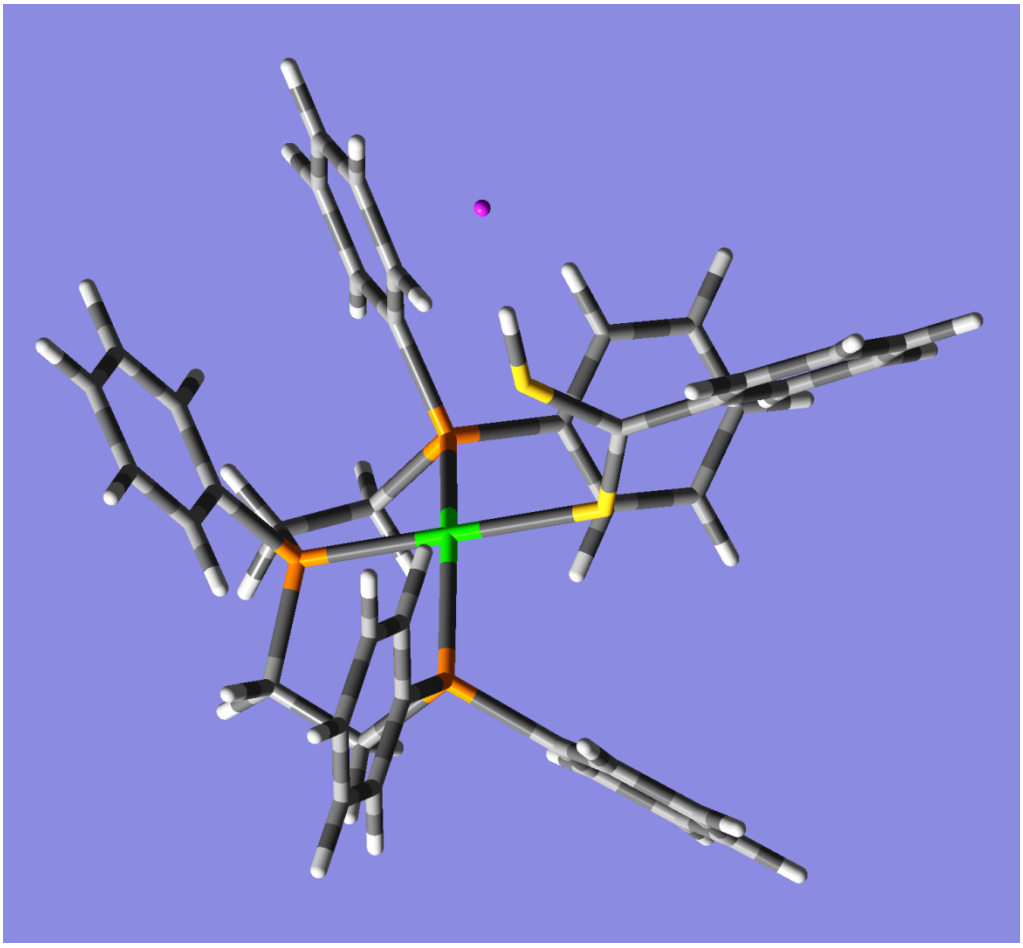

Fig. S7. Picture of the optimised structure of $[Ni(HS_2CPh)(triphos)]^{2+}$ (**E^{Ph}**) showing the protonated carboxydithioate ligand has undergone chelate ring opening. Key: Ni = green; P = orange; S = yellow; H = white, C = grey and Cl = magenta.