Electronic Supplementary Information

A highly efficient [Ni{*i*PrHNC(S)NP(S)(O*i*Pr)$_2$-1,3-*N*,*S'*}$_2$]/PR$_3$ (R$_3$ = Me$_3$, Me$_2$Ph) complex system for the generation of Ni^0 for catalysis

Damir A. Safin,*[a] Maria G. Babashkina,[a] Michael Bolte[b] and F. Ekkehardt Hahn[c]

[a] *Institut für Chemie, Anorganische Festkörperchemie, Albert-Einstein-Str. 3a, D-18059 Rostock, Germany. Fax: +49 381 4986390; Tel: +49 381 4986381; E-mail: maria.babashkina@ksu.ru*

[b] *Institut für Anorganische Chemie J.-W.-Goethe-Universität, Frankfurt/Main, Germany.*

[c] *Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 36, D-48149, Münster, Germany.*

Physical measurements: Infrared spectra (Nujol) were recorded with a Thermo Nicolet 380 FT-IR spectrometer in the range 400–3600 cm^{-1}. NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to SiMe$_4$ (^{1}H) and 85% H$_3$PO$_4$ (^{31}P{^{1}H}). Electronic spectra of absorption in 10^{-4} M solution were measured on a Lambda-35 spectrometer in the range 200−1000 nm. Elemental analyses were performed on a Thermoquest Flash EA 1112 Analyzer from CE Instruments.

Synthesis of [NiL$^{I,II}_2$]: A suspension of **HL^{I,II}** (3 mmol; 0.895 or 0.937 g, respectively) in aqueous EtOH (10 mL) was mixed with an aqueous EtOH (10 mL) solution of KOH (3.3 mmol, 0.185 g). An aqueous EtOH (10 mL) solution of NiCl$_2$ (1.9 mmol, 0.247 g) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further 3 h and left overnight. The resulting complex was extracted with CH$_2$Cl$_2$, washed with water and dried with anhydrous MgSO$_4$. The solvent was then removed in vacuo. Dark violet **[NiL$^{I,II}_2$]** crystals were isolated by recrystallisation from a 1:5 mixture of CH$_2$Cl$_2$ and *n*-hexane.

[NiL$^I_2$]: Yield 0.248 g (91%). IR *ν* (cm^{-1}): 607 (P=S), 972 (POC), 1557 (SCN), 3172 (NH). ^{1}H NMR *δ* (CDCl$_3$, ppm): 1.08 (d, $^3J_{\mathrm{H,H}}$ = 6.5 Hz, CH$_3$, *i*PrN), 1.19 (d, $^3J_{\mathrm{H,H}}$ = 6.6 Hz, CH$_3$, *i*PrN), 1.31 (d, $^3J_{\mathrm{H,H}}$ = 6.1 Hz, CH$_3$, *i*PrO), 1.39 (d, $^3J_{\mathrm{H,H}}$ = 6.2 Hz, CH$_3$, *i*PrO), 1.47 (d, $^3J_{\mathrm{H,H}}$ = 6.1 Hz, CH$_3$, *i*PrO), 1.65 (d, $^3J_{\mathrm{H,H}}$ = 6.1 Hz, CH$_3$, *i*PrO), 3.91 (d. sept, $^3J_{\mathrm{HNCH}}$ = 8.4 Hz, $^3J_{\mathrm{H,H}}$ = 6.5 Hz, NCH), 3.99 (sept, $^3J_{\mathrm{HNCH}}$ = $^3J_{\mathrm{H,H}}$ = 6.6 Hz, NCH), 4.63 (d. sept, $^3J_{\mathrm{POCH}}$ = 10.5 Hz, $^3J_{\mathrm{H,H}}$ = 6.1 Hz, OCH), 4.95 (d sept, $^3J_{\mathrm{POCH}}$ = 10.2 Hz, $^3J_{\mathrm{H,H}}$ = 6.2 Hz, OCH), 5.60 (t, $^4J_{\mathrm{PNCNH}}$ = $^3J_{\mathrm{H,H}}$ = 7.6 Hz, alkylNH), 8.97 (d, $^3J_{\mathrm{H,H}}$ = 8.3 Hz, alkylNH); ^{1}H NMR *δ* (DMF-*d*$_7$, ppm): 1.21 (d, $^3J_{\mathrm{H,H}}$ = 6.4 Hz, 12H, CH$_3$, *i*PrN), 1.39 (d, $^3J_{\mathrm{H,H}}$ = 6.0 Hz, 12H, CH$_3$, *i*PrO), 1.48 (d, $^3J_{\mathrm{H,H}}$ = 6.1 Hz, 12H, CH$_3$, *i*PrO), 4.02 (d. sept, $^3J_{\mathrm{HNCH}}$ = 8.3 Hz, $^3J_{\mathrm{H,H}}$ = 6.4 Hz, 2H, NCH), 4.93 (d. sept, $^3J_{\mathrm{POCH}}$ = 10.1 Hz, $^3J_{\mathrm{H,H}}$ = 6.1 Hz, 4H, OCH), 9.14 (t, $^4J_{\mathrm{PNCNH}}$ = $^3J_{\mathrm{H,H}}$ = 7.2 Hz, 2H, alkylNH); ^{31}P{^{1}H} NMR *δ* (CDCl$_3$, ppm):

51.0 (s, 2.2P), 54.4 (s, 11P), 55.3 (s, 1P), 58.0 (s, 1P); $^{31}P\{^1H\}$ NMR δ (DMF-d_7, ppm): 49.8 (br. s). UV-Vis spectra (CH_2Cl_2), [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 264 (17713), 331 (19005), 532 (171), 649 (164); UV-Vis spectra (DMF), [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 270 (29652), 281 (9162), 533 (159), 644 (156). *Anal.* Calc. for $C_{20}H_{44}N_4NiO_4P_2S_4$ (653.47): C 36.76, H 6.79, N 8.57. Found: C 36.68, H 6.83, N 8.60%.

[NiL$^{II}_2$]: Yield 0.275 g (97%). IR ν (cm^{-1}): 563 (P=S), 978 (POC), 1506 (SCN). ^1H NMR δ ($CDCl_3$, ppm): 1.05 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, CH_3, Et), 1.26 (t, $^3J_{H,H}$ = 7.0 Hz, 6H, CH_3, Et), 1.40 (d, $^3J_{H,H}$ = 6.2 Hz, 12H, CH_3, *i*Pr), 1.49 (d, $^3J_{H,H}$ = 6.2 Hz, 12H, CH_3, *i*Pr), 3.53 (q, $^3J_{H,H}$ = 7.0 Hz, 4H, CH_2, Et), 3.93 (q, $^3J_{H,H}$ = 7.1 Hz, 4H, CH_2, Et), 4.97 (d. sept, $^3J_{POCH}$ = 10.2 Hz, $^3J_{H,H}$ = 6.1 Hz, 4H, OCH); ^1H NMR δ (DMF-d_7, ppm): 1.14 (t, $^3J_{H,H}$ = 7.0 Hz, 6H, CH_3, Et), 1.33 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, CH_3, Et), 1.48 (d, $^3J_{H,H}$ = 6.1 Hz, 12H, CH_3, *i*Pr), 1.53 (d, $^3J_{H,H}$ = 6.0 Hz, 12H, CH_3, *i*Pr), 3.59 (q, $^3J_{H,H}$ = 7.1 Hz, 4H, CH_2, Et), 3.96 (q, $^3J_{H,H}$ = 7.1 Hz, 4H, CH_2, Et), 4.88 (d. sept, $^3J_{POCH}$ = 9.7 Hz, $^3J_{H,H}$ = 6.0 Hz, 4H, OCH); $^{31}P\{^1H\}$ NMR δ ($CDCl_3$, ppm): 42.1 (s); $^{31}P\{^1H\}$ NMR δ (DMF-d_7, ppm): 43.7 (s). UV-Vis spectra (CH_2Cl_2), [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 246 (33118), 265 (sh, 19206), 438 (sh, 1876), 531 (257), 662 (219); UV-Vis spectra (DMF), [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 251 (32247), 271 (sh, 18832), 535 (249), 654 (207). *Anal.* Calc. for $C_{22}H_{48}N_4NiO_4P_2S_4$ (681.53): C 38.77, H 7.10, N 8.22. Found: C 38.84, H 7.03, N 8.14%.

Synthesis of [Ni(PR$_3$)$_2$L$^I_2$]: A solution of the complex **[NiL$^I_2$]** (0.1 mmol, 0.065 g) in toluene (1 mL) was added dropwise to a solution of PMe_3 (0.2 mmol, 0.015 g) or PMe_2Ph (0.2 mmol, 0.028 g) in the same solvent (0.5 mL). After complete addition, the solution was stirred for an hour. The solvent was then removed in vacuo. The residue was recrystallized from a CH_2Cl_2/*n*-hexane mixture. The complexes were isolated as yellow-orange powders.

[Ni(PMe$_3$)$_2$L$^I_2$]: Yield 0.072 g (89%). IR ν (cm^{-1}): 606 (P=S), 984 (POC), 1532 (SCN), 3167 (NH). ^1H NMR δ ($CDCl_3$, ppm): 0.96 (d, $^3J_{H,H}$ = 6.4 Hz, 12H, CH_3, *i*PrN), 1.14 (d, $^3J_{H,H}$ = 6.0 Hz, 12H, CH_3, *i*PrO), 1.16 (d, $^3J_{H,H}$ = 6.1 Hz, 12H, CH_3, *i*PrO), 1.49 (br. s, 18H, CH_3, PMe), 4.06 (d. sept, $^3J_{HNCH}$ = 8.3 Hz, $^3J_{H,H}$ = 6.4 Hz, 2H, NCH), 4.98 (d. sept, $^3J_{POCH}$ = 10.3 Hz, $^3J_{H,H}$ = 6.1 Hz, 4H, OCH), 9.05 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, alkylNH); $^{31}P\{^1H\}$ NMR δ ($CDCl_3$, ppm): 54.8 (s, 2P), –23.7 (br. s, 2P). UV-Vis spectra (CH_2Cl_2), [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 285 (40169), 446 (98), 534 (37), 642 (10), 781 (17). *Anal.* Calc. for $C_{26}H_{62}N_4NiO_4P_4S_4$ (805.63): C 38.76, H 7.76, N 6.95. Found: C 38.89, H 7.65, N 7.03%.

[Ni(PMe$_2$Ph)$_2$L$^I_2$]: Yield 0.086 g (93%). IR ν (cm^{-1}): 608 (P=S), 996 (POC), 1524 (SCN), 3169 (NH). ^1H NMR δ ($CDCl_3$, ppm): 1.13 (d, $^3J_{H,H}$ = 6.6 Hz, 12H, CH_3, *i*PrN), 1.18 (d, $^3J_{H,H}$ = 6.1 Hz, 24H, CH_3, *i*PrO), 1.40 (br. s, 12H, CH_3, PMe), 4.13 (d. sept, $^3J_{HNCH}$ = 8.4 Hz, $^3J_{H,H}$ = 6.5 Hz, 2H, NCH), 5.09 (d. sept, $^3J_{POCH}$ = 10.6 Hz, $^3J_{H,H}$ = 6.0 Hz, 4H, OCH), 7.04–7.71 (m, overlapping with the solvent signal, PPh), 9.11 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, alkylNH); $^{31}P\{^1H\}$ NMR δ ($CDCl_3$, ppm): 55.1 (s, 2P), –12.4 (br. s, 2P). UV-Vis spectra (CH_2Cl_2), [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 281 (38972), 439 (93), 27 (39), 637 (13), 788 (15). *Anal.* Calc. for $C_{36}H_{66}N_4NiO_4P_4S_4$ (929.77): C 46.51, H 7.15, N 6.03. Found: C 46.44, H 7.08, N 6.09%.

HL^I: Colorless crystals. IR *ν* (cm^{-1}): 640 (P=S), 964 (POC), 1543 (S=C–N), 3090, 3382 (NH). ^{1}H NMR *δ* (ppm): 1.26 (d, $^3J_{H,H}$ = 6.6 Hz, 6H, CH_3, *i*PrN), 1.33 (d, $^3J_{H,H}$ = 6.2 Hz, 6H, CH_3, *i*PrO), 1.35 (d, $^3J_{H,H}$ = 6.2 Hz, 6H, CH_3, *i*PrO), 4.47 (d. sept, $^3J_{HNCH}$ = 8.0 Hz, $^3J_{H,H}$ = 6.5 Hz, 1H, NCH), 4.79 (d. sept, $^3J_{POCH}$ = 10.6 Hz, $^3J_{H,H}$ = 6.2 Hz, 2H, OCH), 6.86 (br. s, 1H, NHP), 7.64 (br. s, 1H, alkylNH); ^{31}P{^{1}H} NMR *δ* (ppm): 52.8. *Anal.* Calc. for $C_{10}H_{23}N_2O_2PS_2$ (298.40): C 40.25, H 7.77, N 9.39. Found: C 40.31, H 7.79, N 9.34%.

Catalytic addition of Ph_2S_2 to 1-, 2- and 3-hexynes: The procedure was similar described earlier.[1] A mixture of the complex **[NiL$^I_2$]** (0.01 mmol, 6.53 mg), PMe_3 or PMe_2Ph (0.1 mmol; 7.61 or 13.82 mg, respectively), Ph_2S_2 (0.5 mmol, 109.17 mg) and toluene (1 mL) was stirred for 30 min at 60 °C. The grayish-brown solution was formed. Then 1-, 2- or 3-hexyne (0.75 mmol, 72.13 mg) was added. The resulting mixture was stirred for 1–2 h at 100 °C. The resulting products were obtained by flash column chromatography and characterized by NMR spectroscopy.

X-Ray crystallography: The X-ray data were collected on a STOE IPDS-II diffractometer with graphite-monochromatised Mo-K$_\alpha$ radiation generated by a fine-focus X-ray tube operated at 50 kV and 40 mA. The reflections of the images were indexed, integrated and scaled using the X-Area data reduction package.[2] Data were corrected for absorption using the PLATON program.[3] The structures were solved by direct methods using the SHELXS-97 program[4] and refined first isotropically and then anisotropically using SHELXL-97.[4] Hydrogen atoms were revealed from $\Delta\rho$ maps and those bonded to C were refined using appropriate riding models. H atoms bonded to N were freely refined. Figures were generated using the program Mercury.[5]

[NiL$_2^I$]: $C_{20}H_{44}N_4NiO_4P_2S_4$, M_r = 653.48 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 8.81660(10), b = 9.81210(10), c = 10.7912(2) Å, α = 103.5394(7), β = 107.5586(6), γ = 102.1174(7)°, V = 824.72(2) Å^3, Z = 1, ρ = 1.316 g cm^{-3}, μ(Mo-Kα) = 0.968 mm^{-1}, reflections: 19504 collected, 4795 unique, R_{int} = 0.0224, R_1(all) = 0.0395, wR_2(all) = 0.0910.

Selected bond lengths (Å) and angles (deg): Ni(1)–N(1) 1.9141(12), Ni(1)–S(2) 2.2149(3), P(1)–N(1) 1.6527(12), P(1)–S(1) 1.9409(5), N(1)–C(1) 1.3461(18), N(2)–C(1) 1.3195(18), S(2)–C(1) 1.7266(14); N(1)–Ni(1)–N(1)#1 179.999(1), N(1)–Ni(1)–S(2) 74.35(4), N(1)–Ni(1)–S(2)#1 105.65(4), S(2)–Ni(1)–S(2)#1 180.000(1), C(1)–N(1)–Ni(1) 98.79(9), C(1)–S(2)–Ni(1) 77.74(5), N(1)–C(1)–Ni(1) 49.10(7), N(2)–C(1)–Ni(1) 173.17(11), P(1)–N(1)–Ni(1) 129.14(7), S(2)–C(1)–Ni(1) 59.87(4), C(1)–N(1)–P(1) 131.13(10), N(1)–C(1)–S(2) 108.68(10), N(1)–P(1)–S(1) 114.99(5), N(2)–C(1)–N(1) 127.08(13), N(2)–C(1)–S(2) 124.24(11). Hydrogen bond and hydrogen contact parametres: N(2)–H(2)···S(1) [*d*(N–H) 0.77(2) Å, *d*(H···S) 2.49(2) Å, *d*(N···S) 3.1659(13) Å, ∠(NHS) 148(2)°], C(10)–H(10B)···O(1)a [*d*(C–H) 0.96 Å, *d*(H···O) 2.71 Å, *d*(C···O)

3.512(2) Å, ∠(CHO) 141°], C(10)–H(10B)···O(2)a [*d*(C–H) 0.96 Å, *d*(H···O) 2.72 Å, *d*(C···O) 3.627(2) Å, ∠(CHO) 158°].

[NiL$_2^{II}$]: $C_{22}H_{48}N_4NiO_4P_2S_4$, M_r = 681.53 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 9.0381(6), b = 9.5374(6), c = 9.7949(6) Å, α = 91.109(2), β = 90.152(2), γ = 97.145(3)°, V = 837.60(9) Å^3, Z = 1, ρ = 1.351 g cm^{-3}, μ(Mo-Kα) = 0.956 mm^{-1}, reflections: 27312 collected, 6045 unique, R_{int} = 0.0181, R_1(all) = 0.0226, wR_2(all) = 0.0557.

Selected bond lengths (Å) and angles (deg): Ni(1)–S(1) 2.2231(2), Ni(1)–S(2) 2.2085(2), N(1)–C(1) 1.3225(10), N(2)–C(1) 1.3444(10), P(1)–N(1) 1.5877(7), P(1)–S(1) 2.0004(3), S(2)–C(1) 1.7496(8); S(2)–Ni(1)–S(2)#1 180.0, S(2)–Ni(1)–S(1)#1 81.379(8), S(2)–Ni(1)–S(1) 98.622(8), S(1)–Ni(1)–S(1)#1 179.999(10), N(1)–P(1)–S(1) 115.97(3), P(1)–S(1)–Ni(1) 100.563(10), C(1)–S(2)–Ni(1) 117.88(3), C(1)–N(1)–P(1) 125.25(6), N(1)–C(1)–N(2) 116.50(7), N(1)–C(1)–S(2) 127.49(6), N(2)–C(1)–S(2) 116.01(6). Hydrogen contact parametres: C(11)–H(11A)···S(2)a [*d*(C–H) 0.98 Å, *d*(H···S) 3.00 Å, *d*(C···S) 3.801(3) Å, ∠(CHS) 140°].

HL^{I}: $C_{10}H_{23}N_2O_2PS_2$, M_r = 298.39 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 8.7411(4), b = 9.4953(4), c = 10.2409(5) Å, α = 94.511(2), β = 99.974(2), γ = 94.849(2)°, V = 830.37(7) Å^3, Z = 2, ρ = 1.193 g cm^{-3}, μ(Mo-Kα) = 0.411 mm^{-1}, reflections: 21707 collected, 6020 unique, R_{int} = 0.0171, R_1(all) = 0.0322, wR_2(all) = 0.0811.

Selected bond lengths (Å) and angles (deg): N(1)–C(2) 1.3792(11), N(2)–C(2) 1.3298(11), P(1)–N(1) 1.6685(7), S(1)–P(1) 1.9122(3), S(2)–C(2) 1.6757(8); C(2)–N(1)–P(1) 129.44(6), N(1)–C(2)–S(2) 119.74(6), N(1)–P(1)–S(1) 111.48(3), N(2)–C(2)–N(1) 116.95(8), N(2)–C(2)–S(2) 123.30(7). Hydrogen bond and hydrogen contact parametres: N(1)–H(1)···S(2)a [*d*(N–H) 0.831(15) Å, *d*(H···S) 2.504(15) Å, *d*(N···S) 3.3262(8) Å, ∠(NHS) 170.5(13)°], N(2)–H(2)···O(1) [*d*(N–H) 0.790(16) Å, *d*(H···O) 2.370(16) Å, *d*(N···O) 2.9582(11) Å, ∠(NHO) 132.0(14)°], N(2)–H(2)···O(2) [*d*(N–H) 0.790(16) Å, *d*(H···O) 2.518(16) Å, *d*(N···O) 3.0526(11) Å, ∠(NHO) 126.2(14)°], C(6)–H(6)···S(1)a [*d*(C–H) 1.00 Å, *d*(H···S) 2.86 Å, *d*(C···S) 3.7877(10) Å, ∠(CHS) 155°].

CCDC 805252 (**[NiL$_2^{I}$]**), 805251 (**[NiL$_2^{II}$]**) and 805547 (**HL^{I}**) contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

1 V. P. Ananikov, K. A. Gayduk, Z. A. Starikova and I. P. Beletskaya, *Organometallics,* 2010, **29**, 5098;

2 Stoe & Cie. X-AREA. Area-Detector Control and Integration Software. Stoe & Cie, Darmstadt, Germany, 2001.

3 A. L. Spek, *Acta Crystallogr.,* 2009, **D65**, 148.

4 G. M. Sheldrick, *Acta Crystallogr.,* 2008, **A64**, 112.

5 I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr.,* 2002, **B58**, 389.

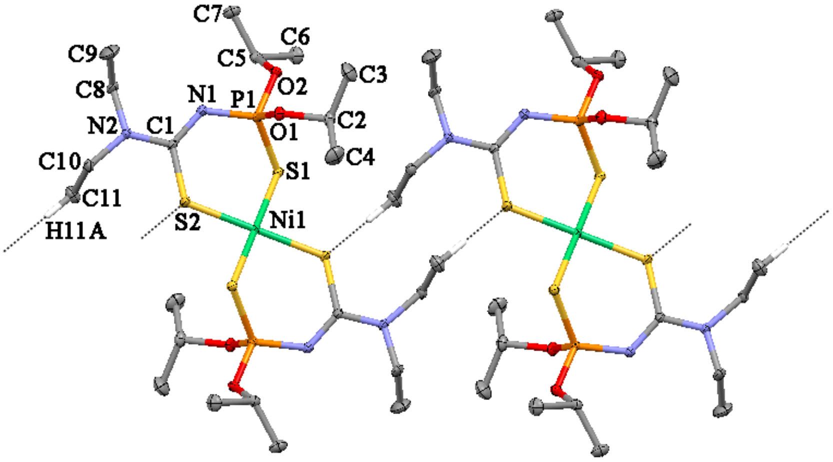

Fig. S1 Thermal ellipsoid (30%) plot of the complex **[NiL^{II}$_2$]**. H-atoms, not involved in hydrogen bonding and short contacts, have been omitted for clarity.

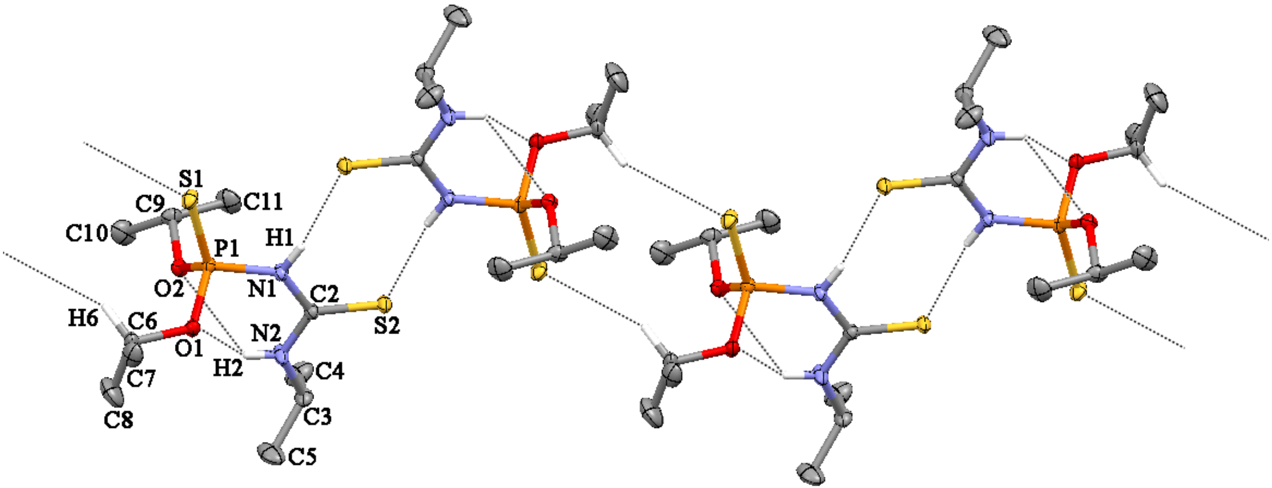

Fig. S2 Thermal ellipsoid (30%) plot of the *N*-thiophosphorylated thiourea **HL^I**. H-atoms, not involved in hydrogen bonding and short contacts, have been omitted for clarity.