

## **Part 1: Experimental Procedures.**

**Experimental Section: General Considerations:** All operations were performed under a nitrogen atmosphere unless otherwise stated. Benzene, THF, toluene, and hexanes were distilled from dark purple solutions of benzophenone ketyl. MeCN was dried and distilled over CaH<sub>2</sub>. Neutral alumina was heated to 200°C under vacuum for two days and stored under nitrogen. Thiophene (99+%) was purchased from Aldrich Chemical Co. and purified as previously reported.<sup>1</sup> Butyl lithium, potassium *tert*-butoxide, KPF<sub>6</sub>, Super-Hydride® and hydrogen sulfide was purchased from Aldrich Chemical Co. and used without further purification. 2, 2'-dibromobiphenyl was purchased from Alfa Aesar and used without further purification. Dibenzothiophene was purchased from Aldrich Chemical Co. and purified by passage through a neutral alumina column before use. A Siemens-SMART 3-Circle CCD diffractometer was used for X-ray crystal structure determination. Elemental analyses were obtained from Desert Analytics. All <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C spectra were recorded on a Bruker AMX400 NMR spectrometer, and all <sup>1</sup>H chemical shifts are reported relative to the residual proton resonance in the deuterated solvent. Dippe<sup>2</sup> and (dippe)NiCl<sub>2</sub><sup>3</sup> were synthesized according to published procedures. The synthesis of [(dippe)Ni(μ-S)]<sub>2</sub> will be reported elsewhere.

**Preparation of [(dippe)NiH]<sub>2</sub> (1):** (dippe)NiCl<sub>2</sub> (755 mg, 1.92 mmol) was added to a stirred solution of Super Hydride® (4.2 mL, 1M solution in THF) in benzene (100 mL) and stirred at room temperature for 1.5 h. The solution was then filtered through a frit packed with a small amount (2 cm) of neutral alumina. 20 mL toluene was added to the filtrate and the solvents were removed on the vacuum line leaving a deep red residue. This was dried overnight on the vacuum line and then the product was extracted with hexanes. The solvents were removed and the dark

red solid was dried overnight under vacuum. Yield: 558 mg (90%).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  1.19 (br s, 8H), 1.34 - 1.26 (m, 32 H), 1.11 (br s, 24 H), -9.81 (quin,  $J = 24.2$  Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ , 100 MHz):  $\delta$  25.29 (br s), 22.76 - 22.34 (m), 20.12 (s), 19.28 (s).  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_{12}$ ,  $25^\circ\text{C}$ , 162 MHz): 79.57 (s). Anal. Calcd (found) for  $\text{C}_{28}\text{H}_{66}\text{NiP}_4$ : 52.06 (52.38) %C, 10.44 (10.05) %H.

**Preparation of (dippe)Ni( $\eta^2$ -C,S-dibenzothiophene) (2):** **1** (620 mg, 0.96 mmol) was dissolved in a minimum amount of hexanes and added to a stirred solution of DBT (709 mg, 3.85 mmol) in 150 mL hexanes. The solution was stirred for 3 hours and the orange precipitate was then collected, washed with hexanes, and dried under vacuum. Yield 468 mg (48%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-78^\circ\text{C}$ ):  $\delta$  7.53 - 7.43 (m, 2H), 7.39 (d,  $J = 7.3$  Hz, 1H), 7.17 (d,  $J = 6.4$  Hz, 1H), 7.00 - 6.83 (m, 4H), 2.77 (br s, 1H), 2.41 (br s, 1H), 2.25 - 0.84 (m, 24 H), 0.63 (br s, 3H), 0.12 (br s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-78^\circ\text{C}$ , 100 MHz):  $\delta$  156.11 (dd,  $J = 27.7, 25.8$  Hz), 147.44 (s), 143.03 (s), 138.95 (s), 133.59 (d,  $J = 8.1$  Hz), 128.81 (s), 125.25 (s), 124.68 (s), 123.94 (s), 122.05 (s), 121.42 (s), 25.02 (d,  $J = 27.2$  Hz), 23.78 (d,  $J = 20.2$  Hz), 22.06 - 21.46 (m), 19.99 - 19.66 (m), 18.91 - 17.10 (m), 15.46 - 15.26 (m), 14.81 (s).  $^{31}\text{P}\{^1\text{H}\}$  (THF- $d_8$ ,  $-78^\circ\text{C}$ , 162 MHz)  $\delta$  75.55 (d,  $J = 10.2$  Hz), 74.39 (d,  $J = 10.2$  Hz) Anal. Calcd (found) for  $\text{C}_{26}\text{H}_{40}\text{NiP}_2\text{S}$ : 61.57 (61.80) %C, 7.74 (7.98) %H.

**Reaction of 2 with thiophene:** **2** (15 mg, 0.03 mmol) was dissolved in 0.5 mL thiophene and allowed to stand at room temperature for 1 h. Excess thiophene was then removed under vacuum, and the residue was dissolved in THF- $d_8$ . Yield of the new C-S insertion complex (**3**) was quantitative by NMR.

**Alternate preparation of (dippe)Ni( $\eta^2$ -C,S-thiophene) (3):** Thiophene (1 mL) was added to a stirred solution of **1** (70 mg, 0.11 mmol) in 13 mL hexanes. The solution was stirred at room temperature for 3 h and the yellow precipitate was filtered and rinsed with hexanes. Yield: 60 mg (68.1%)  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ , 25°C):  $\delta$  7.46 (t,  $J$  = 10 Hz, 1H), 7.37 (t,  $J$  = 11.1 Hz, 1H), 6.91-6.82 (m, 1H), 6.58 (t,  $J$  = 8.1 Hz, 1H), 2.46 (oct,  $J$  = 7.5 Hz, 2H), 2.32 (oct,  $J$  = 6.9 Hz, 2H), 1.94 (sext,  $J$  = 8.7 Hz, 2H), 1.78 (sext,  $J$  = 8.1 Hz, 2H), 1.31-1.15 (m, 24H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , -35°C, 100 MHz):  $\delta$  142.01 (dd,  $J$  = 68.8, 27.7 Hz), 125.85 (s), 121.59 (d,  $J$  = 13.3 Hz), 120.03 (s), 24.24 - 23.67 (m), 22.40 (t,  $J$  = 19.6 Hz), 19.76 (dd,  $J$  = 22.3, 13.7 Hz), 18.65 (s), 18.32 (s), 17.90 (s), 17.79 (s).  $^{31}\text{P}\{^1\text{H}\}$  (THF- $d_8$ , 25°C, 162 MHz)  $\delta$  82.33 (d,  $J$  = 20.4 Hz), 73.24 (d,  $J$  = 20.4 Hz) Anal. Calcd (found) for  $\text{C}_{18}\text{H}_{36}\text{NiP}_2\text{S}$ : 52.98 (53.36) %C, 9.11 (8.96) %H.

**Preparation of (dippe)Ni(2, 2'-biphenyl) (4):** To a stirred solution of 2, 2'- dibromobiphenyl (175 mg) in 50 mL THF (0°C) was added *n*-butyl lithium (0.54 mL, 2.5 M solution in THF). The solution was warmed to room temperature and stirred for 45 minutes. A suspension of (dippe)NiCl<sub>2</sub> in THF was then added and the resulting solution was stirred at room temperature for 25 min. The solvents were then removed under vacuum and the residue was extracted with benzene and filtered. Removal of benzene under vacuum and recrystallization of the residue (THF/hexanes, -30°C) left yellow-orange crystals. Yield: 154 mg (64%).  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ , 25°C):  $\delta$  7.23 (t,  $J$  = 6.9 Hz, 2H), 7.10 (d,  $J$  = 7.7 Hz, 2H), 6.74 (t,  $J$  = 7.1 Hz, 2H), 6.57 (t,  $J$  = 6.9 Hz, 2H), 2.47 (oct,  $J$  = 7.3 Hz, 4H), 1.72 (d,  $J$  = 14.1 Hz, 4H), 1.35 - 1.26 (m, 24H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25°C, 100 MHz):  $\delta$  168.49 (dd,  $J$  = 76.3, 21.6 Hz), 159.88 (t,  $J$  = 1.9 Hz), 140.45 (br s), 124.71 (s), 124.45 (s), 118.89 (s), 26.30 - 25.99 (m), 22.39 (br s), 18.90, (s),

18.57 (t,  $J = 19.39$ ).  $^{31}\text{P}\{^1\text{H}\}$  (THF- $d_8$ , 25°C, 162 MHz)  $\delta$  70.09 (s). Anal. Calcd (found) for  $\text{C}_{26}\text{H}_{40}\text{NiP}_2$ : 65.89 (65.99) %C, 8.55 (8.52) %H.

**Isolation of [(dippe)Ni( $\mu$ -S)] $_2$ Ni(2, 2'-biphenyl) (6):** Dissolution of **2** in  $\text{C}_6\text{D}_6$  for ca. 3 weeks in an NMR tube led to the precipitation of trace quantities of **6** which could be recovered for analysis.  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ , 25°C):  $\delta$  7.50 (d,  $J = 7.2$  Hz), 6.88 (d,  $J = 6.8$  Hz), 6.50 (t,  $J = 7.4$  Hz), 6.36 (t,  $J = 7.0$  Hz), 2.40 - 2.21 (m, 8H), 1.70 - 1.14 (m, 56 H).  $^{31}\text{P}\{^1\text{H}\}$  (THF- $d_8$ , 25°C, 162 MHz)  $\delta$  79.79 (s) Anal. Calcd (found) for  $\text{C}_{40}\text{H}_{72}\text{Ni}_3\text{P}_4\text{S}_2$ : 52.49 (52.39) %C, 7.55 (7.91) %H.

**Preparation of (dippe) $_2$ Ni (7):** To a stirred solution of [(dippe)NiH] $_2$  (70 mg, 0.11 mmol) in 25 mL benzene was added dippe (62.8 mg, 0.23 mmol) and the solution was stirred for 1 hour at room temperature. The solvents were removed under vacuum leaving a clear residue of analytically pure product. Yield: quantitative.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25°C):  $\delta$  1.99 (sept,  $J = 7.09$  Hz, 8H), 1.35 - 1.32 (br s, 8H), 1.27 - 1.22 (br s, 24 H), 1.22 - 1.16 (br s, 24 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25°C, 100 MHz):  $\delta$  27.39 (quin,  $J = 5.8$  Hz), 22.66 - 22.14 (m), 20.92 (s), 19.11 (s);  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ , 25°C, 162 MHz)  $\delta$  54.50 (s) Anal. Calcd (found) for  $\text{C}_{28}\text{H}_{64}\text{NiP}_4$ : 57.46 (57.65) %C, 11.34 (11.06) %H.

**Preparation of [(dippe) $_2$ Ni $_2$ ( $\mu$ -S)( $\mu$ -H)][PF $_6$ ] (8):** **1** (50 mg, 0.08 mmol) was dissolved 15 mL THF and added to a stirred suspension of (dippe)Ni(SH) $_2$  (60 mg, 0.16 mmol) in THF (30 mL). KPF $_6$  (28 mg, 0.16 mmol) in MeCN (10 mL) was quickly added to the mixture and the resulting solution was stirred for 25 min. The solvents were removed under vacuum and the residue was

rinsed with hexanes. The remaining residue was extracted with THF and the filtrate was then pumped dry leaving 119 mg (93.5%) crude product. The product can be purified of all residual (dippe)Ni(SH)<sub>2</sub> by dissolution in the minimum amount of THF and cooling to -30°C overnight. The precipitate was collected and pumped dry leaving 94 mg (74%) pure **8**. <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>, 25°C): δ 2.52 - 2.35 (m, 8H), 2.26 - 2.05 (m, 8H), 1.30 - 1.13 (m, 48 H), -11.27 (tt, J = 45.6, 25.7 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 25°C, 100 MHz): δ 29.81 - 29.47 (m), 28.09 (d, J = 22.0 Hz), 24.52 - 24.05 (m), 21.59 - 21.16 (m), 21.09 (virtual t, J = 3 Hz), 19.80 (s), 19.21 (s), 19.11 (s). <sup>31</sup>P{<sup>1</sup>H} (THF-d<sub>8</sub>, 25°C, 162 MHz) δ 100.60 (dd, J = 14.4, 8.53 Hz), 91.44 (dd, J = 15.3, 8.5 Hz), -141.70 (sept, J = 709.5 Hz). Anal. Calcd (found) for C<sub>28</sub>H<sub>65</sub>Ni<sub>2</sub>P<sub>3</sub>F<sub>6</sub>S: 41.19 (41.01) %C, 8.02 (7.99) %H.

**Deprotonation of 8 to yield 5:** In a resealable vessel 1 eq of potassium *tert*-butoxide in THF (1M solution) was added to a solution of **8** (16 mg, 0.02 mmol) in THF-d<sub>8</sub> (0.9 mL). The solution was then heated to 70°C for 2 h yielding **5** in *ca.* 80% yield by NMR. Analytical data for the fluxional complex **5**: <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>, 25°C): δ 2.14 (br s, 8H), 1.55 (br s, 8H), 1.22 (br s, 24 H), 1.08 (br s, 24 H). <sup>31</sup>P{<sup>1</sup>H} (THF-d<sub>8</sub>, -35°C, 162 MHz) δ 77.86 (t, J = 22.7 Hz), 73.64 (t, J = 22.1 Hz). Anal. Calcd (found) for C<sub>28</sub>H<sub>64</sub>Ni<sub>2</sub>P<sub>4</sub>S: 50.73 (49.89) %C, 9.57 (9.97) %H

**Preparation of (dippe)Ni(SH)<sub>2</sub>:** To a stirred solution of (dippe)<sub>2</sub>Ni (169 mg, 0.29 mmol) in benzene was added 1 atm H<sub>2</sub>S (*caution! Poisonous gas!*). The solution was stirred at room temperature for 1 hour, and then all solvents were removed under vacuum. The residue was washed with hexanes and dried under vacuum leaving an orange solid. Yield 79 mg (70%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25°C): δ 2.32 (m, 4H), 1.71 (d, J = 11.5 Hz, 4H), 1.39 (dd, J = 16.1,

7.2 Hz, 12 H), 1.23 (dd,  $J = 13.5, 7.0$  Hz, 12 H), -1.08 (d,  $J = 12.0$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25°C, 100 MHz):  $\delta$  26.54 - 26.15 (m), 21.68 (t,  $J = 19.7$  Hz), 20.05 (s), 18.68 (s).  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ , 25°C, 162 MHz)  $\delta$  86.82 (s) Anal. Calcd (found) for  $\text{C}_{28}\text{H}_{64}\text{NiP}_4$ : 43.57 (43.43) %C, 8.74 (8.85) %H.

**Monitoring the decomposition of 2 in THF:** **2** (15.4 mg, 0.03 mmol) was dissolved in 0.85 mL THF- $d_8$  (and 1  $\mu\text{L}$  DME as an internal standard) and the NMR tube was spun at room temperature for 5 days. The reaction was followed by both  $^1\text{H}$  and inverse gated decoupled  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. NMR yields of the resulting products (relative to starting amount of **2**: dibenzothiophene 40%, (dippe)Ni(2, 2'-biphenyl) (**4**) 23.3% ,  $[\text{Ni}_2(\mu\text{-S})(\text{dippe})_2]$  (**5**) 23.3%,  $[(\text{dippe})\text{Ni}(\mu\text{-S})]_2\text{Ni}(2, 2'\text{-biphenyl})$  (**6**) 8.3%,  $(\text{dippe})_2\text{Ni}$  (**7**) 2.0%.

**X-ray Structural Determination of (dippe)Ni( $\eta^2\text{-C,S-DBT}$ ) **2**.** **2** was dissolved in cold (-30°C) THF and layered with hexanes. Slow diffusion of hexanes in THF at -30°C produced orange prisms. The A single crystal of dimensions 0.20 x 0.20 x 0.20  $\text{mm}^3$  was mounted on a glass fiber with Paratone-N oil. Data were collected at -80 °C on a Siemens SMART CCD area detector system employing a 3kW sealed tube X-ray source operating at 2.0 kW. 1 quadrant of data were collected over approximately 6 h, yielding 13076 total data after integration using SAINT (see Table 2). Laue symmetry revealed an orthorhombic crystal system, and cell parameters were determined from 3529 unique reflections.<sup>4</sup> The space group was assigned as *Pbca* on the basis of systematic absences using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a Z value of 8 there is one independent molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined

anisotropically (full matrix on  $F^2$ ), with hydrogens included in idealized locations. The structure refined with final residuals of  $R_1 = 0.0485$  and  $wR_2 = 0.0820$ .<sup>5</sup> Fractional coordinates and thermal parameters are given in the Supporting Information.

**X-ray Structural Determination of  $[(\text{dippe})_2\text{Ni}_2(\mu\text{-S})(\mu\text{-H})][\text{PF}_6]$  **8**.** Slow cooling of a THF solution of **8** produced small, orange plates. A single crystal of dimensions 0.10 x 0.25 x 0.40 mm<sup>3</sup> was mounted on a glass fiber with Paratone-N oil. Data were collected at -80 °C on a Siemens SMART CCD area detector system employing a 3kW sealed tube X-ray source operating at 2.0 kW. 1.3 hemispheres of data were collected over 7 h, yielding 18127 total data after integration using SAINT (see Table 2). Laue symmetry revealed an triclinic crystal system, and cell parameters were determined from 12178 unique reflections.<sup>iv</sup> The space group was assigned as *P1* on the basis of systematic absences using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a *Z* value of 4 there are two independent molecules within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on  $F^2$ ), with hydrogens included in idealized locations. A bridging hydride ligand, located in a difference Fourier map, was included and refined isotropically. The structure refined with final residuals of  $R_1 = 0.0558$  and  $wR_2 = 0.1176$ .<sup>v</sup> Fractional coordinates and thermal parameters are given in the Supporting Material.

---

**References and Notes**

- <sup>1</sup> Spies, G. H. and Angelici, R.J. *Organometallics*, **1987**, *6*, 1897.
- <sup>2</sup> Cloke, F. G. N.; Gibson, V. C.; Green, M. L. H. *J. Chem. Soc. Dalton Trans.* **1988**, 2227.
- <sup>3</sup> Scott, F.; Krüger, C.; Betz, P. *J. Organomet. Chem.* **1990**, *387*, 113.
- <sup>4</sup> It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10x the listed values.
- <sup>5</sup> Using the SHELXTL 5.04 package,  $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$ ,  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ , where  $w = 1/[\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$  and  $P = [f \cdot (\text{Maximum of } 0 \text{ or } F_o^2) + (1-f) \cdot F_c^2]$



**Part 2: Crystallographic Information****Table S-1. Crystallographic Data for 2 and 8.**

<b>Crystal Parameters</b>	<b>2</b>	<b>8</b>
chemical formula	C <sub>26</sub> H <sub>40</sub> NiP <sub>2</sub> S	C <sub>28</sub> H <sub>65</sub> F <sub>6</sub> Ni <sub>2</sub> P <sub>5</sub> S
formula weight	505.29	820.13
cryst syst	orthorhombic	triclinic
space group (No.)	<i>Pbca</i>	<i>P1</i>
Z	8	4
a, Å	16.0335(3)	16.3477(1)
b, Å	17.4135(1)	16.6742(2)
c, Å	18.3742(3)	17.2145(1)
β, deg	90	92.7060 (10)
vol., Å <sup>3</sup>	5130.06(1)	3905.40(6)
ρ <sub>calc</sub> , g cm <sup>-3</sup>	1.308	1.395
cryst dimens, mm <sup>3</sup>	0.20 x 0.20 x 0.20	0.10 x 0.25 x 0.40
temp, °C	-80	-80
<b>Measurement of Intensity Data</b>		
diffractometer	Siemens SMART	Siemens SMART
radiation	Mo, 0.71073 Å	Mo, 0.71073 Å
frame range/time, deg/sec	0.3/30	0.3/10
2θ range, deg	4.10-50	2.64-50
data collected	-15 ≤ h ≤ 4, -19 ≤ k ≤ 18, -24 ≤ l ≤ 24	-15 ≤ h ≤ 21, -21 ≤ k ≤ 19, -21 ≤ l ≤ 22
no. of data collected	13076	18127
no. of unique data	3529	12178
no. of obs data (F <sub>o</sub> >4σ(F <sub>o</sub> ))	3065	8893
agreement between equivalent data (R <sub>int</sub> )	0.0360	0.0200
no. of params varied	271	765
μ, mm <sup>-1</sup>	0.974	1.269
abs cor	empirical (SADABS)	empirical (SADABS)
range of trans. factors	0.928 - 0.836	0.928 - 0.756
R <sub>1</sub> (F <sub>o</sub> ), wR <sub>2</sub> (F <sub>o</sub> <sup>2</sup> ), (F <sub>o</sub> >4σ(F <sub>o</sub> ))	0.0485, 0.0820	0.0558, 0.1176
R <sub>1</sub> (F <sub>o</sub> ), wR <sub>2</sub> (F <sub>o</sub> <sup>2</sup> ), (all data)	0.0616, 0.0860	0.0796, 0.1297
goodness of fit	1.226	1.045

**Table S2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ni (1)	7513 (1)	835 (1)	7514 (1)	23 (1)
P (1)	7861 (1)	1238 (1)	6413 (1)	25 (1)
P (2)	8802 (1)	490 (1)	7675 (1)	26 (1)
S (1)	6479 (1)	1629 (1)	7548 (1)	35 (1)
C (1)	9209 (2)	965 (3)	8498 (2)	35 (1)
C (2)	8948 (3)	542 (3)	9186 (2)	53 (1)
C (3)	8940 (3)	1800 (3)	8540 (2)	52 (1)
C (4)	9208 (2)	-500 (2)	7732 (2)	35 (1)
C (5)	10128 (2)	-544 (3)	7960 (3)	49 (1)
C (6)	9075 (2)	-932 (3)	7015 (2)	45 (1)
C (7)	9431 (2)	928 (2)	6951 (2)	30 (1)
C (8)	8956 (2)	985 (2)	6237 (2)	30 (1)
C (9)	7760 (2)	2255 (2)	6169 (2)	30 (1)
C (10)	8263 (2)	2749 (3)	6690 (2)	44 (1)
C (11)	7971 (2)	2449 (3)	5379 (2)	42 (1)
C (12)	7267 (2)	710 (2)	5713 (2)	31 (1)
C (13)	7276 (2)	-145 (3)	5879 (2)	47 (1)
C (14)	6375 (2)	999 (3)	5681 (2)	45 (1)
C (15)	7051 (2)	194 (2)	8269 (2)	24 (1)
C (16)	7156 (2)	-583 (3)	8148 (2)	29 (1)
C (17)	6756 (2)	-1152 (2)	8549 (2)	35 (1)
C (18)	6208 (2)	-934 (3)	9090 (2)	36 (1)
C (19)	6085 (2)	-174 (3)	9225 (2)	30 (1)
C (20)	6497 (2)	405 (2)	8835 (2)	24 (1)
C (21)	6269 (2)	1210 (2)	9007 (2)	28 (1)
C (22)	6209 (2)	1768 (2)	8465 (2)	30 (1)
C (23)	5875 (2)	2487 (3)	8639 (2)	38 (1)
C (24)	5616 (2)	2657 (3)	9329 (2)	47 (1)
C (25)	5710 (2)	2124 (3)	9877 (2)	46 (1)
C (26)	6033 (2)	1416 (3)	9714 (2)	35 (1)

**Table S3.** Bond lengths [Å] and angles [deg] for **2**.

Ni (1) -C (15)	1.928 (3)	C (8) -P (1) -Ni (1)	109.01 (12)
Ni (1) -S (1)	2.1591 (10)	C (12) -P (1) -Ni (1)	110.41 (12)
Ni (1) -P (2)	2.1716 (9)	C (7) -P (2) -C (1)	102.3 (2)
Ni (1) -P (1)	2.2140 (10)	C (7) -P (2) -C (4)	103.6 (2)
P (1) -C (9)	1.835 (4)	C (1) -P (2) -C (4)	104.3 (2)
P (1) -C (8)	1.838 (3)	C (7) -P (2) -Ni (1)	108.09 (11)
P (1) -C (12)	1.845 (4)	C (1) -P (2) -Ni (1)	108.93 (12)
P (2) -C (7)	1.835 (3)	C (4) -P (2) -Ni (1)	126.98 (12)
P (2) -C (1)	1.843 (4)	C (22) -S (1) -Ni (1)	107.80 (13)
P (2) -C (4)	1.847 (4)	C (3) -C (1) -C (2)	110.0 (4)
S (1) -C (22)	1.756 (4)	C (3) -C (1) -P (2)	111.8 (3)
C (1) -C (3)	1.518 (6)	C (2) -C (1) -P (2)	111.6 (3)
C (1) -C (2)	1.522 (5)	C (6) -C (4) -C (5)	110.1 (3)
C (4) -C (6)	1.532 (5)	C (6) -C (4) -P (2)	111.2 (3)
C (4) -C (5)	1.536 (5)	C (5) -C (4) -P (2)	113.6 (3)
C (7) -C (8)	1.521 (5)	C (8) -C (7) -P (2)	112.1 (2)
C (9) -C (10)	1.519 (5)	C (7) -C (8) -P (1)	110.1 (2)
C (9) -C (11)	1.528 (5)	C (10) -C (9) -C (11)	110.9 (3)
C (12) -C (14)	1.517 (5)	C (10) -C (9) -P (1)	110.2 (3)
C (12) -C (13)	1.519 (6)	C (11) -C (9) -P (1)	115.2 (3)
C (15) -C (16)	1.382 (5)	C (14) -C (12) -C (13)	110.0 (3)
C (15) -C (20)	1.416 (4)	C (14) -C (12) -P (1)	110.5 (3)
C (16) -C (17)	1.390 (5)	C (13) -C (12) -P (1)	110.1 (3)
C (17) -C (18)	1.381 (5)	C (16) -C (15) -C (20)	116.6 (3)
C (18) -C (19)	1.360 (5)	C (16) -C (15) -Ni (1)	113.9 (2)
C (19) -C (20)	1.402 (5)	C (20) -C (15) -Ni (1)	128.2 (3)
C (20) -C (21)	1.482 (5)	C (15) -C (16) -C (17)	123.8 (3)
C (21) -C (22)	1.394 (5)	C (18) -C (17) -C (16)	118.6 (4)
C (21) -C (26)	1.400 (5)	C (19) -C (18) -C (17)	119.4 (4)
C (22) -C (23)	1.399 (5)	C (18) -C (19) -C (20)	122.6 (3)
C (23) -C (24)	1.368 (5)	C (19) -C (20) -C (15)	118.9 (4)
C (24) -C (25)	1.378 (6)	C (19) -C (20) -C (21)	117.1 (3)
C (25) -C (26)	1.371 (6)	C (15) -C (20) -C (21)	123.8 (3)
		C (22) -C (21) -C (26)	117.7 (4)
C (15) -Ni (1) -S (1)	93.12 (11)	C (22) -C (21) -C (20)	121.6 (3)
C (15) -Ni (1) -P (2)	96.20 (10)	C (26) -C (21) -C (20)	120.4 (4)
S (1) -Ni (1) -P (2)	154.62 (5)	C (21) -C (22) -C (23)	119.2 (4)
C (15) -Ni (1) -P (1)	159.68 (11)	C (21) -C (22) -S (1)	124.8 (3)
S (1) -Ni (1) -P (1)	91.01 (4)	C (23) -C (22) -S (1)	115.9 (3)
P (2) -Ni (1) -P (1)	88.37 (3)	C (24) -C (23) -C (22)	121.4 (4)
C (9) -P (1) -C (8)	105.8 (2)	C (23) -C (24) -C (25)	119.9 (4)
C (9) -P (1) -C (12)	105.4 (2)	C (26) -C (25) -C (24)	119.2 (4)
C (8) -P (1) -C (12)	104.6 (2)	C (25) -C (26) -C (21)	122.4 (4)
C (9) -P (1) -Ni (1)	120.45 (12)		

**Table S4.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **2**. The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	U11	U22	U33	U23	U13	U12
Ni (1)	18 (1)	26 (1)	24 (1)	1 (1)	4 (1)	-1 (1)
P (1)	22 (1)	28 (1)	25 (1)	2 (1)	3 (1)	0 (1)
P (2)	19 (1)	31 (1)	28 (1)	4 (1)	2 (1)	0 (1)
S (1)	30 (1)	43 (1)	33 (1)	8 (1)	7 (1)	1 (1)
C (1)	27 (2)	47 (3)	32 (2)	2 (2)	-3 (2)	-2 (2)
C (2)	50 (2)	81 (4)	29 (2)	1 (3)	-4 (2)	-12 (2)
C (3)	57 (3)	49 (4)	48 (3)	-1.2 (3)	-9 (2)	0 (2)
C (4)	26 (2)	36 (3)	42 (2)	9 (2)	3 (2)	2 (2)
C (5)	33 (2)	43 (3)	70 (3)	15 (3)	-1 (2)	6 (2)
C (6)	48 (2)	40 (3)	48 (3)	3 (2)	8 (2)	9 (2)
C (7)	22 (2)	32 (3)	36 (2)	8 (2)	6 (1)	1 (2)
C (8)	26 (2)	36 (3)	29 (2)	6 (2)	9 (1)	1 (2)
C (9)	31 (2)	29 (3)	32 (2)	8 (2)	5 (1)	0 (2)
C (10)	58 (3)	27 (3)	48 (3)	3 (2)	-1 (2)	-3 (2)
C (11)	51 (2)	34 (3)	42 (2)	15 (2)	6 (2)	1 (2)
C (12)	33 (2)	37 (3)	23 (2)	1 (2)	2 (1)	0 (2)
C (13)	56 (3)	35 (4)	49 (3)	-8 (3)	-14 (2)	-3 (2)
C (14)	35 (2)	50 (3)	50 (3)	-4 (2)	-1 (2)	-1 (2)
C (15)	21 (2)	29 (3)	21 (2)	1 (2)	-2 (1)	-4 (2)
C (16)	28 (2)	34 (3)	25 (2)	-2 (2)	3 (1)	-3 (2)
C (17)	35 (2)	26 (3)	43 (2)	2 (2)	-3 (2)	-4 (2)
C (18)	35 (2)	40 (4)	32 (2)	16 (2)	2 (2)	-9 (2)
C (19)	29 (2)	32 (3)	28 (2)	6 (2)	3 (2)	-1 (2)
C (20)	19 (2)	31 (3)	22 (2)	3 (2)	-6 (1)	-3 (2)
C (21)	21 (2)	30 (3)	34 (2)	5 (2)	-4 (1)	-7 (2)
C (22)	20 (2)	34 (3)	35 (2)	-6 (2)	-1 (1)	-5 (2)
C (23)	36 (2)	28 (3)	49 (3)	-7 (2)	-4 (2)	1 (2)
C (24)	44 (2)	43 (4)	53 (3)	-13 (3)	-2 (2)	3 (2)
C (25)	39 (2)	59 (4)	40 (3)	-20 (3)	3 (2)	-4 (2)
C (26)	32 (2)	40 (3)	34 (2)	-5 (2)	0 (2)	-3 (2)

**Table S5.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **2**.

	x	y	z	U(eq)
H(1A)	9832 (2)	954 (3)	8471 (2)	42
H(2A)	9124 (3)	4 (3)	9154 (2)	80
H(2B)	8340 (3)	567 (3)	9238 (2)	80
H(2C)	9212 (3)	784 (3)	9609 (2)	80
H(3A)	9110 (3)	2067 (3)	8095 (2)	77
H(3B)	9204 (3)	2044 (3)	8962 (2)	77
H(3C)	8332 (3)	1827 (3)	8591 (2)	77
H(4A)	8876 (2)	-773 (2)	8113 (2)	42
H(5A)	10207 (2)	-266 (3)	8419 (3)	73
H(5B)	10477 (2)	-311 (3)	7582 (3)	73
H(5C)	10289 (2)	-1083 (3)	8026 (3)	73
H(6A)	8487 (2)	-901 (3)	6874 (2)	68
H(6B)	9233 (2)	-1472 (3)	7078 (2)	68
H(6C)	9421 (2)	-700 (3)	6634 (2)	68
H(7A)	9607 (2)	1448 (2)	7105 (2)	36
H(7B)	9941 (2)	616 (2)	6875 (2)	36
H(8A)	8984 (2)	488 (2)	5977 (2)	36
H(8B)	9216 (2)	1382 (2)	5924 (2)	36
H(9A)	7161 (2)	2395 (2)	6242 (2)	36
H(10A)	8118 (2)	2614 (3)	7192 (2)	67
H(10B)	8136 (2)	3291 (3)	6604 (2)	67
H(10C)	8859 (2)	2658 (3)	6611 (2)	67
H(11A)	7640 (2)	2125 (3)	5053 (2)	63
H(11B)	8566 (2)	2357 (3)	5293 (2)	63
H(11C)	7843 (2)	2991 (3)	5285 (2)	63
H(12A)	7536 (2)	797 (2)	5229 (2)	37
H(13A)	7854 (2)	-326 (3)	5899 (2)	70
H(13B)	6976 (2)	-422 (3)	5496 (2)	70
H(13C)	7005 (2)	-238 (3)	6349 (2)	70
H(14A)	6374 (2)	1550 (3)	5574 (2)	67
H(14B)	6102 (2)	908 (3)	6150 (2)	67
H(14C)	6072 (2)	724 (3)	5297 (2)	67
H(16A)	7522 (2)	-738 (3)	7769 (2)	35
H(17A)	6858 (2)	-1679 (2)	8452 (2)	42
H(18A)	5920 (2)	-1311 (3)	9367 (2)	43
H(19A)	5705 (2)	-30 (3)	9597 (2)	36
H(23A)	5827 (2)	2866 (3)	8269 (2)	45
H(24A)	5372 (2)	3143 (3)	9431 (2)	56
H(25A)	5553 (2)	2245 (3)	10362 (2)	55
H(26A)	6100 (2)	1051 (3)	10094 (2)	42

**Table S6.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ni (1)	13416 (1)	9665 (1)	7194 (1)	30 (1)
Ni (2)	12079 (1)	9174 (1)	6069 (1)	28 (1)
Ni (3)	3420 (1)	4570 (1)	2147 (1)	28 (1)
Ni (4)	2045 (1)	4055 (1)	1031 (1)	27 (1)
P (1)	14783 (1)	10368 (1)	7580 (1)	47 (1)
P (2)	13446 (1)	9343 (1)	8269 (1)	41 (1)
P (3)	11614 (1)	9116 (1)	4852 (1)	31 (1)
P (4)	10816 (1)	8288 (1)	5985 (1)	38 (1)
P (5)	7904 (1)	5454 (1)	3558 (1)	43 (1)
P (6)	4782 (1)	5344 (1)	2522 (1)	34 (1)
P (7)	3539 (1)	4246 (1)	3216 (1)	40 (1)
P (8)	1593 (1)	3994 (1)	-196 (1)	29 (1)
P (9)	736 (1)	3321 (1)	1031 (1)	33 (1)
P (10)	-2030 (1)	570 (1)	-1374 (1)	43 (1)
S (1)	13332 (1)	10003 (1)	6165 (1)	41 (1)
S (2)	3295 (1)	4858 (1)	1089 (1)	39 (1)
F (1)	7023 (2)	4988 (3)	3770 (2)	62 (1)
F (2)	8322 (3)	4785 (4)	3713 (3)	97 (2)
F (3)	7466 (3)	6126 (3)	3418 (3)	93 (1)
F (4)	8209 (3)	6242 (3)	4603 (3)	88 (1)
F (5)	8781 (2)	5931 (3)	3358 (3)	73 (1)
F (6)	7582 (3)	4694 (3)	2525 (2)	101 (2)
F (7)	-2383 (4)	1356 (4)	-1368 (5)	141 (2)
F (8)	-1155 (2)	1013 (3)	-1594 (3)	74 (1)
F (9)	-2910 (2)	129 (3)	-1148 (2)	66 (1)
F (10)	-2421 (3)	-75 (5)	-2382 (3)	142 (3)
F (11)	-1666 (3)	1249 (4)	-336 (3)	117 (2)
F (12)	-1686 (3)	-203 (4)	-1357 (5)	131 (2)
C (1)	15127 (4)	11650 (4)	7928 (5)	61 (2)
C (2)	14630 (6)	12193 (5)	8627 (5)	96 (3)
C (3)	16108 (5)	12151 (6)	8229 (6)	104 (3)
C (4)	15463 (4)	9836 (5)	6772 (5)	62 (2)
C (5)	15441 (4)	10047 (5)	6006 (5)	70 (2)
C (6)	15220 (6)	8758 (6)	6397 (7)	123 (4)
C (7)	12840 (5)	9903 (4)	9165 (4)	57 (2)
C (8)	13100 (6)	10981 (5)	9537 (5)	107 (3)
C (9)	11883 (4)	9434 (5)	8819 (4)	67 (2)
C (10)	13106 (4)	8076 (4)	7962 (4)	51 (2)
C (11)	13203 (5)	7908 (5)	8760 (5)	70 (2)
C (12)	13578 (5)	7524 (5)	7252 (5)	82 (2)
C (13)	15177 (5)	10353 (7)	8584 (6)	114 (4)
C (14)	14574 (4)	9827 (6)	8870 (5)	79 (2)
C (15)	10186 (3)	8868 (4)	6840 (4)	44 (1)
C (16)	10490 (4)	9953 (4)	7248 (4)	61 (2)
C (17)	9211 (4)	8464 (5)	6504 (5)	79 (2)
C (18)	10851 (5)	7223 (4)	6090 (6)	84 (3)
C (19)	11491 (6)	6760 (6)	5512 (7)	117 (4)
C (20)	10063 (5)	6524 (6)	5895 (6)	100 (3)
C (21)	11663 (3)	10244 (4)	4868 (3)	38 (1)
C (22)	12490 (3)	10692 (4)	4651 (4)	47 (1)

C(23)	11527(4)	10970(5)	5775(4)	56(2)
C(24)	12081(3)	8448(4)	3880(3)	37(1)
C(25)	11553(4)	8166(5)	2976(4)	60(2)
C(26)	12252(4)	7587(4)	3861(4)	52(2)
C(27)	10446(3)	8474(5)	4536(4)	53(2)
C(28)	10198(5)	7847(6)	4886(4)	104(3)
C(29)	5073(3)	6593(4)	2784(4)	45(1)
C(30)	4552(5)	7137(4)	3445(5)	69(2)
C(31)	6038(4)	7141(4)	3109(5)	69(2)
C(32)	5487(3)	4821(4)	1749(4)	44(1)
C(33)	5312(4)	3765(4)	1479(4)	63(2)
C(34)	5401(4)	4915(5)	912(4)	55(2)
C(35)	3068(4)	4859(5)	4200(4)	57(2)
C(36)	3454(5)	5942(5)	4674(5)	93(3)
C(37)	2095(5)	4548(5)	3927(4)	76(2)
C(38)	3152(4)	2976(4)	2913(4)	52(2)
C(39)	3472(5)	2363(4)	2079(4)	74(2)
C(40)	3355(5)	2793(5)	3678(5)	79(2)
C(41)	5221(4)	5458(4)	3587(4)	49(2)
C(42)	4699(4)	4615(4)	3676(4)	51(2)
C(43)	2113(3)	3425(4)	-1156(3)	38(1)
C(44)	2286(4)	2541(4)	-1218(4)	53(2)
C(45)	1591(4)	3177(4)	-2046(3)	53(2)
C(46)	1581(3)	5133(4)	-122(3)	40(1)
C(47)	1381(4)	5799(4)	778(4)	53(2)
C(48)	2395(4)	5656(4)	-291(4)	51(2)
C(49)	432(3)	2060(4)	771(4)	42(1)
C(50)	646(4)	1422(4)	-132(4)	59(2)
C(51)	864(5)	1980(5)	1507(5)	75(2)
C(52)	288(3)	3926(4)	2045(4)	48(1)
C(53)	547(4)	5004(4)	2418(4)	65(2)
C(54)	-692(4)	3498(5)	1901(5)	78(2)
C(55)	455(3)	3224(4)	-616(4)	41(1)
C(56)	3(3)	3295(4)	160(4)	42(1)

---

**Table S7.** Bond lengths [Å] and angles [deg] for **8**.

Ni (1) -S (1)	2.1080 (14)	C (10) -C (11)	1.537 (7)
Ni (1) -P (1)	2.142 (2)	C (13) -C (14)	1.415 (9)
Ni (1) -P (2)	2.161 (2)	C (15) -C (16)	1.519 (8)
Ni (1) -Ni (2)	2.5228 (8)	C (15) -C (17)	1.524 (8)
Ni (2) -S (1)	2.106 (2)	C (18) -C (20)	1.395 (10)
Ni (2) -P (3)	2.1428 (14)	C (18) -C (19)	1.568 (10)
Ni (2) -P (4)	2.161 (2)	C (21) -C (23)	1.522 (7)
Ni (3) -S (2)	2.1071 (14)	C (21) -C (22)	1.524 (7)
Ni (3) -P (6)	2.1517 (14)	C (24) -C (26)	1.515 (7)
Ni (3) -P (7)	2.1647 (14)	C (24) -C (25)	1.535 (7)
Ni (3) -Ni (4)	2.5518 (8)	C (27) -C (28)	1.424 (8)
Ni (4) -S (2)	2.1044 (14)	C (29) -C (31)	1.525 (8)
Ni (4) -P (8)	2.1516 (14)	C (29) -C (30)	1.531 (8)
Ni (4) -P (9)	2.1753 (14)	C (32) -C (34)	1.527 (7)
P (1) -C (13)	1.828 (7)	C (32) -C (33)	1.531 (8)
P (1) -C (1)	1.837 (6)	C (35) -C (36)	1.511 (9)
P (1) -C (4)	1.852 (7)	C (35) -C (37)	1.514 (9)
P (2) -C (10)	1.831 (6)	C (38) -C (40)	1.527 (7)
P (2) -C (14)	1.839 (6)	C (38) -C (39)	1.525 (8)
P (2) -C (7)	1.864 (6)	C (41) -C (42)	1.527 (8)
P (3) -C (27)	1.839 (5)	C (43) -C (44)	1.526 (7)
P (3) -C (24)	1.844 (5)	C (43) -C (45)	1.529 (7)
P (3) -C (21)	1.850 (5)	C (46) -C (48)	1.517 (7)
P (4) -C (28)	1.804 (6)	C (46) -C (47)	1.527 (7)
P (4) -C (15)	1.858 (5)	C (49) -C (51)	1.499 (8)
P (4) -C (18)	1.883 (7)	C (49) -C (50)	1.527 (7)
P (5) -F (2)	1.561 (4)	C (52) -C (53)	1.519 (8)
P (5) -F (6)	1.570 (4)	C (52) -C (54)	1.531 (8)
P (5) -F (3)	1.576 (4)	C (55) -C (56)	1.526 (7)
P (5) -F (5)	1.590 (4)		
P (5) -F (4)	1.592 (4)		
P (5) -F (1)	1.599 (3)		
P (6) -C (29)	1.828 (5)		
P (6) -C (41)	1.839 (5)		
P (6) -C (32)	1.848 (5)		
P (7) -C (38)	1.839 (6)		
P (7) -C (35)	1.838 (6)		
P (7) -C (42)	1.843 (6)		
P (8) -C (55)	1.843 (5)		
P (8) -C (43)	1.845 (5)		
P (8) -C (46)	1.847 (5)		
P (9) -C (49)	1.848 (5)		
P (9) -C (52)	1.850 (5)		
P (9) -C (56)	1.851 (5)		
P (10) -F (10)	1.528 (4)		
P (10) -F (12)	1.545 (4)		
P (10) -F (7)	1.557 (5)		
P (10) -F (11)	1.567 (4)		
P (10) -F (8)	1.585 (4)		
P (10) -F (9)	1.596 (3)		
C (1) -C (2)	1.534 (9)		
C (1) -C (3)	1.536 (9)		
C (4) -C (5)	1.520 (9)		
C (4) -C (6)	1.520 (9)		
C (7) -C (9)	1.502 (9)		
C (7) -C (8)	1.518 (9)		
C (10) -C (12)	1.523 (8)		



S(1)-Ni(1)-P(1)	91.30(6)	F(5)-P(5)-F(1)	179.2(2)
S(1)-Ni(1)-P(2)	177.11(7)	F(4)-P(5)-F(1)	88.8(2)
P(1)-Ni(1)-P(2)	90.69(6)	C(29)-P(6)-C(41)	103.1(3)
S(1)-Ni(1)-Ni(2)	53.19(4)	C(29)-P(6)-C(32)	104.8(3)
P(1)-Ni(1)-Ni(2)	144.38(5)	C(41)-P(6)-C(32)	104.3(3)
P(2)-Ni(1)-Ni(2)	124.91(5)	C(29)-P(6)-Ni(3)	115.8(2)
S(1)-Ni(2)-P(3)	91.50(5)	C(41)-P(6)-Ni(3)	108.9(2)
S(1)-Ni(2)-P(4)	177.65(6)	C(32)-P(6)-Ni(3)	118.4(2)
P(3)-Ni(2)-P(4)	90.23(5)	C(38)-P(7)-C(35)	104.0(3)
S(1)-Ni(2)-Ni(1)	53.26(4)	C(38)-P(7)-C(42)	103.0(3)
P(3)-Ni(2)-Ni(1)	144.26(5)	C(35)-P(7)-C(42)	104.9(3)
P(4)-Ni(2)-Ni(1)	124.83(5)	C(38)-P(7)-Ni(3)	117.9(2)
S(2)-Ni(3)-P(6)	90.60(5)	C(35)-P(7)-Ni(3)	117.6(2)
S(2)-Ni(3)-P(7)	178.93(6)	C(42)-P(7)-Ni(3)	107.8(2)
P(6)-Ni(3)-P(7)	89.99(6)	C(55)-P(8)-C(43)	103.6(2)
S(2)-Ni(3)-Ni(4)	52.66(4)	C(55)-P(8)-C(46)	104.5(2)
P(6)-Ni(3)-Ni(4)	143.25(5)	C(43)-P(8)-C(46)	105.3(2)
P(7)-Ni(3)-Ni(4)	126.76(5)	C(55)-P(8)-Ni(4)	107.6(2)
S(2)-Ni(4)-P(8)	89.86(5)	C(43)-P(8)-Ni(4)	116.8(2)
S(2)-Ni(4)-P(9)	175.94(6)	C(46)-P(8)-Ni(4)	117.5(2)
P(8)-Ni(4)-P(9)	90.34(5)	C(49)-P(9)-C(52)	103.7(2)
S(2)-Ni(4)-Ni(3)	52.75(4)	C(49)-P(9)-C(56)	104.7(2)
P(8)-Ni(4)-Ni(3)	142.18(4)	C(52)-P(9)-C(56)	101.4(3)
P(9)-Ni(4)-Ni(3)	127.38(5)	C(49)-P(9)-Ni(4)	120.2(2)
C(13)-P(1)-C(1)	104.3(4)	C(52)-P(9)-Ni(4)	117.4(2)
C(13)-P(1)-C(4)	104.5(4)	C(56)-P(9)-Ni(4)	107.2(2)
C(1)-P(1)-C(4)	105.5(3)	F(10)-P(10)-F(12)	92.1(4)
C(13)-P(1)-Ni(1)	108.1(3)	F(10)-P(10)-F(7)	89.1(4)
C(1)-P(1)-Ni(1)	115.1(2)	F(12)-P(10)-F(7)	178.5(3)
C(4)-P(1)-Ni(1)	118.1(2)	F(10)-P(10)-F(11)	177.4(4)
C(10)-P(2)-C(14)	104.5(3)	F(12)-P(10)-F(11)	90.0(3)
C(10)-P(2)-C(7)	104.2(3)	F(7)-P(10)-F(11)	88.8(4)
C(14)-P(2)-C(7)	104.4(3)	F(10)-P(10)-F(8)	90.3(2)
C(10)-P(2)-Ni(1)	118.0(2)	F(12)-P(10)-F(8)	90.6(2)
C(14)-P(2)-Ni(1)	107.7(2)	F(7)-P(10)-F(8)	90.3(2)
C(7)-P(2)-Ni(1)	116.7(2)	F(11)-P(10)-F(8)	91.2(2)
C(27)-P(3)-C(24)	106.5(3)	F(10)-P(10)-F(9)	90.0(2)
C(27)-P(3)-C(21)	102.4(3)	F(12)-P(10)-F(9)	89.4(2)
C(24)-P(3)-C(21)	105.4(2)	F(7)-P(10)-F(9)	89.7(2)
C(27)-P(3)-Ni(2)	106.8(2)	F(11)-P(10)-F(9)	88.5(2)
C(24)-P(3)-Ni(2)	114.8(2)	F(8)-P(10)-F(9)	179.7(2)
C(21)-P(3)-Ni(2)	119.6(2)	Ni(2)-S(1)-Ni(1)	73.55(5)
C(28)-P(4)-C(15)	107.9(4)	Ni(4)-S(2)-Ni(3)	74.59(5)
C(28)-P(4)-C(18)	108.4(4)	C(2)-C(1)-C(3)	112.3(6)
C(15)-P(4)-C(18)	103.7(3)	C(2)-C(1)-P(1)	111.2(5)
C(28)-P(4)-Ni(2)	106.3(2)	C(3)-C(1)-P(1)	114.5(5)
C(15)-P(4)-Ni(2)	117.4(2)	C(5)-C(4)-C(6)	110.2(7)
C(18)-P(4)-Ni(2)	112.9(2)	C(5)-C(4)-P(1)	113.4(4)
F(2)-P(5)-F(6)	91.7(3)	C(6)-C(4)-P(1)	111.1(5)
F(2)-P(5)-F(3)	178.5(2)	C(9)-C(7)-C(8)	111.6(6)
F(6)-P(5)-F(3)	88.9(3)	C(9)-C(7)-P(2)	111.0(4)
F(2)-P(5)-F(5)	90.5(2)	C(8)-C(7)-P(2)	110.4(5)
F(6)-P(5)-F(5)	90.0(2)	C(12)-C(10)-C(11)	110.1(5)
F(3)-P(5)-F(5)	90.8(2)	C(12)-C(10)-P(2)	110.4(4)
F(2)-P(5)-F(4)	90.2(3)	C(11)-C(10)-P(2)	114.7(4)
F(6)-P(5)-F(4)	178.1(3)	C(14)-C(13)-P(1)	117.0(5)
F(3)-P(5)-F(4)	89.2(3)	C(13)-C(14)-P(2)	116.2(5)
F(5)-P(5)-F(4)	90.5(2)	C(16)-C(15)-C(17)	110.2(5)
F(2)-P(5)-F(1)	89.9(2)	C(16)-C(15)-P(4)	111.5(4)
F(6)-P(5)-F(1)	90.7(2)	C(17)-C(15)-P(4)	114.6(4)
F(3)-P(5)-F(1)	88.7(2)	C(20)-C(18)-C(19)	110.8(7)

C(20)-C(18)-P(4)	117.0(7)	C(40)-C(38)-P(7)	114.9(4)
C(19)-C(18)-P(4)	108.9(5)	C(39)-C(38)-P(7)	110.1(4)
C(23)-C(21)-C(22)	110.2(5)	C(42)-C(41)-P(6)	110.6(4)
C(23)-C(21)-P(3)	109.9(4)	C(41)-C(42)-P(7)	111.7(4)
C(22)-C(21)-P(3)	114.3(4)	C(44)-C(43)-C(45)	111.2(5)
C(26)-C(24)-C(25)	111.5(5)	C(44)-C(43)-P(8)	111.3(4)
C(26)-C(24)-P(3)	112.9(3)	C(45)-C(43)-P(8)	112.0(4)
C(25)-C(24)-P(3)	112.8(4)	C(48)-C(46)-C(47)	110.6(5)
C(28)-C(27)-P(3)	112.9(4)	C(48)-C(46)-P(8)	114.2(4)
C(27)-C(28)-P(4)	114.2(5)	C(47)-C(46)-P(8)	111.0(4)
C(31)-C(29)-C(30)	111.2(5)	C(51)-C(49)-C(50)	110.4(5)
C(31)-C(29)-P(6)	114.4(4)	C(51)-C(49)-P(9)	111.5(4)
C(30)-C(29)-P(6)	111.1(4)	C(50)-C(49)-P(9)	110.7(4)
C(34)-C(32)-C(33)	110.4(5)	C(53)-C(52)-C(54)	110.6(5)
C(34)-C(32)-P(6)	113.2(4)	C(53)-C(52)-P(9)	111.5(4)
C(33)-C(32)-P(6)	110.2(4)	C(54)-C(52)-P(9)	113.7(4)
C(36)-C(35)-C(37)	111.1(6)	C(56)-C(55)-P(8)	111.3(3)
C(36)-C(35)-P(7)	112.3(4)	C(55)-C(56)-P(9)	109.8(3)
C(37)-C(35)-P(7)	110.4(4)		
C(40)-C(38)-C(39)	111.5(6)		

**Table S8.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8**. The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	U11	U22	U33	U23	U13	U12
Ni (1)	31 (1)	36 (1)	24 (1)	15 (1)	1 (1)	15 (1)
Ni (2)	26 (1)	41 (1)	24 (1)	19 (1)	6 (1)	15 (1)
Ni (3)	28 (1)	38 (1)	23 (1)	17 (1)	4 (1)	11 (1)
Ni (4)	22 (1)	36 (1)	25 (1)	18 (1)	6 (1)	11 (1)
P (1)	33 (1)	55 (1)	53 (1)	31 (1)	-7 (1)	10 (1)
P (2)	55 (1)	44 (1)	24 (1)	17 (1)	-1 (1)	19 (1)
P (3)	24 (1)	46 (1)	28 (1)	23 (1)	4 (1)	10 (1)
P (4)	43 (1)	37 (1)	27 (1)	17 (1)	6 (1)	2 (1)
P (5)	36 (1)	60 (1)	42 (1)	32 (1)	6 (1)	15 (1)
P (6)	27 (1)	37 (1)	33 (1)	15 (1)	0 (1)	11 (1)
P (7)	51 (1)	49 (1)	26 (1)	22 (1)	4 (1)	16 (1)
P (8)	26 (1)	37 (1)	27 (1)	17 (1)	4 (1)	13 (1)
P (9)	28 (1)	36 (1)	34 (1)	18 (1)	1 (1)	9 (1)
P (10)	38 (1)	55 (1)	43 (1)	30 (1)	6 (1)	14 (1)
S (1)	26 (1)	68 (1)	42 (1)	39 (1)	4 (1)	12 (1)
S (2)	24 (1)	65 (1)	42 (1)	39 (1)	4 (1)	9 (1)
F (1)	50 (2)	72 (2)	73 (2)	45 (2)	24 (2)	16 (2)
F (2)	106 (3)	141 (4)	134 (4)	109 (4)	66 (3)	90 (3)
F (3)	68 (3)	122 (4)	158 (4)	113 (4)	32 (3)	45 (2)
F (4)	74 (3)	94 (3)	59 (2)	19 (2)	11 (2)	9 (2)
F (5)	39 (2)	115 (3)	79 (3)	64 (3)	14 (2)	15 (2)
F (6)	94 (3)	114 (4)	43 (2)	22 (2)	5 (2)	-8 (3)
F (7)	150 (5)	171 (5)	243 (7)	174 (6)	114 (5)	112 (4)
F (8)	48 (2)	103 (3)	81 (3)	61 (2)	17 (2)	11 (2)
F (9)	46 (2)	87 (3)	68 (2)	45 (2)	15 (2)	13 (2)
F (10)	93 (3)	205 (6)	41 (2)	38 (3)	-2 (2)	-35 (4)
F (11)	107 (4)	128 (4)	50 (2)	33 (3)	-1 (2)	-37 (3)
F (12)	109 (4)	134 (4)	257 (7)	151 (5)	92 (4)	84 (3)
C (1)	53 (4)	46 (4)	63 (4)	21 (3)	-6 (3)	0 (3)
C (2)	137 (8)	58 (5)	62 (5)	14 (4)	33 (5)	16 (5)
C (3)	61 (5)	76 (5)	133 (8)	49 (5)	-38 (5)	-26 (4)
C (4)	36 (3)	66 (4)	104 (6)	51 (4)	16 (3)	29 (3)
C (5)	52 (4)	84 (5)	87 (5)	45 (4)	33 (4)	35 (4)
C (6)	120 (8)	81 (6)	221 (12)	93 (7)	104 (8)	69 (6)
C (7)	95 (5)	61 (4)	27 (3)	24 (3)	19 (3)	38 (4)
C (8)	171 (9)	49 (4)	71 (5)	7 (4)	57 (6)	31 (5)
C (9)	80 (5)	84 (5)	53 (4)	39 (4)	29 (4)	39 (4)
C (10)	73 (4)	52 (4)	46 (3)	33 (3)	15 (3)	31 (3)
C (11)	93 (5)	76 (5)	73 (5)	57 (4)	26 (4)	35 (4)
C (12)	130 (7)	56 (4)	89 (5)	45 (4)	51 (5)	52 (5)
C (13)	60 (5)	183 (10)	131 (8)	128 (8)	-34 (5)	-5 (5)
C (14)	63 (5)	116 (6)	64 (5)	58 (5)	-18 (4)	18 (4)
C (15)	38 (3)	52 (3)	50 (3)	28 (3)	18 (3)	18 (3)
C (16)	69 (4)	53 (4)	57 (4)	19 (3)	29 (3)	28 (3)
C (17)	39 (4)	75 (5)	120 (7)	46 (5)	21 (4)	21 (3)
C (18)	106 (6)	34 (3)	102 (6)	25 (4)	67 (5)	20 (4)
C (19)	162 (9)	97 (7)	155 (9)	89 (7)	101 (8)	75 (7)
C (20)	103 (7)	86 (6)	120 (7)	58 (6)	44 (6)	29 (5)
C (21)	42 (3)	48 (3)	33 (3)	24 (3)	1 (2)	20 (3)
C (22)	49 (3)	40 (3)	49 (3)	21 (3)	7 (3)	12 (3)
C (23)	61 (4)	70 (4)	48 (4)	30 (3)	8 (3)	37 (3)
C (24)	43 (3)	43 (3)	24 (3)	17 (2)	1 (2)	1 (2)
C (25)	79 (5)	66 (4)	28 (3)	17 (3)	4 (3)	28 (4)
C (26)	62 (4)	52 (4)	49 (4)	23 (3)	26 (3)	31 (3)
C (27)	28 (3)	82 (4)	62 (4)	53 (4)	-5 (3)	6 (3)
C (28)	64 (5)	148 (8)	53 (4)	64 (5)	-28 (4)	-59 (5)

C(29)	41(3)	38(3)	51(3)	19(3)	5(3)	14(3)
C(30)	91(5)	47(4)	73(5)	26(4)	24(4)	35(4)
C(31)	53(4)	46(4)	86(5)	26(4)	-9(4)	1(3)
C(32)	26(3)	54(3)	49(3)	23(3)	6(2)	16(2)
C(33)	79(5)	57(4)	64(4)	30(3)	28(4)	38(4)
C(34)	45(4)	79(4)	52(4)	36(3)	22(3)	28(3)
C(35)	75(5)	72(4)	32(3)	30(3)	21(3)	26(4)
C(36)	113(7)	71(5)	55(4)	0(4)	42(4)	26(5)
C(37)	84(5)	92(5)	54(4)	32(4)	39(4)	39(4)
C(38)	59(4)	57(4)	50(4)	37(3)	5(3)	13(3)
C(39)	114(6)	42(4)	59(4)	23(3)	22(4)	20(4)
C(40)	103(6)	88(5)	78(5)	67(5)	12(4)	31(5)
C(41)	45(3)	60(4)	33(3)	20(3)	-5(3)	15(3)
C(42)	61(4)	64(4)	31(3)	26(3)	-2(3)	26(3)
C(43)	39(3)	42(3)	33(3)	19(2)	15(2)	15(2)
C(44)	65(4)	53(4)	53(4)	26(3)	22(3)	33(3)
C(45)	74(4)	59(4)	24(3)	17(3)	14(3)	24(3)
C(46)	44(3)	39(3)	37(3)	19(2)	-1(2)	16(2)
C(47)	56(4)	48(3)	55(4)	22(3)	11(3)	28(3)
C(48)	56(4)	46(3)	57(4)	33(3)	4(3)	9(3)
C(49)	37(3)	34(3)	49(3)	19(3)	17(3)	9(2)
C(50)	85(5)	45(3)	56(4)	27(3)	24(3)	31(3)
C(51)	112(6)	61(4)	64(4)	43(4)	14(4)	21(4)
C(52)	41(3)	54(4)	51(3)	25(3)	25(3)	19(3)
C(53)	73(5)	45(4)	64(4)	17(3)	34(4)	18(3)
C(54)	55(4)	70(5)	101(6)	34(4)	51(4)	21(4)
C(55)	27(3)	50(3)	44(3)	24(3)	-1(2)	9(2)
C(56)	29(3)	44(3)	51(3)	21(3)	7(2)	15(2)

---

**Table S9.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8**.

	x	y	z	U(eq)
H(1)	12419 (29)	9112 (33)	6876 (31)	41 (14)
H(2)	2389 (40)	3952 (44)	1815 (42)	87 (21)
H(1A)	14951 (4)	11678 (4)	7379 (5)	73
H(2A)	14010 (6)	11848 (5)	8407 (5)	144
H(2B)	14750 (6)	12843 (5)	8721 (5)	144
H(2C)	14815 (6)	12233 (5)	9198 (5)	144
H(3A)	16398 (5)	11781 (6)	7764 (6)	156
H(3B)	16308 (5)	12191 (6)	8796 (6)	156
H(3C)	16244 (5)	12801 (6)	8320 (6)	156
H(4A)	16073 (4)	10131 (5)	7114 (5)	75
H(5A)	15598 (4)	10744 (5)	6255 (5)	105
H(5B)	14858 (4)	9733 (5)	5632 (5)	105
H(5C)	15853 (4)	9801 (5)	5636 (5)	105
H(6A)	15236 (6)	8630 (6)	6896 (7)	184
H(6B)	15630 (6)	8507 (6)	6027 (7)	184
H(6C)	14636 (6)	8440 (6)	6025 (7)	184
H(7A)	13000 (5)	9798 (4)	9670 (4)	69
H(8A)	13727 (6)	11264 (5)	9757 (5)	160
H(8B)	12807 (6)	11271 (5)	10035 (5)	160
H(8C)	12935 (6)	11103 (5)	9059 (5)	160
H(9A)	11737 (4)	8741 (5)	8586 (4)	100
H(9B)	11707 (4)	9542 (5)	8334 (4)	100
H(9C)	11580 (4)	9712 (5)	9311 (4)	100
H(10A)	12478 (4)	7799 (4)	7678 (4)	61
H(11A)	12897 (5)	8266 (5)	9212 (5)	105
H(11B)	13816 (5)	8130 (5)	9030 (5)	105
H(11C)	12958 (5)	7219 (5)	8545 (5)	105
H(12A)	13513 (5)	7637 (5)	6747 (5)	123
H(12B)	13334 (5)	6834 (5)	7033 (5)	123
H(12C)	14193 (5)	7745 (5)	7518 (5)	123
H(13A)	15663 (5)	10087 (7)	8468 (6)	137
H(13B)	15411 (5)	11027 (7)	9088 (6)	137
H(14A)	14595 (4)	10250 (6)	9520 (5)	94
H(14B)	14760 (4)	9283 (6)	8808 (5)	94
H(15A)	10308 (3)	8745 (4)	7340 (4)	53
H(16A)	11117 (4)	10204 (4)	7462 (4)	91
H(16B)	10208 (4)	10245 (4)	7755 (4)	91
H(16C)	10340 (4)	10109 (4)	6789 (4)	91
H(17A)	9022 (4)	7764 (5)	6243 (5)	118
H(17B)	9057 (4)	8615 (5)	6043 (5)	118
H(17C)	8925 (4)	8753 (5)	7010 (5)	118
H(18A)	11111 (5)	7483 (4)	6734 (6)	101
H(19A)	12040 (6)	7262 (6)	5661 (7)	175
H(19B)	11241 (6)	6448 (6)	4870 (7)	175
H(19C)	11593 (6)	6280 (6)	5646 (7)	175
H(20A)	9674 (5)	6828 (6)	6263 (6)	150
H(20B)	10158 (5)	6043 (6)	6030 (6)	150
H(20C)	9804 (5)	6210 (6)	5254 (6)	150
H(21A)	11171 (3)	10088 (4)	4398 (3)	46
H(22A)	12570 (3)	10219 (4)	4066 (4)	71
H(22B)	12983 (3)	10890 (4)	5121 (4)	71
H(22C)	12448 (3)	11256 (4)	4626 (4)	71
H(23A)	10994 (4)	10674 (5)	5908 (4)	85
H(23B)	11483 (4)	11534 (5)	5753 (4)	85
H(23C)	12017 (4)	11168 (5)	6248 (4)	85
H(24A)	12657 (3)	8900 (4)	3959 (3)	45
H(25A)	11454 (4)	8737 (5)	3011 (4)	90

H(25B)	10996 (4)	7682 (5)	2845 (4)	90
H(25C)	11871 (4)	7901 (5)	2496 (4)	90
H(26A)	12589 (4)	7791 (4)	4446 (4)	79
H(26B)	12575 (4)	7317 (4)	3387 (4)	79
H(26C)	11701 (4)	7098 (4)	3737 (4)	79
H(27A)	10132 (3)	8950 (5)	4760 (4)	64
H(27B)	10274 (3)	8093 (5)	3870 (4)	64
H(28A)	10260 (5)	7216 (6)	4460 (4)	124
H(28B)	9580 (5)	7742 (6)	4922 (4)	124
H(29A)	4897 (3)	6571 (4)	2208 (4)	54
H(30A)	3936 (5)	6769 (4)	3220 (5)	104
H(30B)	4652 (5)	7769 (4)	3502 (5)	104
H(30C)	4735 (5)	7220 (4)	4037 (5)	104
H(31A)	6354 (4)	6778 (4)	2674 (5)	103
H(31B)	6231 (4)	7224 (4)	3698 (5)	103
H(31C)	6148 (4)	7774 (4)	3164 (5)	103
H(32A)	6098 (3)	5179 (4)	2086 (4)	52
H(33A)	5370 (4)	3716 (4)	2023 (4)	94
H(33B)	5729 (4)	3514 (4)	1120 (4)	94
H(33C)	4725 (4)	3389 (4)	1121 (4)	94
H(34A)	5515 (4)	5594 (5)	1096 (4)	83
H(34B)	4815 (4)	4543 (5)	551 (4)	83
H(34C)	5819 (4)	4669 (5)	551 (4)	83
H(35A)	3199 (4)	4654 (5)	4638 (4)	69
H(36A)	4083 (5)	6124 (5)	4843 (5)	140
H(36B)	3217 (5)	6236 (5)	5217 (5)	140
H(36C)	3314 (5)	6167 (5)	4269 (5)	140
H(37A)	1861 (5)	3845 (5)	3621 (4)	114
H(37B)	1946 (5)	4764 (5)	3516 (4)	114
H(37C)	1849 (5)	4833 (5)	4465 (4)	114
H(38A)	2508 (4)	2761 (4)	2738 (4)	63
H(39A)	3333 (5)	2498 (4)	1602 (4)	110
H(39B)	3190 (5)	1680 (4)	1867 (4)	110
H(39C)	4099 (5)	2517 (4)	2231 (4)	110
H(40A)	3142 (5)	3197 (5)	4202 (5)	119
H(40B)	3981 (5)	2950 (5)	3842 (5)	119
H(40C)	3072 (5)	2113 (5)	3479 (5)	119
H(41A)	5831 (4)	5473 (4)	3604 (4)	59
H(41B)	5204 (4)	6070 (4)	4101 (4)	59
H(42A)	4781 (4)	4802 (4)	4321 (4)	61
H(42B)	4916 (4)	4063 (4)	3351 (4)	61
H(43A)	2685 (3)	3903 (4)	-1043 (3)	45
H(44A)	2621 (4)	2721 (4)	-640 (4)	80
H(44B)	2612 (4)	2292 (4)	-1695 (4)	80
H(44C)	1736 (4)	2044 (4)	-1359 (4)	80
H(45A)	1489 (4)	3756 (4)	-1988 (3)	80
H(45B)	1036 (4)	2684 (4)	-2193 (3)	80
H(45C)	1913 (4)	2932 (4)	-2528 (3)	80
H(46A)	1095 (3)	4965 (4)	-604 (3)	48
H(47A)	853 (4)	5449 (4)	875 (4)	79
H(47B)	1298 (4)	6356 (4)	769 (4)	79
H(47C)	1863 (4)	6018 (4)	1267 (4)	79
H(48A)	2513 (4)	5218 (4)	-870 (4)	77
H(48B)	2882 (4)	5875 (4)	194 (4)	77
H(48C)	2317 (4)	6212 (4)	-305 (4)	77
H(49A)	-207 (3)	1826 (4)	720 (4)	50
H(50A)	360 (4)	1482 (4)	-605 (4)	88
H(50B)	444 (4)	750 (4)	-278 (4)	88
H(50C)	1272 (4)	1624 (4)	-91 (4)	88
H(51A)	721 (5)	2393 (5)	2081 (5)	113
H(51B)	1491 (5)	2184 (5)	1554 (5)	113

H(51C)	662 (5)	1310 (5)	1367 (5)	113
H(52A)	553 (3)	3831 (4)	2518 (4)	58
H(53A)	1175 (4)	5265 (4)	2506 (4)	97
H(53B)	367 (4)	5313 (4)	2997 (4)	97
H(53C)	266 (4)	5131 (4)	1992 (4)	97
H(54A)	-847 (4)	2803 (5)	1660 (5)	117
H(54B)	-979 (4)	3617 (5)	1472 (5)	117
H(54C)	-877 (4)	3799 (5)	2478 (5)	117
H(55A)	150 (3)	3421 (4)	-972 (4)	49
H(55B)	427 (3)	2547 (4)	-1018 (4)	49
H(56A)	-528 (3)	2736 (4)	-70 (4)	50
H(56B)	-165 (3)	3887 (4)	428 (4)	50

---