## **Electronic Supplementary Information**

Experimental and theoretical investigations of the Ni<sup>II</sup> complex with *N*-phosphorylated thiourea *i*PrNHC(S)NHP(O)(OPh)<sub>2</sub>

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*Physical measurements:* Infrared spectra (KBr) were recorded with a FTIR-8400S SHIMADZU spectrophotometer in the range 400–3600 cm<sup>-1</sup>. NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded at 299.948, and 121.420 MHz, respectively. Chemical shifts are reported with reference to SiMe<sub>4</sub> (<sup>1</sup>H) and 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P{<sup>1</sup>H}). UV-vis absorption spectra of 10<sup>-4</sup> M solutions were recorded on a Lambda-35 spectrometer in the range 200–1000 nm. Diffuse reflectance spectra were obtained with a Varian Cary 5E spectrometer using polytetrafluoroethylene (PTFE) as a reference. The spectra were measured on a pure solid to avoid matrix effects. Eventual distortions in the Kubelka-Munk spectra that could result from the study of pure compounds have not been considered because no comparison with absorption spectra was necessary. Thermogravimetric analyses (TGA) were performed by a SDT 2960 Simultaneous DTA-TGA instrument in a dynamic air atmosphere (100 mL min<sup>-1</sup>) from laboratory temperature to 900 °C with a 10 °C min<sup>-1</sup> heating rate. Electrospray ionization mass spectra were recorded on a Thermo Fisher Scientific LCQ mass spectrometer on a 10<sup>-6</sup> M solution in a MeOH. The spray voltage was 5 kV. The capillary temperature was 260 °C. Elemental analyses were performed on a Thermoquest Flash EA 1112 Analyzer from CE Instruments.

*Synthesis of HL and [iPrNH<sub>3</sub>]<sup>+</sup>[P(O)<sub>2</sub>(OPh)<sub>2</sub>]*: A solution of isopropylamine (0.295 g, 5 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was treated under vigorous stirring with a solution of (PhO)<sub>2</sub>P(O)NCS (1.746 g, 6 mmol) in the same solvent. The mixture was stirred for 1 h. The solvent was removed in a vacuum, and the product was purified by recrystallisation from a 1:5 (v/v) mixture of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane. Yield 1.628 g (93%). IR, *v*: 962 (POC), 1238 (P=O), 1551 (S=C–N), 3149, 3289 (NH) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>),  $\delta$ : 1.10 (d, <sup>3</sup>*J*<sub>H,H</sub> = 6.4 Hz, 6H, CH<sub>3</sub>, *i*Pr), 4.22 (d. sept, <sup>3</sup>*J*<sub>HNCH</sub> = 7.6 Hz, <sup>3</sup>*J*<sub>H,H</sub> = 6.4 Hz, 1H, CH, *i*Pr), 7.21–7.36 (m, 6H, *o*-H + *p*-H, Ph), 7.44 (t, <sup>3</sup>*J*<sub>H,H</sub> = 8.5 Hz, 4H, *m*-H, Ph), 8.30 (d, <sup>3</sup>*J*<sub>HNCH</sub> = 7.6 Hz, 1H, *i*PrNH), 9.71 (br. s, 1H, NHP) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub>),  $\delta$ : – 10.6 ppm. *Anal*. Calc. for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub>PS (350.37): C 54.85, H 5.47, N 8.00. Found: C 54.73, H 5.51, N 8.07%.

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Recrystallization of **HL** (0.525 g, 1.5 mmol) from an aqueous acetone (15 mL) solution leads to the formation of the salt  $[iPrNH_3]^+[P(O)_2(OPh)_2]^-$ . Yield 0.408 g (88%). IR, *v*: 922 (POC), 1083 (P=O), 2968, 3042 (NH) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>),  $\delta$ : 1.15 (d, <sup>3</sup>*J*<sub>H,H</sub> = 6.7 Hz, 6H, CH<sub>3</sub>, *i*Pr), 3.20 (sept, <sup>3</sup>*J*<sub>H,H</sub> = 6.5 Hz, 1H, CH, *i*Pr), 6.98 (t, <sup>3</sup>*J*<sub>H,H</sub> = 7.1 Hz, 2H, *p*-H, Ph), 7.13 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.2 Hz, 4H, *o*-H, Ph), 7.24 (t, <sup>3</sup>*J*<sub>H,H</sub> = 7.2 Hz, 4H, *m*-H, Ph), 7.92 (br. s, 3H, NH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub>),  $\delta$ : -11.8 ppm. *Anal*. Calc. for C<sub>15</sub>H<sub>20</sub>NO<sub>4</sub>P (309.30): C 58.25, H 6.25, N 4.53. Found: C 58.33, H 6.30, N 4.51%.

*Synthesis of [NiL<sub>2</sub>]:* A suspension of **HL** (3 mmol, 1.050 g) in MeOH (10 mL) was mixed with a MeOH (10 mL) solution of KOH (3.3 mmol, 0.185 g). An aqueous (10 mL) solution of NiCl<sub>2</sub> (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<sub>2</sub>Cl<sub>2</sub>, washed with water and dried with anhydrous MgSO<sub>4</sub>. The solvent was removed in a vacuum, and the product was purified by recrystallisation from a 1:3 (v/v) mixture of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane. Yield 1.033 g (91%). IR, *v*: 939 (POC), 1564 (SCN), 1231 (P=O), 3248 (NH) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 1.08 (d, <sup>3</sup>*J*<sub>H,H</sub> = 6.4 Hz, 12H, CH<sub>3</sub>, *i*Pr), 3.87 (d. sept, <sup>3</sup>*J*<sub>HNCH</sub> = 7.8 Hz, <sup>3</sup>*J*<sub>H,H</sub> = 6.4 Hz, 2H, CH, *i*Pr), 7.25 (t, <sup>3</sup>*J*<sub>H,H</sub> = 7.3 Hz, 4H, *p*-H, Ph), 7.42 (t, <sup>3</sup>*J*<sub>H,H</sub> = 7.8 Hz, 8H, *m*-H, Ph), 7.53 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.8 Hz, 8H, *o*-H, Ph), 8.05 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.8 Hz, 2H, *i*PrNH) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>),  $\delta$ : -5.0 ppm. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>),  $\delta$ : 1.00 (br. s, 2H, CH, *i*Pr), 2.81 (br. s, 12H, CH<sub>3</sub>, *i*Pr), 3.89 (br. s, 2H, *i*PrNH), 6.80–7.64 (m, 20H, Ph) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub>),  $\delta$ : -7.5 ppm. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max} (\varepsilon, M^{-1} cm^{-1})$ : 264 (26865), 318 (18470), 502 (213), 634 (191) nm. UV-vis (DMSO),  $\lambda_{max} (\varepsilon, M^{-1} cm^{-1})$ : 248 (25490), 306 (2385), 437 (68), 722 (10) 1118 (12) nm. ESI-MS<sup>+</sup>, *m/z* (*I*, %): 407.01 (20.6) [M – L]<sup>+</sup>, 756.97 (33.8) [M + H]<sup>+</sup>, 779.09 (15.1) [M + Na]<sup>+</sup>, 1164.95 (100) [Ni<sub>2</sub>L<sub>3</sub>]<sup>+</sup>, 1534.57 (8.5) [Ni<sub>2</sub>L<sub>4</sub> + Na]<sup>+</sup>, 1922.37 (4.7) [Ni<sub>3</sub>L<sub>5</sub>]<sup>+</sup>. ESI-MS<sup>-</sup>, *m/z* (*I*, %): 755.08 (100) [M – H]<sup>-</sup>. *Anal.* Calc. for C<sub>32</sub>H<sub>36</sub>N<sub>4</sub>NiO<sub>6</sub>P<sub>2</sub>S<sub>2</sub> (757.42): C 50.74, H 4.79, N 7.40. Found: C 50.64, H 4.73, N 7.36%.

*Static DFT calculations:* We have applied in DFT-based geometry optimizations the hybrid exchange-correlation functional B3LYP<sup>1</sup> and Grimme's B97D functional<sup>2</sup> with empirical correction for dispersion interactions and the 6-311G\*\* basis set as implemented in the Gaussian 09 package.<sup>3</sup> Deformation density map as well as deformation density contributions of the ETS-NOCV method were plotted based on the ADF-GUI interface.<sup>4</sup>

*ETS-NOCV bonding analysis:* Historically the Natural Orbitals for Chemical Valence (NOCV) have been derived from the Nalewajski-Mrozek valence theory as eigenvectors that diagonalizes the deformation density matrix. It was shown that the natural orbitals for chemical valence pairs ( $\psi_{-k}, \psi_k$ ) decompose the differential density  $\Delta \rho$  into NOCV-contributions ( $\Delta \rho_k$ ):

$$\Delta \rho(r) = \sum_{k=1}^{M/2} v_k [-\psi_{-k}^2(r) + \psi_k^2(r)] = \sum_{k=1}^{M/2} \Delta \rho_k(r),$$

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where  $v_k$  and M stand for the NOCV eigenvalues and the number of basis functions, respectively. Visual inspection of deformation density plots ( $\Delta \rho_k$ ) helps to attribute symmetry and the direction of the charge flow. In addition, these pictures are enriched by providing the energetic estimations,  $\Delta E_{orb}(k)$ , for each  $\Delta \rho_k$  within ETS-NOCV scheme. The exact formula, which links the ETS and NOCV methods, will be given in the next paragraph, after we briefly present the basic concept of ETS scheme. In this method the total bonding energy  $\Delta E_{total}$  between interacting fragments, exhibiting the geometry as in the combined complex, is divided into the three components:

$$\Delta E_{\text{total}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$$

The first term,  $\Delta E_{\text{elstat}}$ , corresponds to the classical electrostatic interaction between the promoted fragments as they are brought to their positions in the final complex. The second term,  $\Delta E_{\text{Pauli}}$ , accounts for the repulsive Pauli interaction between occupied orbitals on the two fragments in the combined molecule. Finally, the last stabilizing term,  $\Delta E_{orb}$  represents the interactions between the occupied molecular orbitals of one fragment with the unoccupied molecular orbitals of the other fragment as well as mixing of occupied and virtual orbitals within the same fragment (inner-fragment polarization). This energy term may be linked to the electronic bonding effect coming from the formation of a chemical bond. The three last terms ( $\Delta E_{\text{elstat}}$ ,  $\Delta E_{\text{pauli}}$ ,  $\Delta E_{\text{orb}}$ ) very often are combined into the instantaneous interaction energy,  $\Delta E_{\text{int}}$ , as it describes the interaction between the fragments in the geometry of the complex.

In the combined ETS-NOCV scheme the orbital interaction term ( $\Delta E_{orb}$ ) is expressed in terms of NOCV's eigenvalues ( $v_k$ ) as:

$$\Delta E_{orb} = \sum_{k} \Delta E_{orb}(k) = \sum_{k=1}^{M/2} v_k [-F_{-k,-k}^{TS} + F_{k,k}^{TS}],$$

where  $F_{i,i}^{TS}$  are diagonal Kohn-Sham matrix elements defined over NOCV with respect to the transition state (TS) density (at the midpoint between density of the molecule and the sum of fragment densities). The above components  $\Delta E_{orb}(k)$  provide the energetic estimation of  $\Delta \rho_k$  that may be related to the importance of a particular electron flow channel for the bonding between the considered molecular fragments. ETS-NOCV analysis was done based on the Amsterdam Density Functional (ADF) package in which this scheme was implemented.

*Molecular Dynamics Study*: We have applied the Born-Oppenheimer approach based on DFT method (CP2K package,<sup>5</sup> the Becke Perdew functional with Grimme's dispersion correction). The 5 ps trajectory for monomer and dimer was analyzed. The combination of DZVP basis sets centered on atoms and the plane waves (cutoff = 260) were applied as implemented in CP2K program. The time step was 1 fs. The trajectory was analyzed based on the VMD program.<sup>5</sup>

*X-Ray crystallography:* X-ray data collection was performed on a Mar345 image plate detector using Mo-K<sub> $\alpha$ </sub> radiation (rotation anode, multilayer mirror). The data were integrated with the CrysAlisPro software.<sup>6</sup> The

implemented empirical absorption correction was applied. The structures were solved by direct methods using the SHELXS-97 program<sup>7</sup> and refined by full-matrix least squares on  $|F^2|$  using SHELXL-97.<sup>7</sup> Non-hydrogen atoms were anisotropically refined and the hydrogen atoms were placed on calculated positions in riding mode with temperature factors fixed at 1.2 times U<sub>eq</sub> of the parent atoms and 1.5 times U<sub>eq</sub> for methyl groups. Figures were generated using the program Mercury.<sup>8</sup>

**Crystal data for HL.**  $C_{16}H_{19}N_2O_3PS$ ,  $M_r = 350.36 \text{ g mol}^{-1}$ , triclinic, space group *P*-1, a = 9.8501(12), b = 11.0661(18), c = 17.707(2) Å, a = 92.032(11),  $\beta = 92.940(10)$ ,  $\gamma = 111.728(13)$  °, V = 1787.5(4) Å<sup>3</sup>, Z = 4,  $\rho = 1.302 \text{ g cm}^{-3}$ ,  $\mu$ (Mo-K $\alpha$ ) = 0.285 mm<sup>-1</sup>, reflections: 17578 collected, 6210 unique,  $R_{int} = 0.053$ ,  $R_1(all) = 0.0855$ ,  $wR_2(all) = 0.1693$ .

**Crystal data for**  $[i\mathbf{PrNH_3}]^+[\mathbf{P(O)_2(OPh)_2}]^-$ . C<sub>15</sub>H<sub>20</sub>NO<sub>4</sub>P,  $M_r = 309.29 \text{ g mol}^{-1}$ , orthorhombic, space group *Pna*2<sub>1</sub>, *a* = 14.327(2), *b* = 17.039(3), *c* = 6.4900(11) Å, *V* = 1584.3(4) Å<sup>3</sup>, *Z* = 4,  $\rho = 1.297 \text{ g cm}^{-3}$ ,  $\mu$ (Mo-K $\alpha$ ) = 0.188 mm<sup>-1</sup>, reflections: 8565 collected, 1926 unique,  $R_{int} = 0.134$ ,  $R_1(all) = 0.0858$ ,  $wR_2(all) = 0.1706$ .

**Crystal data for [NiL<sub>2</sub>].**  $C_{32}H_{36}N_4NiO_6P_2S_2$ ,  $M_r = 757.42 \text{ g mol}^{-1}$ , monoclinic, space group  $P2_1/n$ , a = 12.060(2), b = 10.7171(10), c = 13.9639(13) Å,  $\beta = 90.435(11)^\circ$ , V = 1804.8(4) Å<sup>3</sup>, Z = 2,  $\rho = 1.394$  g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.789 mm<sup>-1</sup>, reflections: 9499 collected, 3334 unique,  $R_{int} = 0.045$ ,  $R_1(all) = 0.0507$ ,  $wR_2(all) = 0.1049$ .

CCDC 894844 (HL), 894843 ( $[iPrNH_3]^+[P(O)_2(OPh)_2]^-$ ) and 894845( $[NiL_2]$ ) 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 (a) J. P. Perdew, *Phys. Rev. B: Condens. Matter.*, 1986, **33**, 8822; (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372.
- 2 S. Grimme, J. Comp. Chem., 2006, 27, 1787.
- (a) P. J. Hay, W. R. Wadt, J. Chem. Phys., 1985, 82, 270; (b) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Gaussian Inc., Wallingford CT, 2009.

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- 4 ADF-GUI 2009.01, SCM, Amsterdam, The Netherlands, http://www.scm.com (O. Visser, P. Leyronnas, W. J. van Zeist and M. Lupki).
- (a) J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, *Comp. Phys. Comm.*, 2005, 167, 103; (b) M. Krack and M. Parrinello, *Forschungszentrum Jülich, NIC Series*, 2004, 25, 29; (c) J. VandeVondele and J. Hutter, *J. Chem. Phys.*, 2003, 118, 4365; (d) W. Humphrey, A. Dalke and K. Schulten, *J. Molec. Graphics*, 1996, 14, 33.
- 6 Oxford Diffraction Data collection and data reduction, Version 171.34.40.
- 7 G. M. Sheldrick, Acta Crystallogr., 2008, A64, 112.
- 8 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.

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*trans*-[Ni(L-1,3-*N*,*S*)<sub>2</sub>] 0.0 kcal/mol and 0.0 kcal/mol



*cis*-[Ni(L-1,3-*N*,*S*)<sub>2</sub>] 13.3 kcal/mol and 11.4 kcal/mol



*trans*-[Ni(L-1,5-*O*,*S*)<sub>2</sub>] 9.6 kcal/mol and 26.0 kcal/mol



*cis*-[Ni(L-1,5-*O*,*S*)<sub>2</sub>] 13.3 kcal/mol and 23.1 kcal/mol

**Fig. S1** Energies of the possible conformations of [NiL<sub>2</sub>] based on the B3LYP/6-311G\*\* (black) and B97D/6-311G\*\* (red calculations.

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Bond	trans-1,3-N,S-isomer	trans-1,5-0,S-isomer		
Ni–N	2x, 0.1059			
Ni–S	2x, 0.0827	2x, 0.0777		
Ni–O	—	2x, 0.0993		
N−H···O=P	2x, 0.0163	—		
$C_{Ph}$ -H····S=C	4x, 0.0052	2x, 0.0077		
$C_{Ph}$ – $H$ ··· $\pi_{Ph}$	2x, 0.0020	—		
$C_{Ph}$ -H···O	—	2x, 0.0103		
RCP (Ring Critical Point)	Ni–N–C–S, 0.0483	Ni–S–C–N–P–O, 0.0143		
nx is the number of given interactions				

**Fig. S2** QTAIM molecular graphs for the *trans*-1,3-*N*,*S*-isomer (A) and *trans*-1,5-*O*,*S*-isomer (B) of [NiL<sub>2</sub>], obtained from the ADF/TZP/BP86 calculations. Molecular graphs were plotted with the help of ADF-GUI interface. In addition the density values at bond critical points are presented.

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**Fig. S3** Triplet and singlet octahedral complexes of [NiL<sub>2</sub>] with two axially coordinated DMSO molecules and their relative energies calculated at the B3LYP/6-311G\*\* (black) and B97D/6-311G\*\* (red) levels.

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**Fig. S4** Simultaneous TG/DTA analyses of **HL** (top),  $[iPrNH_3]^+[P(O)_2(OPh)_2]^-$  (middle) and  $[NiL_2]$  (bottom) performed in a dynamic air atmosphere.

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Fig. S5 Normalised IR spectrum (top) and PXRD diffractogram (bottom) of NiPS<sub>3</sub> obtained from annealing of [NiL<sub>2</sub>] at 850 °C.

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Fig. S6 Changes in the selected parameters observed during the CP2K molecular dynamics simulations for dimer of  $[NiL_2]$ . Parts a and b show the C<sub>Ph</sub>-H···O intermolecular hydrogen bonding distance. Parts c and d show the variation in the C<sub>Me</sub>-H···Ph distance (with respect to the middle of the Ph ring).

The molecular dynamics calculations show a significant dynamic effect of the intermolecular interactions. Figure S6a shows the presence of week hydrogen bonding of the type  $C_{Ph}$ -H···O=P (qualitative picture from the ETSNOCV method is presented in part A of Figure below). Figure S6b depicts the formation of two new intermolecular hydrogen bonds between the oxygen atom directly connected with Ph of one monomer and *ortho*-(red line), *meta*- (black line) hydrogen atoms of the Ph ring of the other [NiL<sub>2</sub>] unit. Figure S6c,d present the C<sub>Me</sub>-H···*π* bonding formed by two methyl groups of the *i*Pr unit and the *π*-electrons of the Ph ring (see the  $\Delta \rho_{rest}$  contour in the part b of Figure below).

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 $\Delta E_{orb}(rest) = -2.15kcal/mol$ 

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Bond lengths					
S(19)–C(18)	1.674(2)	P(31)-O(32)	1.4675(17)	N(17)–C(18)	1.387(3)
S(49)–C(48)	1.676(2)	P(31)-O(33)	1.5739(17)	N(20)–C(18)	1.320(3)
P(1)-O(2)	1.4652(18)	P(31)-O(40)	1.5748(18)	N(47)–C(48)	1.401(3)
P(1)-O(3)	1.5694(17)	P(1)–N(17)	1.655(2)	N(50)–C(48)	1.331(3)
P(1)-O(10)	1.5642(17)	P(31)–N(47)	1.643(2)		
Bond angles					
O(2)–P(1)–O(3)	115.64(10)	O(3)–P(1)–N(17)	108.78(10)	N(17)-C(18)-N(20)	116.5(2)
O(2)–P(1)–O(10)	118.01(10)	O(10)–P(1)–N(17)	105.51(10)	N(47)-C(48)-N(50)	117.29(19)
O(3)–P(1)–O(10)	96.10(9)	O(32)–P(31)–N(47)	110.73(10)	S(19)-C(18)-N(17)	117.61(17)
O(32)–P(31)–O(33)	118.38(9)	O(33)–P(31)–N(47)	105.91(10)	S(19)-C(18)-N(20)	125.89(19)
O(32)–P(31)–O(40)	115.72(10)	O(40)-P(31)-N(47)	108.07(10)	S(49)-C(48)-N(47)	117.70(16)
O(33)–P(31)–O(40)	96.72(10)	P(1)-N(17)-C(18)	130.26(16)	S(49)-C(48)-N(50)	125.01(17)
O(2)-P(1)-N(17)	111.40(10)	P(31)-N(47)-C(48)	128.80(16)		

Table S2. Selected bond lengths (Å) and angles (°) for  $[iPrNH_3]^+[P(O)_2(OPh)_2]^-$ 

Bond lengths					
P(1)-O(2)	1.482(2)	P(1)-O(4)	1.627(2)	N(21)–C(22)	1.517(4)
P(1)–O(3)	1.451(2)	P(1)–O(11)	1.6167(19)		
Bond angles					
O(2)–P(1)–O(3)	119.48(13)	O(2)–P(1)–O(11)	105.37(12)	O(3)–P(1)–O(11)	111.42(11)
O(2)–P(1)–O(4)	111.55(11)	O(3)–P(1)–O(4)	103.72(12)	O(4)–P(1)–O(11)	104.44(11)

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Bond lengths					
Ni(1)–S(2)	2.2301(8)	N(8)–C(3)	1.350(3)	P(9)–O(10)	1.4690(17)
Ni(1)–N(8)	1.902(2)	S(2)–C(3)	1.731(2)	P(9)–O(11)	1.5961(18)
N(4)–C(3)	1.314(3)	P(9)–N(8)	1.635(2)	P(9)–O(18)	1.5858(17)
Bond angles					
Ni(1)–N(8)–C(3)	99.65(14)	S(2)–Ni(1)–S(2)a	180.00	O(10)–P(9)–O(18)	115.27(10)
Ni(1)–N(8)–P(9)	132.27(12)	N(4)-C(3)-N(8)	126.3(2)	O(11)–P(9)–O(18)	96.11(9)
Ni(1)-S(2)-C(3)	77.51(8)	P(9)-N(8)-C(3)	126.63(16)	O(10)-P(9)-N(8)	114.21(10)
N(8)–Ni(1)–N(8)a	180.00	S(2)-C(3)-N(4)	125.56(19)	O(11)–P(9)–N(8)	106.65(10)
S(2)-Ni(1)-N(8)	74.19(6)	S(2)-C(3)-N(8)	108.17(16)	O(18)–P(9)–N(8)	107.09(10)
S(2)-Ni(1)-N(8)a	105.81(6)	O(10)–P(9)–O(11)	115.70(10)		

Table S3. Selected bond lengths (Å) and angles (°) for [NiL<sub>2</sub>]

Table S4. Selected hydrogen bond lengths (Å) and angles (°) for HL, [*i*PrNH<sub>3</sub>]<sup>+</sup>[P(O)<sub>2</sub>(OPh)<sub>2</sub>]<sup>-</sup> and [NiL<sub>2</sub>]

	D−H…A	<i>d</i> (D–H)	$d(\mathbf{H}^{\dots}\mathbf{A})$	$d(\mathbf{D}\cdots\mathbf{A})$	∠(DHA)
$\mathrm{HL}^{a}$	N(20)-H(20)···O(2)	0.88	2.03	2.784(3)	143
	N(50)-H(50)···O(32)	0.88	2.06	2.814(2)	143
	N(17)-H(17)···O(32)	0.88	2.05	2.801(3)	142
	N(47)–H(47)···O(42)#1	0.88	2.13	2.821(3)	135
$[i PrNH_3]^+ [P(O)_2(OPh)_2]^-$	N(21)-H(21A)····O(2)#1	0.91	1.92	2.819(4)	172
	N(21)-H(21B)····O(3)	0.91	1.98	2.891(4)	177
	N(21)-H(21C)···O(3)#2	0.91	1.93	2.829(3)	167
$[NiL_2]^c$	N(4)–H(4)····O(10)	0.86	2.21	2.882(3)	135
	C(17)-H(17)····O(10)#1	0.93	2.54	3.419(3)	158

<sup>*a*</sup>Symmetry transformations used to generate equivalent atoms: #1 1 + x, y, z<sup>*b*</sup>Symmetry transformations used to generate equivalent atoms: #1 x, y, 1 + z; #2 2 - x, 1 - y, 1/2 + z<sup>*c*</sup>Symmetry transformations used to generate equivalent atoms: #1 -x, 1 - y, 1 - z