Phosphine-promoted ring-opening of benzisothiazolinate ligands at a nickel(II) centre: A convenient synthesis of Ni(II)-thiolate complexes

Electronic Supplementary Information

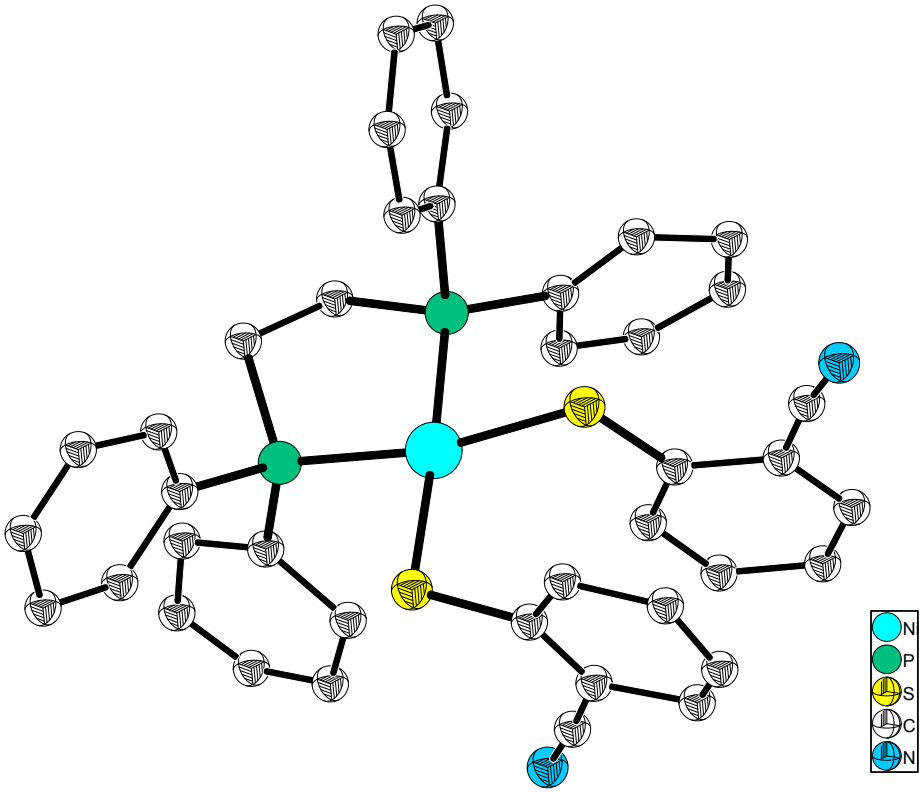

Fig. S1. Molecular structure of **2a**

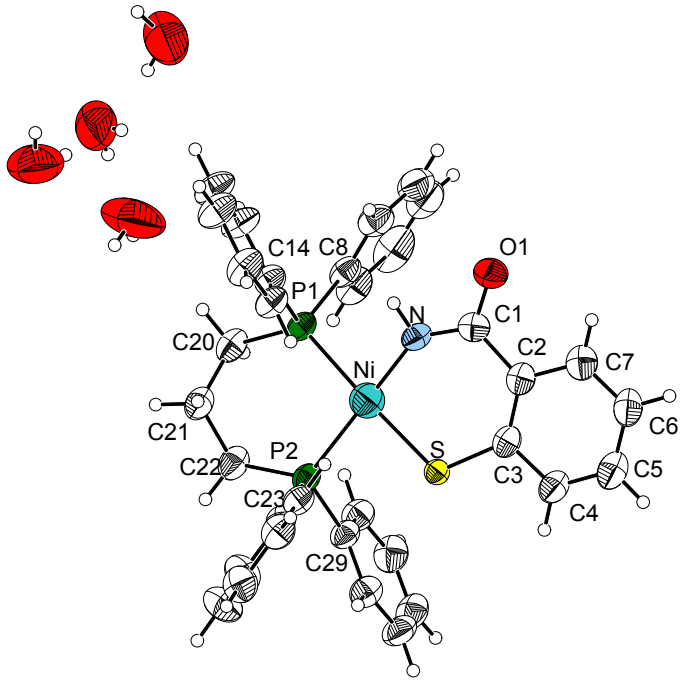

Fig. S2. Molecular structure of **3b**.4H_2O.

General methods, reagents and instrumentation - ^{1}H NMR spectra were recorded on a Varian Unity spectrometer using d^{6}-DMSO as solvent. IR spectra were recorded on Shimadzu FT-IR 8400 spectrophotometer in the 400-4000 cm^{-1} range as KBr discs and in the 200-600 cm^{-1} as CsI discs Elemental analyses were carried out at Al Al-Bayt University, Jorden using a Euro vector EURO EA300 elemental analyzer. Melting points measured on a Gallenkamp melting point apparatus and are uncorrected. Conductivity measurements were carried out on 10^{-3} molar solutions using a digital conductivity meter. $[Ni_2(\mu\text{-bit})_4(H_2O)_2]$ (**1**).3H_2O was prepared by the literature method.

Synthesis of 2a and 3a - Three slightly different procedures have been employed. **(a)** EtOH (20 cm^3) and CH_2Cl_2 (5 cm^3) were added to a mixture of dppe (0.30 g, 0.74 mmol) and **1** (0.30 g, 0.37 mmol). The mixture was stirred for 30 mins then heated at reflux for 4 h. Filtration gave an orange solid which was dried under vacuum and recrystallized from CH_2Cl_2/EtOH to afford orange needles crystals of **3a** (0.30 g, 58%). The maroon mother liquor was left to evaporate at room temperature to give a maroon solid, which was recrystallized from CH_2Cl_2/EtOH to afford maroon plate-like crystals of **2a** (0.10 g, 18%). **(b)** CH_2Cl_2 (20 cm^3) was added to a mixture of dppe (0.58 g 1.46 mmol) and **1** (0.30 g, 0.37 mmol). The mixture was stirred at room temperature for 30 mins to afford a maroon solution. The solution was heated at reflux for 4 h, filtered and the filtrate was set aside to evaporate at room temperature. The resulting maroon solid was recrystallized from CH_2Cl_2/EtOH to give a mixture of orange needles of **3a** (5%) and maroon plates of **2a** (95%). Combined yield 0.30 g, 80%. **(c)** EtOH (20 cm^3) was added to a mixture of dppe (0.30 g, 0.74 mmol and **1** (0.30 g, 0.37 mmol). The mixture was stirred for 4h at room temperature to afford an orange precipitate which was collected and dried under vacuum. Recrystallisation from CH_2Cl_2/EtOH afforded orange needle crystals of **3a**. Yield 0.10 g, 76%. Characterising data for **2a**: Dark maroon plates. *Anal*. Calc. for $C_{40}H_{32}N_2NiP_2S_2$: C 66.22, H 4.45, N 3.86, S 8.84. Found: C 66.55, H 4.97, N 3.80, S 8.59. IR: 3053w, 2921w, 2858w, 2214m, 1579m, 1483w, 1429s, 1101m, 876w, 810w, 748s, 700s, 528s, 478m cm^{-1}. UV-Vis (λ_{max} nm): 540, 376, 310. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): 55.6 (s) ppm. ^{1}H NMR (dmso-d$_6$): δ 8.01 (d, J 7.6 Hz, 1H, Ph), 7.91-7.45 (m, 20H, Ph), 7.36 (d, J 7.6 Hz, 1H, Ph), 7.25 (d, J 7.6, 1H, Ph), 7.17 (d, J 7.6 Hz, 1H, Ph), 7.02 (d, J 7.6 Hz, 1H, Ph), 6.94 (t, J 4.0 Hz, 1H, Ph), 6.86 (t, J 4.0 Hz, 1H, Ph), 6.80 (t, J 4.0 Hz, 1H, Ph), 2.50 (s, 4H, 2CH_2). Mp: 244 ^{o}C. Characterising data for **3a**: Orange needles. *Anal*. Calc. for $C_{33}H_{29}NNiOP_2S$: C 65.16, H 4.81, N 2.30, S 5.52. Found: C 65.55, H 4.84, N

2.02, S 5.59. IR: 3299w, 3051w, 2908w, 1589s, 1573s, 1535m,1483w, 1434s, 1375m, 1101s, 746s, 692m, 532vs, 484m cm^{-1}. UV-Vis (λ_{max} nm): 530, 380, 305. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): 59.3 (d, J 51 Hz), 56.1 (d, J 51) ppm. ^{1}H NMR ($CDCl_3$): δ 7.91-7.78 (m, 6H, Ph), 7.57-7.38 (m, 14H, Ph), 7.32 (d, 8.0 Hz, 1H, Ph), 6.94 (dd, J 8.0, 4.0 Hz, 1H, Ph), 6.77 (td, J 4.0, 8.0 Hz, 1H, Ph), 6.69 (td, J 4.0, 8.0 Hz, 1H, Ph), 2.35 (d, J 4.0 Hz, 4H, $2CH_2$). Mp: 173 °C decomposes.

Synthesis of 2b and 3b - EtOH (25 cm^3) and CH_2Cl_2 (5 cm^3) was added to dppp (0.37 g 0.89 mmol) and **1** (0.30 g, 0.37 mmol). The resulting mixture was stirred for 30 mins then heated at reflux for 4 h to give a maroon suspension. This was filtered to give a light maroon solid which was dried under vacuum and recrystallized from CH_2Cl_2/EtOH to afford light maroon crystals of **2b** (Yield 0.25 g, 40%). The filtrate was left to evaporate at room temperature to give a dark maroon solid which was recrystallized from CH_2Cl_2/EtOH to afford dark maroon crystals **3b** (Yield 0.17 g, 26%). Characterising data for **2b**: Light maroon. *Anal*. Calc. for $C_{41}H_{34}N_2NiP_2S_2$: C 65.01, H 4.97, N 3.70, S 8.46. Found: C 65.00, H 4.77, N 3.66, S 8.40. IR: 3062w, 2925m, 2856w, 2221m, 1674w, 1581s, 1494s, 1429m, 1166w, 1060w, 894w, 750s, 570w, 499w cm^{-1}. UV-Vis (λ_{max} nm): 510, 380, 305. $^{31}P\{^{1}H\}$ NMR (dmso-d_6) 29.9 ppm. ^{1}H NMR (dmso-d_6): δ 8.0-7.15 (m, 26H, Ph), 6.95 (bs, 2H, Ph), 6.74 (bs, 2H, Ph), 2.50 (s, 4H, $2CH_2$), 1.61 (bs, 2H, CH_2) Mp: 184 °C decomposed. Characterising data for **3b**: Dark maroon. *Anal*. Calc. for $C_{34}H_{31}NNiOP_2S$: C 65.62, H 5.02, N 2.25, S 5.15. Found: C 65.67, H 5.10, N 2.22, S 5.10. IR: 3049w, 2920w, 2852w , 1575vs, 1521m, 1483w, 1434s, 1305m, 1097m, 981w, 844w, 748s, 698s, 513m cm^{-1}. UV-Vis (λ_{max} nm): 538, 351, 322. $^{31}P\{^{1}H\}$ NMR (dmso-d^6): 13.8 (d, J 90 Hz), 11.42(d, J 90 Hz). ^{1}H NMR (dmso-d^6): δ 7.85 (d, 1H, Ph), 7.82-7.73 (m, 8H, Ph), 7.60-7.35 (m, 12H, Ph), 7.02 (d, J 8.0 Hz, 1H, Ph), 6.92 (d, J 8.0 Hz, 2H, Ph), 2.60 (d, J 8.0 Hz, 4H, $2CH_2$), 1.75 (s, 2H, CH_2). Mp: 246 °C.

Synthesis of 4 - A solution of dppm (0.25 g, 0.65 mmol) in CH_2Cl_2 (3 cm^3) was added to **1** (0.20 g, 0.25 mmol) suspended in EtOH (15 cm^3). The mixture was heated under reflux for 3 h to afford a maroon suspension. The suspension was filtered and the solid dried under vacuum. It was then extracted into $CHCl_3$ (ca. 10 cm^3) and EtOH (10 cm^3) was added. The mixture was left to evaporate at room temperature to afford a mixture of maroon needles and plate-like crystals. Yield 0.28 g, 80%. Characterising data for **4**: *Anal*. Calc. for $C_{39}H_{30}N_2NiO_2P_2S_2$: C 64.39, H 4.16, N 3.85, S 8.85. Found: C 64.35, H 4.12, N 3.84, S 8.81. IR: 3049w, 2910, 2212, 1583m, 1556s, 1527m,1425s, 1321m, 1101m, 1062w, 773m, 738s,

686s, 509w, 478w cm^{-1}. UV-Vis (λ_{max} nm): 530, 365, 300. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): 45.3 (d, J 57 Hz), 15.5 (d, J 57 Hz) ppm. ^{1}H NMR ($CDCl_3$): δ 7.8-7.11 (m, 24H, Ph), 7.02 (t, J 7.8 Hz, 1H, Ph), 6.95 (d, J 7.8 Hz, 1H, Ph), 6.84 (t, J 4.0 Hz, 1H, Ph), 6.76 (t, J 4.0 Hz, 1H, Ph), 2.99 (dd, J 7.6, 1.8 Hz 2H, CH_2). Mp: 237-238°C.

Synthesis of 5 - PPh_3 (1.02 g, 3.90 mmol) and **1** (0.45 g, 0.56 mmol) were dissolved in a mixed of EtOH (7 cm^3), isopropanol (3 cm^3) and $CHCl_3$ (3 cm^3). The mixture was stirred for 30 min then heated at reflux for 6 h to give a maroon solid. This was filtered off and dried under vacuum. Yield 0.60 g, 60%. Characterising data for **5**: Maroon solid *Anal*. Calc. for $C_{50}H_{40}N_2NiOP_2S_2$: C 69.06, H 4.64, N 3.22, S 7.37. Found: C 69.10, H 4.59, N 3.20, S 7.30. μ_{eff}: 3.95 BM. IR: 3334w, 3269m, 3056w, 2220m, 1633m, 1577s, 1490s, 1429s, 1062w, 891w, 750s, 484m cm^{-1}. UV-Vis (λ_{max} nm): 700, 510, 318, 280. Mp: 320 °C decomposes.

Crystal structure determinations - Crystals of suitable for X-ray crystallography were mounted on a glass fiber and all geometric and intensity data were taken from this sample using a STOE-IPDS diffractometer. Absorption corrections were made using the IPDS software package. All structures were solved by direct methods and refined using full-matrix least-square routines against F^2 with SHELXL-97. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the models by calculating the positions (riding model) and refined with calculated isotropic displacement parameters. Illustrations were generated using DIAMOND 3.0. Crystallographic data is summarised in Table 1.

Table S1. Crystallographic data and structure refinement details

Compound	**3a**.(2EtOH)	**3b**.($4H_2O$)	**4**
Empirical formula	$C_{37}H_{41}NNiO_3P_2S$	$C_{34}H_{38}NNiO_5P_2S$	$C_{39}H_{30}N_2NiOP_2S_2$
Formula weight	700.42	694.37	727.42
Temperature (K)	213(2)	200(2)	213(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system,	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
Unit cell dimensions			
a (Å)	15.7991(6)	15.5162(7)	10.9912(4)
b (Å)	14.1552(5)	13.4129(6)	27.0617(12)
c (Å)	16.1484(6)	16.3229(6)	11.4178(4)
α (°)	90	90	90
β (°)	106.07(8)	104.39(2)	98.521(3)
γ (°)	90	90	90
Volume ($Å^3$)	3470.3(2)	3290.5(2)	3358.6(2)
Z	4	4	4
Density (calc.) (g/cm^3)	1.341	1.400	1.439
Absorption coefficient (mm^{-1})	0.748	0.793	0.833
F(000)	1472	1456	1504
Crystal size (mm)	0.21 x 0.09 x 0.06	0.46 x 0.45 x 0.37	0.33 x 0.28 x 0.05
Theta range for data collection (°)	1.596 to 25.000°.	1.991 to 26.857°.	1.505 to 24.999
Limiting indices	-17<=h<=18, -16<=k<=16, -19<=l<=19	-17<=h<=19, -16<=k<=16, -20<=l<=20	-13<=h<=12, -30<=k<=32, -13<=l<=13
Refln collected/ Indep.refln	31463/6114	19782/6939	17246/5910
R_{int}	0.0570	0.1023	0.0301
Completeness to θ	100.0 %	99.7 %	100.0 %
Data / restraints / parameters	6114 / 1 / 420	6939 / 4 / 409	5910 / 0 / 424
Goodness-of-fit on F2	1.012	0.956	1.015
Final R indices [I>2σ(I)]	R1 = 0.0329, wR2 = 0.06995	R1 = 0.0549, wR2 = 0.1482	R1 = 0.0292, wR2 = 0.0677
R indices (all data)	R1 = 0.0520, wR2 = 0.0759	R1 = 0.0719, wR2 = 0.1561	R1 = 0.0416, wR2 = 0.0724
Largest diff. peak/hole ($e\cdot Å^{-3}$)	0.350 and -0.250	1.075 and -0.674	0.379 /-0.185

Table S2. Selected bond lengths (Å) and bond angles (°)

4				**3a**			
Bond lengths		**Bond angles**		**Bond lengths**		**Bond angles**	
Ni-S(1)	215.17(6)	N(1)-Ni-S(1)	96.63(5)	Ni-N	189.60(19)	N-Ni-S	95.31(6)
Ni-S(2)	222.18(5)	N(1)-Ni-P(1)	92.97(5)	Ni-S	213.78(6)	N-Ni-P(2)	169.35(7)
Ni-P(1)	215.99(6)	S(1)-Ni-P(1)	170.16(2)	Ni-P(1)	219.10(6)	S-Ni-P(2)	86.53(2)
Ni-N(1)	193.27(15)	N(1)-Ni-S(2)	174.22(5)	Ni-P(2)	215.66(6)	N-Ni-P(1)	93.85(6)
N(1)-P(2)	167.98(8)	S(1)-Ni-S(2)	85.75(2)			S-Ni-P(1)	169.13(3)
		P(1)-Ni-S(2)	84.88(2)			P(2)-Ni-P(1)	85.54(2)
		C(1)-N(1)-Ni	130.30(13)			C(28)-P(2)-Ni	121.12(8)
		P(2)-N(1)-Ni	117.82(9)			C(22)-P(2)-Ni	107.48(8)
		C(3)-S(1)-Ni	112.66(8)			C(9)-P(2)-Ni	110.20(8)
		C(8)-S(2)-Ni	106.60(7)				
		C(22)-P(1)-Ni	118.24(7)				
		C(16)-P(1)-Ni	118.43(7)				
		C(15)-P(1)-Ni	102.90(7)				

3b			
Bond lengths		**Bond angles**	
Ni-S	215.98(8)	N-Ni-S	93.40(8)
Ni-P(1)	220.56(8)	N-Ni-P(2)	171.68(8)
Ni-P(2)	218.14(9)	S-Ni-P(2)	85.26(3)
Ni-N	188.5(3)	N-Ni-P(1)	87.58(8)
		S-Ni-P(1)	171.70(3)
		P(2)-Ni-P(1)	94.92(3)
		C(22)-P(2)-Ni	120.67(12)
		C(23)-P(2)-Ni	109.74(11)
		C(29)-P(2)-Ni	113.23(11)
		C(1)-N-Ni	139.6(2)