Electronic Supplementary Information of

Thioiminium and thiaphospholanium derived from acetonitrile *via* nickel(II)–(2-mercaptophenyl)phosphine complexations

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A. General Methods

All manipulations were performed under nitrogen using Schlenk techniques or glovebox. Acetonitrile was distilled once from P₂O₅, and freshly distilled from CaH₂ before usage; CH₂Cl₂ was distilled from CaH₂; Et₂O and THF were dried by distillation from sodium/benzophenone prior to use. All reagents were obtained from commercial sources and used as received without further purification. Bis(2-mercaptophenyl)phenylphosphine (H₂PS2) and (2-mercaptophenyl)diphenylphosphine (HPS1) were synthesized as reported procedure.¹ [Ni(CH₃CN)₆](ClO₄)₂ was prepared and crystallized from Ni(ClO₄)₂·6H₂O as literature.² NMR spectra were recorded on Bruker Avance-400 MHz or Avance-500 MHz FT NMR spectrometers. UV-vis spectra were recorded on Agilent 8453 spectrophotometers. IR spectra were recorded using KBr pellets on a Perkin-Elmer Paragon 500 spectrometer. Elemental analyses were performed on a Heraeus varioIII-NCH analyzer at the Instrumental Center at National Taiwan University, or Elementar vario EL III (CHN-OS rapid) at the Instrumental Center at National Chung Hsing University. ESI-MS spectra were recorded on a Thermo Finnigan LCQ Advantage spectrometer; isotope patterns were simulated by *IsoPro* 3.1 freeware.³

B. Synthetic Procedure

$Ni(P(o-C_6H_4S)(o-C_6H_4SH)(C_6H_5))_2$ (1)

A 3-mL CH₃CN solution of $[Ni(CH_3CN)_6](ClO_4)_2$ (99.4 mg, 0.20 mmol) was gradually transferred to a 12-mL CH₃CN solution of H₂PS2 (129.3 mg, 0.40 mmol) in a Schlenk flask. The reaction mixture became green immediately, and then green precipitate was formed. Supernatant liquid was removed after excess Et₂O adding to the reaction solution. The green solid was washed twice with Et₂O. Crystallization via vapor diffusion of Et₂O into a CH₂Cl₂ solution of **1** at room temperature over three days gave green crystals in 64% yield (89.3 mg). ¹H NMR (400 MHz, CDCl₃, δ): 8.03–7.95 (m, 2H), 7.79–7.72 (m, 2H), 7.53–7.46 (m, 4H), 7.46–7.29 (m, 6H), 7.26–7.14 (m, 6H), 7.14–7.07 (m, 1H), 7.06–6.97 (m, 2H), 6.97–6.91 (m, 1H), 6.91–6.85 (m, 2H). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 53.6, 48.4. IR (KBr) $\bar{\nu}_{max}$: 2345 (w, SH) cm⁻¹. Anal. Calcd for **1**: C, 60.94; H, 3.98; S, 18.08. Found: C, 61.30; H, 3.92; N, 18.05. UV-vis (CH₂Cl₂) λ_{max} , nm (ϵ): 299 (40000), 410 (5800), 612 (180).



Fig. S1 UV/vis spectrum of 1 in CH₂Cl₂.

$[Ni(P(o-C_6H_4S)(o-C_6H_4SC(CH_3)=NH_2)(C_6H_5))_2](ClO_4)_2$ (2)

A 5-mL CH₃CN Solution of $[Ni(CH_3CN)_6](ClO_4)_2$ (100.8 mg, 0.20 mmol) was charged into an addition funnel and added dropwise to a 10-mL pre-heated CH₃CN solution (55–60 °C) of H₂PS2 (130.6 mg, 0.40 mmol) in a Schlenk flask for few hours. An olive solution was resulted and separated from green and brown precipitates which was assigned as a mixture of **1** and dinuclear $[Ni(PS2)]_2$ by ³¹P NMR.⁴ Excess Et₂O was added into the filtrate to precipitate and to wash the product twice. Yellow-green crystals suitable for X-ray analysis were obtained in 61% yield (122.1 mg) by vapor diffusion of Et₂O into the CH₃CN solution of **2** at -20 °C over one week. The structures of **2** and its geometric isomer **2'** were determined by X-ray crystallography. ¹H NMR (400 MHz, CD₃CN, δ): 9.44(br), 9.12 (br), 8.28 (br), 7.92–6.94 (m, 26H), 1.86 (s, 6H), 2.24 (s, minor signal for **2'**) ppm. ³¹P{¹H} NMR (162 MHz, CD₃CN, δ): 47.0, 52.5 (minor signal for **2'**) ppm. IR (KBr) $\bar{\nu}_{max}$: 1647 (C=N) cm⁻¹. Anal. Calcd for **2**·CH₃CN: C, 48.81; H, 3.80; N, 4.07. Found: C, 48.8; H, 4.07; N, 4.36. UV-vis (CH₂Cl₂) λ_{max} , nm (ϵ): 302 (37000), 368 (6600), 618 (75).



Fig. S2 UV/vis spectrum of 2 in CH₃CN.

$[(C_6H_5)P(C_6H_4SC(CH_3)(NHCOCH_3))(o-C_6H_4SH)](ClO_4) (3)$

A 10-mL CH₃CN solution of H₂PS2 (65.3 mg, 0.20 mmol) was injected with 2 equivalents of HClO₄(aq) (70%, ca. 57 μ L) and stired at 60 °C for 12 hours. The solvent was evaporated. Dry CH₂Cl₂ was added to the residual slurry, making it become white suspension. The insoluble was separated, evaporated, and redissolved in dry CH₃CN. After vapor diffusion of Et₂O into the CH₃CN solution at room temperature, colorless crystals of **3** were obtained in 48% yield (98.6 mg) over three days. ¹H NMR (400 MHz, CD₃CN, δ): 8.04 (br d, ${}^{3}J_{\text{HP}} = 9.2 \text{ Hz}, 1\text{H}, -\text{NHAc}), 7.93 \text{ (dd, } J = 14.4, 8.1 \text{ Hz}, 1\text{H}), 7.88-7.81 \text{ (m, 1H)}, 7.81-7.70 \text{ (m, 1H$ 3H), 7.64–7.54 (m, 7H), 7.41 (td, J = 7.8, 3.8 Hz, 1H) 4.88 (br s, 1H, SH), 2.31 (d, ${}^{2}J_{\text{HP}} = 16.2$ Hz, 3H, -CH₃) 1.56 (s, 3H, -COCH₃). ¹³C NMR (100 MHz, CD₃CN, δ): 171.9 (-NHC=O), 148.4 (d, J = 16.6 Hz), 137.9 (d, J = 11.0 Hz), 137.6 (d, J = 10.0 Hz), 137.2 (d, J = 7.3 Hz), 136.5 (d, J = 2.7 Hz), 136.4 (d, J = 3.0 Hz), 136.2 (d, J = 3.4 Hz), 135.2 (d, J = 10.3 Hz), 134.2 (d, J = 9.2 Hz), 131.2 (d, J = 13.2 Hz), 130.9 (d, J = 13.3 Hz), 129.4 (d, J = 12.7 Hz), 127.5 (d, J = 10.8 Hz), 124.1 (d, J = 8.3 Hz), 120.9 (d, ${}^{1}J_{CP} = 79.2$ Hz), 120.5 (d, ${}^{1}J_{CP} = 102.7$ Hz), 120.1 (d, ${}^{1}J_{CP} = 90.3$ Hz), 67.2 (d, ${}^{1}J_{CP} = 59.2$ Hz), 26.6 (d, J = 1.7 Hz), 22.0. ${}^{31}P{}^{1}H{}$ NMR (162 MHz, CD₃CN, δ): 54.8. Anal. Calcd for **3**: C, 51.71; H, 4.34; N, 2.74; S, 12.55. Found: C, 51.83; H, 4.08; N, 2.53; S, 12.86. A minor component observed in NMR (³¹P: 46.2 ppm) has a ca. 1:6 ratio to compound **3**. Accroding to the similar set of signals, including nitrile-derived carbons (¹³C: 68.1 25.8, 22.8 ppm), the minor one is probably a diasteromer of **3**. Notably, (R,R)- and (S,S)-form of **3** are packing together in the lattice.

$[(C_6H_5)_2P(C_6H_4SC(CH_3)(NH_3))](ClO_4)_2$ (5)

Three equivalents of HPS1 (352.6 mg, 1.20 mmol) was dissolved in 10 mL CH₃CN in a Schlenk flask. A 3-mL CH₃CN solution of [Ni(CH₃CN)₆](ClO₄)₂ (200.8 mg, 0.40 mmol) was then transferred into the HPS1 solution and reacted overnight at 55–60 °C. After cooling, a green precipitate of Ni(P(o-C₆H₄S)(C₆H₅)₂)₂ was removed by filtration. The filtrate was concentrated to minimum volume, following by addition of 10 mL anhydrous CH₂Cl₂ with stirring. A resulting white precipitate was isolated from the pale green CH₂Cl₂ solution. The precipitate was washed twice by dry CH₂Cl₂ and dissolved in anhydrous CH₃CN for crystallization by Et₂O vapor diffusion at room temperature. Hygroscopic compound **5** was isolated as colorless crystals in 56% yield (121.2 mg) over one week. ¹H NMR (400 MHz, CD₃CN, δ): 8.24–8.07 (m, 3H), 8.07–7.88 (m, 7H), 7.83 (dd, *J* = 8.1, 3.7 Hz, 1H), 7.83–7.77 (m, 2H), 7.74 (dt, *J* = 7.7, 4.1 Hz, 1H), 7.60 (br, NH), 2.18 (d, *J* = 14.2 Hz, 3H, –CH₃). ¹³C NMR (100 MHz, CD₃CN, δ): 145.6 (d, *J*_{CP} = 15.1 Hz), 139.6, 139.1, 138.4, 136.7, 136.6, 136.5 (d, *J*_{CP} = 10.8 Hz), 135.9, 135.8, 132.9, 132.8, 132.2, 132.1, 130.7 (d, *J*_{CP} = 11.7 Hz),

128.0 (d, J_{CP} = 9.0 Hz), 114.5 (d, ${}^{1}J_{CP}$ = 102.1 Hz), 112.9 (d, ${}^{1}J_{CP}$ = 83.9 Hz), 110.3 (d, ${}^{1}J_{CP}$ = 77.6 Hz), 69.5 (d, ${}^{1}J_{CP}$ = 58.0 Hz), 21.0. 31 P NMR (162 MHz, CD₃CN, δ): 47.2. Anal. Calcd for **5**: C, 44.79; H, 3.76; N, 2.61. Found: C, 44.79; H, 3.54; N, 2.45. ESI-MS m/z: 336.1 [**5**-H]⁺.



Fig. S3 ESI-MS spectrum of 5 (left) and simulation result (right).

$[(C_6H_5)_2P(C_6H_4SC(CD_3)(NH_3))](ClO_4)_2$ (5D)

As the same procedure of compound **5**, 179.4 mg HPS1 (0.61 mmol) and 101.9 mg $[Ni(CH_3CN)_6](ClO_4)_2$ (0.20 mmol) were reacted in 5 mL CD₃CN for 24 hours at 60 °C. After work-up, compound **5D** was crystallized by vapor diffusion method (CD₃CN/Et₂O) at room temperature. Yield: 52.5 mg (48%). 8.21–8.08 (m, 3H), 8.07–7.87 (m, 7H), 7.84 (dd, *J* = 8.2, 3.7 Hz, 1H), 7.84–7.77 (m, 2H), 7.74 (dt, *J* = 7.7, 4.1 Hz, 1H), 7.56 (br, NH). ³¹P NMR (162 MHz, CD₃CN, δ): 46.8. ESI-MS m/z: 339.3 [**5D**–H]⁺.



Fig. S4 ESI-MS spectrum of 5D (left) and simulation result (right).

Supporting information

Alternative way for **5**: HClO₄(aq) (70%, 150 μ L) was injected into the Schlenk flask charged with 7-mL CH₃CN solution of HPS1 (203.8 mg, 0.69 mmol). Then the reaction stired at about 65 °C for 20 hours. After cooling, solvent was evaporated. Glue-like product was washed with anhydrous CH₂Cl₂/Et₂O (5/10 mL) mixed solvent and resulted as white precipitate. The precipitate was washed again by dry Et₂O, dissolved in dry CH₃CN, and crystallized via vapor diffusion with Et₂O at room temperature. Colorless crystals were obtained two days later. By X-ray diffraction and NMR spectra, the crystal is identified as compound **5** (128.7 mg, 35% yield).

C. X-ray Structure Determination.

Crystals suitable for CCD X-ray diffractometer were selected under a microscope and mounted on the tip of a glass fiber fashioned on a copper pin. X-ray data for complexes 1, 2, 2', 3 and 5 were collected by a Brucker-Nonius Kappa CCD diffractometer employing graphite monochromated Mo K α radiation ($\lambda = 0.7107$ Å) at 200 or 296 K and a θ -2 θ scan mode. The space groups for complexes were determined on the basis of systematic absences and intensity statistics, and the structures of 1, 2, 2', 3 and 5 were solved by direct methods using SIR92 or SIR97, and refined using SHELXL-97. An empirical absorption correction by multiscans was applied to all structures. All non-hydrogen atoms were refined with anisotropic displacement factors. Hydrogen atoms were placed in ideal positions and fixed with relative isotropic displacement parameters. CIFs of 1, 2, 2', 3 and 5 are provided as supporting information.

References

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Crystallographic Data

$Ni(P(o-C_6H_4S)(o-C_6H_4SH)(C_6H_5))_2$ (1)



Table 1. Crystallographic parameters of 1

Empirical formula	$C_{36}H_{28}NiP_2S_4$	
Formula weight	709.47	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	$a = 11.1450(7) \text{ Å} \qquad \alpha = 90^{\circ}$	
	$b = 16.9903(10) \text{ Å} \qquad \beta = 90^{\circ}$	
	$c = 17.4117(10) \text{ Å} \qquad \gamma = 90^{\circ}$	
Volume	3297.0(3) Å ³	
Z	4	
Density (calculated)	1.429 Mg/m ³	
Absorption coefficient	0.964 mm^{-1}	
F(000)	1464	
Crystal size	$0.35 \ge 0.30 \ge 0.11 \text{ mm}^3$	
Theta range for data collection	2.48 to 25.06°.	
Index ranges	$-12 \le h \le 13, -20 \le k \le 20, -18 \le l \le 20$	
Reflections collected	16125	
Independent reflections	2920 [R(int) = 0.0462]	
Completeness to theta = 25.06°	99.6%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9013 and 0.7289	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2920 / 0 / 196	
Goodness-of-fit on F ²	1.013	
Final R indices [I>2sigma(I)]	$R^1 = 0.0376, wR^2 = 0.0877$	
R indices (all data)	$R^1 = 0.0596$, $wR^2 = 0.0984$	
Largest diff. peak and hole	0.361 and -0.315 e.Å $^{-3}$	

[Ni(P(o-C₆H₄S)(o-C₆H₄SC(CH₃)=NH₂)(C₆H₅))₂](ClO₄)₂ (**2**)



Empirical formula C₄₈H₄₈Cl₂N₆NiO₈P₂S₄ Formula weight 1156.71 296(2) K Temperature 0.71073 Å Wavelength Triclinic Crystal system *P*-1 Space group Unit cell dimensions a = 9.5352(3) Å $\alpha = 80.481(2)^{\circ}$ b = 11.8573(5) Å $\beta = 73.240(2)^{\circ}$ c = 13.0288(6) Å $\gamma = 76.247(2)^{\circ}$ 1362.60(10) Å³ Volume Ζ 1 1.410 Mg/m^3 Density (calculated) 0.722 mm^{-1} Absorption coefficient F(000) 598 Crystal size $0.42 \ge 0.12 \ge 0.04 \text{ mm}^3$ 1.64 to 25.02°. Theta range for data collection $-9 \le h \le 11, -14 \le k \le 14, -15 \le l \le 15$ Index ranges Reflections collected 8561 Independent reflections 4672 [R(int) = 0.0404]Completeness to theta = 25.02° 97.0% Absorption correction multi-scan 0.9717 and 0.7514 Max. and min. transmission Full-matrix least-squares on F^2 Refinement method Data / restraints / parameters 4672 / 0 / 325 Goodness-of-fit on F^2 1.043 $R^1 = 0.0651$, $wR^2 = 0.1699$ Final R indices [I>2sigma(I)] $R^1 = 0.1183$, $wR^2 = 0.2237$ R indices (all data) 0.983 and -0.700 e.Å ⁻³ Largest diff. peak and hole

Table 2. Crystallographic parameters of 2

Isomeric [Ni(P(o-C₆H₄S)(o-C₆H₄SC(CH₃)=NH₂)(C₆H₅))₂](ClO₄)₂ (**2'**)



Table 3. Crystallographic parameters of 2'

Empirical formula	$C_{52}H_{47}Cl_2N_8NiO_9P_2S_4$	
Formula weight	1247.77	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>C</i> 2/c	
Unit cell dimensions	$a = 29.5398(18) \text{ Å} \qquad \alpha = 90^{\circ}$	
	$b = 14.4527(9) \text{ Å} \qquad \beta = 92.550(2)^{\circ}$	
	$c = 14.8710(10) \text{ Å} \qquad \gamma = 90^{\circ}$	
Volume	6342.6(7) Å ³	
Z	4	
Density (calculated)	1.307 Mg/m^3	
Absorption coefficient	0.628 mm^{-1}	
F(000)	2572	
Crystal size	0.24 x 0.11 x 0.04 mm ³	
Theta range for data collection	2.06 to 25.38°.	
Index ranges	$-31 \le h \le 35, -16 \le k \le 17, -17 \le l \le 17$	
Reflections collected	21064	
Independent reflections	5775 [R(int) = 0.1575]	
Completeness to theta = 25.38°	99.1%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0445 and 0.8735	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5775 / 0 / 354	
Goodness-of-fit on F ²	1.099	
Final R indices [I>2sigma(I)]	$R^1 = 0.1098, wR^2 = 0.2648$	
R indices (all data)	$R^1 = 0.2123$, $wR^2 = 0.3394$	
Largest diff. peak and hole	0.961 and -0.780 e.Å $^{-3}$	

[P(C₆H₄SC(CH₃)(NHCOCH₃)](*o*-C₆H₄SH)(C₆H₅)](ClO₄) (**3**)



Table 4. Crystallographic parameters of 3

Empirical formula	C ₂₂ H ₂₁ ClNO ₅ PS ₂	$C_{22}H_{21}CINO_5PS_2$	
Formula weight	509.94		
Temperature	200(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	<i>P</i> -1		
Unit cell dimensions	a = 8.6493(3) Å	$\alpha = 109.381(2)^{\circ}$	
	b = 10.7076(4) Å	$\beta = 90.385(2)^{\circ}$	
	c = 13.9856(6) Å	$\gamma = 105.756(2)^{\circ}$	
Volume	1169.24(8) Å ³		
Z	2		
Density (calculated)	1.448 Mg/m^3		
Absorption coefficient	0.445 mm^{-1}		
F(000)	528		
Crystal size	0.3 x 0.18 x 0.05 mm ³		
Theta range for data collection	2.11 to 25.66°.		
Index ranges	$-10 \le h \le 10, -13 \le k \le 12, -17 \le l \le 17$		
Reflections collected	17425		
Independent reflections	4409 [R(int) = 0.0878]		
Completeness to theta = 25.66°	99.6%		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	1.0682 and 0.7373		
Refinement method	Full-matrix least-squ	Full-matrix least-squares on F ²	
Data / restraints / parameters	4409 / 0 / 290	4409 / 0 / 290	
Goodness-of-fit on F ²	1.060		
Final R indices [I>2sigma(I)]	$R^1 = 0.0635, wR^2 = 0.1600$		
R indices (all data)	$R^1 = 0.0998, wR^2 = 0.0988, wR^2 = 0.09888, wR^2 = 0.09888, wR^2 = 0.0988, wR^2 = 0.0988, wR^2 = 0.0988, wR^$	$R^1 = 0.0998$, $wR^2 = 0.1981$	
Extinction coefficient	0.020(4)	0.020(4)	
Largest diff. peak and hole	0.810 and -0.503 e.Å	0.810 and –0.503 e.Å $^{-3}$	

$[P(C_6H_4SC(CH_3)(NH_3))(C_6H_5)_2](ClO_4)_2 (5)$



Table 5. Crystallographic parameters of 5

Empirical formula	$C_{20}H_{20}Cl_2NO_8PS$	
Formula weight	536.30	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	$a = 12.0439(7) \text{ Å}$ $\alpha = 90^{\circ}$	
	$b = 11.1901(7) \text{ Å} \qquad \beta = 102.248(2)^{\circ}$	
	$c = 17.4924(15) \text{ Å} \qquad \gamma = 90^{\circ}$	
Volume	2303.8(3) Å ³	
Z	4	
Density (calculated)	1.546 Mg/m^3	
Absorption coefficient	0.490 mm^{-1}	
F(000)	1104	
Crystal size	$0.25 \ge 0.2 \ge 0.07 \text{ mm}^3$	
Theta range for data collection	2.18 to 25.36°.	
Index ranges	$-11 \le h \le 14, -13 \le k \le 13, -21 \le l \le 20$	
Reflections collected	12792	
Independent reflections	4161 [R(int) = 0.0784]	
Completeness to theta = 25.36°	98.5%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9781 and 0.8667	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4161 / 0 / 303	
Goodness-of-fit on F ²	1.038	
Final R indices [I>2sigma(I)]	$R^1 = 0.0655, wR^2 = 0.1540$	
R indices (all data)	$R^1 = 0.1138$, $wR^2 = 0.1795$	
Largest diff. peak and hole	0.937 and -0.419 e.Å^{-3}	