

# {2,6-Bis[(2,6-diisopropylphosphanyl)-oxy]-4-fluorophenyl- $\kappa^3P,C^1,P'$ }(1H-pyrazole- $\kappa N^2$ )nickel(II) hexafluorophosphate

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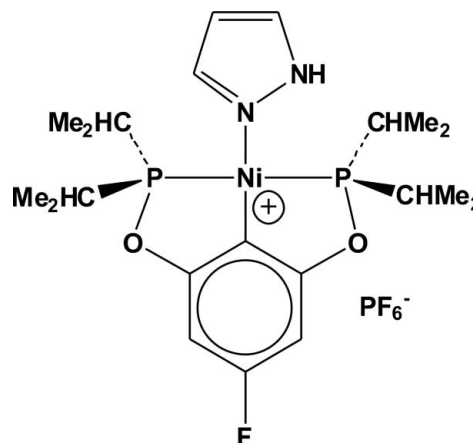
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Key indicators: single-crystal X-ray study;  $T = 290$  K; mean  $\sigma(C-C) = 0.005$  Å;  $R$  factor = 0.037;  $wR$  factor = 0.100; data-to-parameter ratio = 15.8.

The title compound,  $[\text{Ni}(\text{C}_{18}\text{H}_{30}\text{FO}_2\text{P}_2)(\text{C}_3\text{H}_4\text{N}_2)]\text{PF}_6$ , was prepared by halide abstraction with  $\text{TIPF}_6$  in the presence of  $\text{CH}_3\text{CN}$  in  $\text{CDCl}_3$  from the respective neutral pincer chlorido analogue followed by addition of pyrazole. The  $\text{PO}-\text{C}-\text{OP}$  pincer ligand acts in typical  $\text{trans-P}_2$  tridentate fashion to generate a distorted square-planar nickel structure. The  $\text{Ni}-\text{N}(\text{pyrazole})$  distance is 1.925 (2) Å and the plane of the pyrazole ligand is rotated 56.2 (1)° relative to the approximate square plane surrounding the  $\text{Ni}^{\text{II}}$  center in which the pyrazole is bound to the  $\text{Ni}^{\text{II}}$  atom through its  $sp^2$ -hybridized N atom. This  $\text{Ni}-\text{N}$  distance is similar to bond lengths in the other reported  $\text{Ni}^{\text{II}}$  pincer-ligand square-planar pyrazole complex structures; however, its dihedral angle is significantly larger than any of those for the latter set of pyrazole complexes.

## Related literature

For recent studies on the chemistry of  $d$ -block  $\text{PO}-\text{C}-\text{OP}$  pincer complexes, see Chen *et al.* (2012); Zhang *et al.* (2012); Salah & Zargarian (2011); Hoffman *et al.* (2009); Wicker *et al.* (2011). For structures of other  $\text{Ni}^{\text{II}}$  pincer-ligand square-planar pyrazole complexes, see Salem *et al.* (2007, 2008); Peng *et al.* (2010). For information regarding the  $^{19}\text{F}$  NMR reference, see: Ji *et al.* (2005).



## Experimental

### Crystal data

$[\text{Ni}(\text{C}_{18}\text{H}_{30}\text{FO}_2\text{P}_2)(\text{C}_3\text{H}_4\text{N}_2)]\text{PF}_6$   
 $M_r = 631.12$   
 Monoclinic,  $P2_1/n$   
 $a = 9.0380$  (9) Å  
 $b = 20.1878$  (16) Å  
 $c = 16.1480$  (16) Å  
 $\beta = 98.659$  (8)°

$V = 2912.7$  (5) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.90$  mm<sup>-1</sup>  
 $T = 290$  K  
 $0.58 \times 0.52 \times 0.34$  mm

### Data collection

Enraf-Nonius CAD-4  
 diffractometer  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
 $T_{\text{min}} = 0.265$ ,  $T_{\text{max}} = 0.315$   
 5464 measured reflections

5122 independent reflections  
 3432 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$   
 3 standard reflections every 120 min  
 intensity decay: none

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.100$   
 $S = 1.00$   
 5122 reflections

325 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.22$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.29$  e Å<sup>-3</sup>

Data collection: *CAD-4-PC* (Enraf-Nonius, 1993); cell refinement: *CAD-4-PC*; data reduction: *XCAD4-PC* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG5249).

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## supplementary materials

*Acta Cryst.* (2012). E68, m1282–m1283 [doi:10.1107/S1600536812039207]

**{2,6-Bis[(2,6-diisopropylphosphanyl)oxy]-4-fluorophenyl- $\kappa^3P,C^1,P'$ }(1H-pyrazole- $\kappa N^2$ )nickel(II) hexafluorophosphate**

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**Comment**

Considerable attention has recently been devoted to nickel PO—C—OP pincer complexes (*e.g.*, Salah & Zargarian, 2011; Chen *et al.*, 2012; Zhang *et al.*, 2012). Our interest in studying relative binding affinities of metal centers for ligands of moderate donor power using  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectroscopy (Hoffman *et al.*, 2009) to monitor ligand-substitution equilibria led us to prepare the title complex (I). The fluoro-pincer ligand precursor was generated by heating 5-fluoro-resorcinol and diisopropylchlorophosphine in THF in the presence of triethylamine, and then anhydrous  $\text{NiCl}_2$  was added to form the (PO—C—OP)NiCl complex. Chloride abstraction with  $\text{TIPF}_6$  in the presence of  $\text{CH}_3\text{CN}$  from this species followed by addition of pyrazole afforded an excellent yield of the cationic complex whose structure is shown below in Fig 1. Suitable single crystals were grown *via* vapor diffusion of methyl *tert*-butyl ether into a  $\text{CDCl}_3$  solution of the highly soluble reaction product at room temperature. Its Ni—N distance, 1.925 (2) Å, fell within the range of such values for the five square-planar  $\text{Ni}^{\text{II}}$ -pincer unsubstituted-pyrazole complexes found in the Cambridge Structural Database (Salem *et al.* (2008), Peng *et al.* (2010), and Salem *et al.* (2007)). However, its pyrazole-ring/Ni-coordination-plane dihedral angle, 56.2 (1)°, falls significantly outside the range (3–28°) of those for the latter set of pyrazole complexes, in which none of the pendant-ligand arms exert meaningful steric force upon the pyrazole position. The C—F bond length for this complex, 1.355 (4) Å, is identical within experimental error to that, 1.357 (3) Å, of  $\text{Pd}\{(3-2,6-[(\text{C}_6\text{H}_5)_2\text{PO}]_2-\text{C}_6\text{H}_2-4-\text{F})\}(\text{C}_4\text{H}_4\text{NO}_4\text{S})$ , a Pd(II) acesulfamato complex containing a similar fluoro-pincer ligand (Wicker *et al.*, 2011). Detailed lists of dimensions are available in the archived CIF.

**Experimental**

The first step entailed generating a neutral nickel(II) halido pincer complex, abbreviated as  $\text{Pr}\{\text{Ni}_F\}\text{Cl}$ . An anhydrous solution of 5-fluororesorcinol (330 mg, 2.58 mmol) in THF was prepared in a 100-ml Kontes Teflon screw-cap flask inside a glovebox. To this solution was added *via* syringe 1.50 ml  $\text{NEt}_3$  (10.77 mmol) followed by 850  $\mu\text{L}$  of  $\text{ClPPri}_2$  (5.34 mmol); immediately a large volume of white precipitate formed. The flask was brought out of the glovebox and heated for 20 minutes at 80 °C; thereafter the flask was returned to the glovebox, where 0.57 grams of anhydrous  $\text{NiCl}_2$  (4.40 mmol) was added to afford an orange mixture. After 24 h under heavy stirring at 80 °C, the resulting green-yellow mixture was filtered through a plug of Celite and concentrated under vacuum. This solution was layered with pentane and left overnight in a -30 °C freezer to give dark yellow-brown crystals of  $\text{Pr}\{\text{Ni}_F\}\text{Cl}$  (608 mg, 52% yield).

Complex I,  $[\text{Ni}(\text{C}_3\text{H}_2\text{N}_2)(\text{C}_{12}\text{H}_{16}\text{FO}_2\text{P}_2)]\text{PF}_6$ , abbreviated as  $\text{Pr}\{\text{Ni}_F\}(\text{Pz})\text{PF}_6$ , was prepared as follows.  $\text{Pr}\{\text{Ni}_F\}\text{Cl}$  (32.4 mg, 0.0799 mmol) was stirred at ambient temperature for 24 h with  $\text{TIPF}_6$  (Strem Chemicals; 1.15 mol equiv.) in  $\text{CDCl}_3$  (Cambridge Isotopes Lab; 1.25 ml) to which 25  $\mu\text{L}$   $\text{CH}_3\text{CN}$  (Fisher reagent) had been added. The resulting mixture was

filtered to remove insoluble TiCl<sub>4</sub> and excess TiPF<sub>6</sub>. To the resulting yellow-orange solution of Pr{Ni<sub>F</sub>}(CH<sub>3</sub>CN)]PF<sub>6</sub> was added a slight excess of solid pyrazole (Aldrich; 5.7 mg), and the reaction solution was stirred one hour. Then it was subjected to vapor diffusion with 30 ml of methyl *tert*-butyl ether (MTBE; Fisher reagent) at 22 °C for 3 days. The very pale yellow liquid of the resulting mixture was removed from the vial by a small-diameter syringe needle, and the rod-like orange crystals were washed twice with 1.5 ml of MTBE, removed from the vial, and then air-dried overnight in the dark (91% yield). The complex was characterized by NMR at 24 °C in CDCl<sub>3</sub>. Unusual features of the spectra are discussed below the data tabulation.

<sup>1</sup>H: (relative to internal TMS)  $\delta$  11.66 (broad singlet, 0.74 H);  $\delta$  8.07 (overlapping doublet of doublets, 1H);  $\delta$  7.64 (overlapping doublet of doublets, 1H);  $\delta$  6.58 (2H, doublet, <sup>3</sup>J<sub>F-H</sub>=9.6 Hz)  $\delta$  2.34 (4H, septuplet, <sup>3</sup>J<sub>H-H</sub>=7.1 Hz);  $\delta$  1.35 (overlapping inequivalent triplets, 12H);  $\delta$  1.08 (overlapping inequivalent triplets, 12H)

<sup>19</sup>F: (relative to internal C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> at  $\delta$  -63.00; (Ji *et al.*, 2005)) aryl-F at  $\delta$  -109.41 (triplet of triplets, <sup>3</sup>J<sub>H-F</sub>=9.6 Hz, <sup>5</sup>J<sub>P-F</sub>=1.0 Hz) and counterion PF<sub>6</sub><sup>-</sup> at  $\delta$  -72.28 (doublet, <sup>2</sup>J<sub>P-F</sub>=713 Hz)

<sup>31</sup>P: (relative to external 85% aq. phosphoric acid) pincer-P at  $\delta$  190.31 (doublet, <sup>5</sup>J<sub>P-F</sub>=1.0 Hz) and counterion PF<sub>6</sub><sup>-</sup> at  $\delta$  -143.79 (septuplet, <sup>2</sup>J<sub>P-F</sub>=713 Hz)

<sup>13</sup>C: (relative to internal TMS)

Pyrazole:  $\delta$  108.59(s),  $\delta$  135.21(s),  $\delta$  141.43(s).

Pincer Aryl: *ipso*  $\delta$  115.49(t of d; <sup>4</sup>J<sub>F-C</sub>=2.9 Hz, <sup>2</sup>J<sub>P-C</sub>=21 Hz) *ortho*  $\delta$  168.55 (d of t; <sup>3</sup>J<sub>F-C</sub>=15 Hz, <sup>2</sup>J<sub>P-C</sub>~7.4 Hz) *meta*  $\delta$  94.89(d of t; <sup>2</sup>J<sub>F-C</sub>=33 Hz, <sup>4</sup>J<sub>P-C</sub>~6.6 Hz) *para*  $\delta$  165.16 (d; <sup>1</sup>J<sub>F-C</sub>=246 Hz Pr<sub>2</sub>P: methyne,  $\delta$  27.66(t; <sup>1</sup>J<sub>P-C</sub>=11 Hz) methyls  $\delta$  16.58(t; <sup>2</sup>J<sub>P-C</sub>=11 Hz),  $\delta$  16.41(s)

Integrals recorded for <sup>1</sup>H signals of Pr{Ni<sub>F</sub>}(Pz)]PF<sub>6</sub> match expected values except for the low-field pyrazole N—H resonance in which strong hydrogen-bonding to the hexafluorophosphate counterion is likely. Overlap of <sup>1</sup>H triplets for the inequivalent isopropyl methyl groups created by different rotation rates around the Ni—Pz, P—C, and C—C bonds affords pseudo-quartets centered at  $\delta$  1.35 and  $\delta$  1.08 (Fig. 2). The same rotational phenomena generate a more unusual <sup>13</sup>C-NMR methyls pattern (Fig. 3), in which a triplet at  $\delta$  16.58 (<sup>2</sup>J<sub>P-C</sub>=11 Hz) and singlet at  $\delta$  16.41 (no measurable P—C coupling observed) of equal intensity appear. Recording the <sup>13</sup>C-NMR spectrum with longer relaxation delay (4 s *versus* 1 s) or at 44 °C affords no change in this pattern.

## Refinement

Hydrogen atoms were placed in calculated positions and allowed to ride during subsequent refinement, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  and C—H distances of 0.93 Å for the H atoms on the pyrazole carbons,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$  and an N—H distance of 0.86 Å for the H atom on the pyrazole N,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  and C—H distances of 0.98 Å for the H atoms on the tertiary carbons, and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  and C—H distances of 0.96 Å for the methyl H atoms.

## Computing details

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC* (Enraf–Nonius, 1993); data reduction: *XCAD4-PC* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

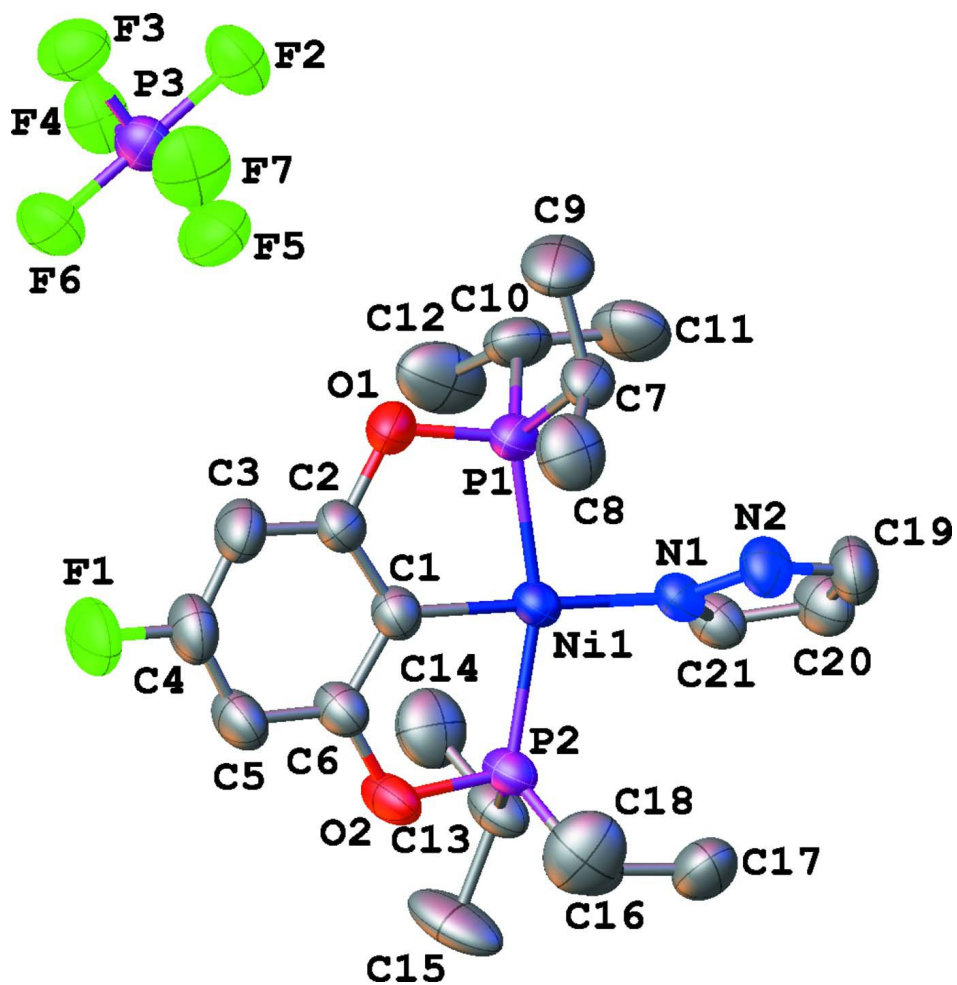
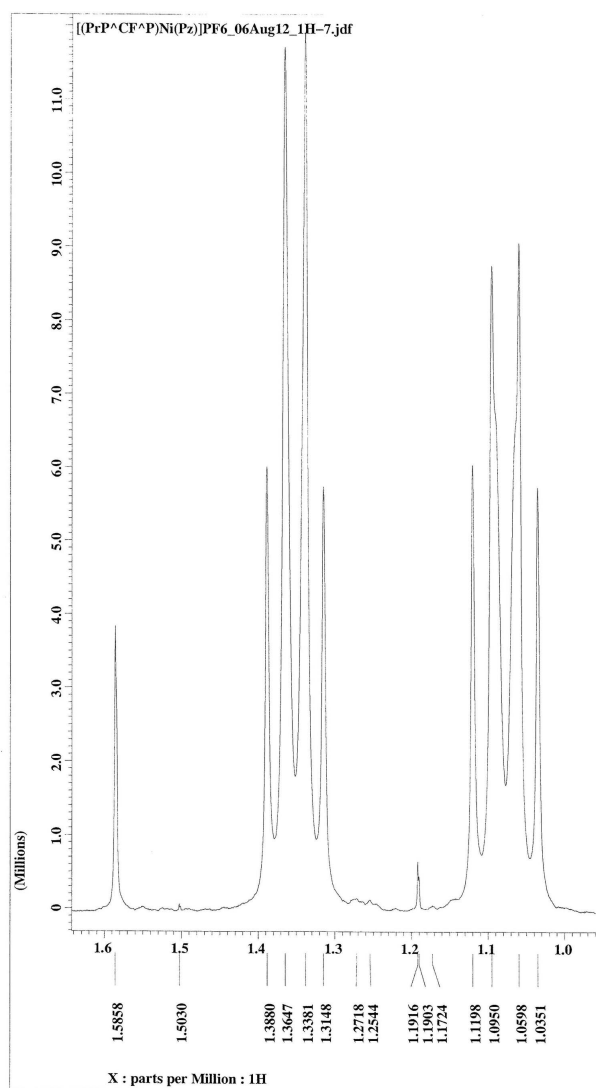
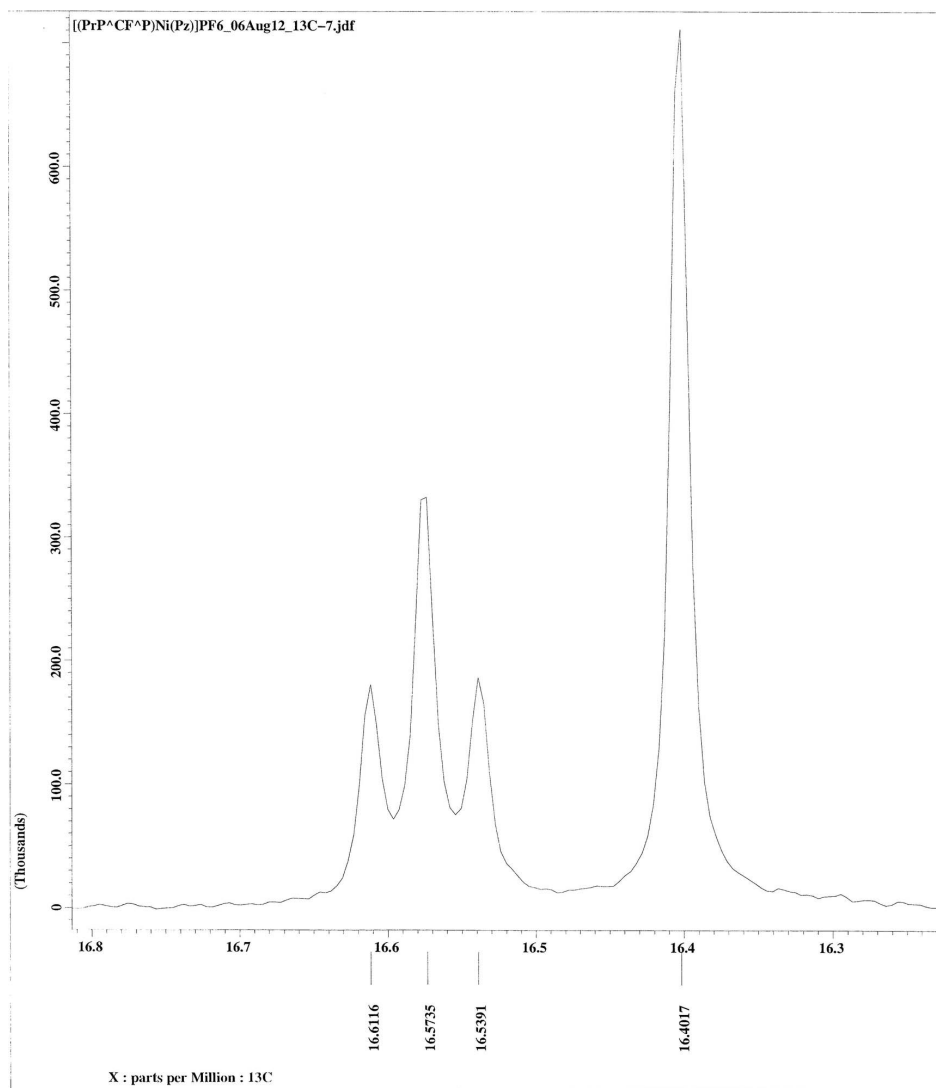


Figure 1

A thermal ellipsoid plot (50%) of the title compound showing the labeling scheme.

**Figure 2**

<sup>1</sup>H NMR spectrum of the title compound at 23 °C.



**Figure 3**

$^{13}\text{C}$  NMR spectrum of the title compound at 23 °C.

**{2,6-Bis[(2,6-diisopropylphosphanyl)oxy]-4-fluorophenyl- $\kappa^3\text{P},\text{C}^1,\text{P}^1$ }(1H-pyrazole- $\kappa\text{N}^2$ )nickel(II) hexafluorophosphate**

*Crystal data*

$[\text{Ni}(\text{C}_{18}\text{H}_{30}\text{FO}_2\text{P}_2)(\text{C}_3\text{H}_4\text{N}_2)]\text{PF}_6$

$M_r = 631.12$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P\ 2_1n$

$a = 9.0380$  (9) Å

$b = 20.1878$  (16) Å

$c = 16.1480$  (16) Å

$\beta = 98.659$  (8)°

$V = 2912.7$  (5) Å<sup>3</sup>

$Z = 4$

$F(000) = 1304$

$D_x = 1.439$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 25 reflections

$\theta = 9.5\text{--}13.0^\circ$

$\mu = 0.90$  mm<sup>-1</sup>

$T = 290$  K

Prism, yellow

$0.58 \times 0.52 \times 0.34$  mm

*Data collection*

|  |  |
|--|--|
| Enraf–Nonius CAD-4<br>diffractometer                               | 5122 independent reflections<br>3432 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube                           | $R_{\text{int}} = 0.024$   |
| Graphite monochromator   | $\theta_{\text{max}} = 25.0^\circ$ , $\theta_{\text{min}} = 2.0^\circ$ |
| $\theta/2\theta$ scans   | $h = 0 \rightarrow 10$   |
| Absorption correction: $\psi$ scan<br>(North <i>et al.</i> , 1968) | $k = 0 \rightarrow 23$   |
| $T_{\text{min}} = 0.265$ , $T_{\text{max}} = 0.315$                | $l = -19 \rightarrow 18$   |
| 5464 measured reflections  | 3 standard reflections every 120 min<br>intensity decay: none          |

*Refinement*

|   |  |
|---|--|
| Refinement on $F^2$   | Secondary atom site location: difference Fourier<br>map      |
| Least-squares matrix: full  | Hydrogen site location: inferred from<br>neighbouring sites  |
| $R[F^2 > 2\sigma(F^2)] = 0.037$                                   | H-atom parameters constrained                                |
| $wR(F^2) = 0.100$   | $w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 0.9656P]$            |
| $S = 1.00$  | where $P = (F_o^2 + 2F_c^2)/3$                               |
| 5122 reflections  | $(\Delta/\sigma)_{\text{max}} < 0.001$                       |
| 325 parameters  | $\Delta\rho_{\text{max}} = 0.22 \text{ e } \text{\AA}^{-3}$  |
| 0 restraints  | $\Delta\rho_{\text{min}} = -0.29 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant<br>direct methods |  |

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

|     | <i>x</i>     | <i>y</i>      | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|--------------|----------------------------------|
| Ni1 | 0.32898 (5)  | 0.127947 (18) | 0.28825 (2)  | 0.04161 (12)                     |
| P1  | 0.23694 (10) | 0.18930 (4)   | 0.37905 (6)  | 0.0479 (2)                       |
| P2  | 0.39378 (11) | 0.04384 (4)   | 0.21782 (5)  | 0.0479 (2)                       |
| P3  | 0.20240 (11) | 0.13469 (5)   | 0.89133 (6)  | 0.0559 (2)                       |
| O1  | 0.1773 (3)   | 0.13751 (11)  | 0.44521 (15) | 0.0617 (7)                       |
| O2  | 0.3652 (3)   | -0.02228 (10) | 0.27213 (14) | 0.0609 (7)                       |
| N1  | 0.3831 (3)   | 0.19614 (12)  | 0.21502 (16) | 0.0446 (6)                       |
| N2  | 0.4812 (3)   | 0.24504 (14)  | 0.23638 (18) | 0.0568 (7)                       |
| H2A | 0.5305       | 0.2502        | 0.2858       | 0.068*                           |
| F1  | 0.1762 (3)   | -0.08905 (11) | 0.51487 (15) | 0.0953 (8)                       |
| F2  | 0.1974 (3)   | 0.21394 (10)  | 0.87960 (15) | 0.0789 (7)                       |
| F3  | 0.1327 (3)   | 0.14307 (11)  | 0.97561 (13) | 0.0792 (7)                       |
| F4  | 0.0382 (2)   | 0.13121 (10)  | 0.84026 (14) | 0.0761 (6)                       |
| F5  | 0.2707 (3)   | 0.12876 (13)  | 0.80763 (16) | 0.0966 (8)                       |
| F6  | 0.2071 (3)   | 0.05746 (10)  | 0.90361 (15) | 0.0837 (7)                       |
| F7  | 0.3643 (3)   | 0.14096 (13)  | 0.94371 (17) | 0.0969 (8)                       |



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|      |             |               |            |             |
|------|-------------|---------------|------------|-------------|
| C1   | 0.2761 (4)  | 0.05995 (15)  | 0.3580 (2) | 0.0487 (8)  |
| C2   | 0.2103 (4)  | 0.07201 (16)  | 0.4286 (2) | 0.0519 (8)  |
| C3   | 0.1765 (4)  | 0.02385 (18)  | 0.4828 (2) | 0.0658 (10) |
| H3A  | 0.1341      | 0.0340        | 0.5303     | 0.079*      |
| C4   | 0.2087 (5)  | -0.04016 (19) | 0.4630 (2) | 0.0680 (11) |
| C5   | 0.2699 (5)  | -0.05769 (17) | 0.3935 (2) | 0.0650 (10) |
| H5A  | 0.2883      | -0.1017       | 0.3813     | 0.078*      |
| C6   | 0.3028 (4)  | -0.00660 (16) | 0.3426 (2) | 0.0527 (8)  |
| C7   | 0.3621 (4)  | 0.24172 (17)  | 0.4498 (2) | 0.0573 (9)  |
| H7A  | 0.4045      | 0.2751        | 0.4161     | 0.069*      |
| C8   | 0.4897 (5)  | 0.1988 (2)    | 0.4920 (3) | 0.0838 (13) |
| H8A  | 0.5581      | 0.2255        | 0.5291     | 0.126*      |
| H8B  | 0.5413      | 0.1794        | 0.4501     | 0.126*      |
| H8C  | 0.4503      | 0.1643        | 0.5233     | 0.126*      |
| C9   | 0.2836 (5)  | 0.2780 (2)    | 0.5141 (3) | 0.0912 (15) |
| H9A  | 0.3545      | 0.3054        | 0.5487     | 0.137*      |
| H9B  | 0.2422      | 0.2463        | 0.5485     | 0.137*      |
| H9C  | 0.2047      | 0.3051        | 0.4855     | 0.137*      |
| C10  | 0.0709 (4)  | 0.23715 (19)  | 0.3406 (3) | 0.0684 (10) |
| H10A | 0.0314      | 0.2559        | 0.3888     | 0.082*      |
| C11  | 0.1109 (5)  | 0.2940 (2)    | 0.2859 (3) | 0.0895 (14) |
| H11A | 0.0225      | 0.3190        | 0.2659     | 0.134*      |
| H11B | 0.1525      | 0.2765        | 0.2392     | 0.134*      |
| H11C | 0.1831      | 0.3223        | 0.3183     | 0.134*      |
| C12  | -0.0481 (5) | 0.1917 (2)    | 0.2934 (3) | 0.1067 (18) |
| H12A | -0.1359     | 0.2171        | 0.2730     | 0.160*      |
| H12B | -0.0734     | 0.1577        | 0.3304     | 0.160*      |
| H12C | -0.0099     | 0.1717        | 0.2470     | 0.160*      |
| C13  | 0.2776 (4)  | 0.02806 (16)  | 0.1181 (2) | 0.0573 (9)  |
| H13A | 0.3016      | 0.0619        | 0.0786     | 0.069*      |
| C14  | 0.1133 (5)  | 0.0365 (2)    | 0.1272 (3) | 0.0880 (14) |
| H14A | 0.0522      | 0.0287        | 0.0742     | 0.132*      |
| H14B | 0.0968      | 0.0808        | 0.1456     | 0.132*      |
| H14C | 0.0875      | 0.0054        | 0.1677     | 0.132*      |
| C15  | 0.3067 (7)  | -0.0397 (2)   | 0.0809 (3) | 0.1052 (18) |
| H15A | 0.2431      | -0.0450       | 0.0281     | 0.158*      |
| H15B | 0.2856      | -0.0740       | 0.1187     | 0.158*      |
| H15C | 0.4095      | -0.0425       | 0.0727     | 0.158*      |
| C16  | 0.5878 (4)  | 0.03345 (18)  | 0.2048 (2) | 0.0621 (10) |
| H16A | 0.5979      | -0.0099       | 0.1789     | 0.074*      |
| C17  | 0.6377 (5)  | 0.0857 (2)    | 0.1476 (3) | 0.0824 (13) |
| H17A | 0.7405      | 0.0783        | 0.1417     | 0.124*      |
| H17B | 0.6274      | 0.1288        | 0.1713     | 0.124*      |
| H17C | 0.5767      | 0.0832        | 0.0936     | 0.124*      |
| C18  | 0.6859 (5)  | 0.0334 (3)    | 0.2900 (3) | 0.1030 (16) |
| H18A | 0.7886      | 0.0275        | 0.2828     | 0.155*      |
| H18B | 0.6562      | -0.0023       | 0.3233     | 0.155*      |
| H18C | 0.6748      | 0.0747        | 0.3177     | 0.155*      |
| C19  | 0.4934 (5)  | 0.28489 (18)  | 0.1717 (2) | 0.0706 (11) |

|      |            |              |            |             |
|------|------------|--------------|------------|-------------|
| H19A | 0.5543     | 0.3221       | 0.1725     | 0.085*      |
| C20  | 0.4012 (5) | 0.26112 (18) | 0.1053 (2) | 0.0665 (10) |
| H20A | 0.3859     | 0.2782       | 0.0512     | 0.080*      |
| C21  | 0.3346 (4) | 0.20647 (16) | 0.1337 (2) | 0.0535 (9)  |
| H21A | 0.2648     | 0.1800       | 0.1008     | 0.064*      |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$      | $U^{13}$     | $U^{23}$      |
|-----|-------------|-------------|-------------|---------------|--------------|---------------|
| Ni1 | 0.0490 (2)  | 0.0336 (2)  | 0.0428 (2)  | -0.00062 (18) | 0.00846 (17) | -0.00333 (17) |
| P1  | 0.0493 (5)  | 0.0408 (4)  | 0.0564 (5)  | -0.0048 (4)   | 0.0168 (4)   | -0.0095 (4)   |
| P2  | 0.0663 (6)  | 0.0357 (4)  | 0.0420 (5)  | 0.0042 (4)    | 0.0095 (4)   | -0.0027 (3)   |
| P3  | 0.0559 (6)  | 0.0504 (5)  | 0.0615 (6)  | 0.0087 (4)    | 0.0092 (4)   | 0.0069 (4)    |
| O1  | 0.0703 (16) | 0.0510 (14) | 0.0714 (16) | -0.0127 (12)  | 0.0351 (13)  | -0.0105 (12)  |
| O2  | 0.0977 (19) | 0.0355 (12) | 0.0512 (14) | 0.0088 (12)   | 0.0169 (13)  | 0.0017 (10)   |
| N1  | 0.0494 (16) | 0.0355 (14) | 0.0489 (16) | -0.0027 (12)  | 0.0070 (13)  | -0.0046 (11)  |
| N2  | 0.0654 (19) | 0.0532 (16) | 0.0511 (17) | -0.0163 (15)  | 0.0069 (14)  | -0.0071 (14)  |
| F1  | 0.145 (2)   | 0.0653 (15) | 0.0830 (16) | -0.0156 (15)  | 0.0418 (16)  | 0.0215 (13)   |
| F2  | 0.0833 (16) | 0.0520 (12) | 0.0982 (17) | 0.0014 (11)   | 0.0041 (13)  | 0.0099 (12)   |
| F3  | 0.0881 (16) | 0.0868 (16) | 0.0655 (14) | 0.0200 (13)   | 0.0205 (12)  | 0.0081 (12)   |
| F4  | 0.0689 (14) | 0.0729 (14) | 0.0799 (15) | -0.0058 (11)  | -0.0105 (11) | 0.0113 (12)   |
| F5  | 0.119 (2)   | 0.0951 (18) | 0.0864 (17) | 0.0124 (15)   | 0.0492 (15)  | 0.0068 (14)   |
| F6  | 0.1030 (19) | 0.0539 (13) | 0.0971 (18) | 0.0157 (12)   | 0.0244 (14)  | 0.0103 (12)   |
| F7  | 0.0593 (14) | 0.109 (2)   | 0.116 (2)   | 0.0090 (14)   | -0.0080 (13) | 0.0128 (16)   |
| C1  | 0.055 (2)   | 0.0428 (17) | 0.0487 (19) | -0.0047 (15)  | 0.0081 (16)  | -0.0002 (14)  |
| C2  | 0.056 (2)   | 0.0430 (18) | 0.058 (2)   | -0.0083 (16)  | 0.0145 (17)  | -0.0068 (16)  |
| C3  | 0.081 (3)   | 0.063 (2)   | 0.057 (2)   | -0.016 (2)    | 0.024 (2)    | 0.0002 (19)   |
| C4  | 0.086 (3)   | 0.057 (2)   | 0.062 (2)   | -0.016 (2)    | 0.014 (2)    | 0.0118 (19)   |
| C5  | 0.092 (3)   | 0.0413 (19) | 0.063 (2)   | -0.0023 (18)  | 0.014 (2)    | 0.0042 (17)   |
| C6  | 0.070 (2)   | 0.0414 (17) | 0.0461 (19) | -0.0010 (16)  | 0.0062 (17)  | 0.0003 (15)   |
| C7  | 0.064 (2)   | 0.053 (2)   | 0.057 (2)   | -0.0149 (17)  | 0.0145 (17)  | -0.0149 (17)  |
| C8  | 0.075 (3)   | 0.086 (3)   | 0.085 (3)   | -0.015 (2)    | -0.006 (2)   | -0.004 (2)    |
| C9  | 0.117 (4)   | 0.084 (3)   | 0.079 (3)   | -0.018 (3)    | 0.034 (3)    | -0.037 (3)    |
| C10 | 0.056 (2)   | 0.067 (2)   | 0.085 (3)   | 0.0098 (19)   | 0.019 (2)    | -0.015 (2)    |
| C11 | 0.092 (3)   | 0.072 (3)   | 0.104 (4)   | 0.032 (3)     | 0.014 (3)    | 0.007 (3)     |
| C12 | 0.058 (3)   | 0.104 (4)   | 0.149 (5)   | 0.007 (3)     | -0.013 (3)   | -0.032 (3)    |
| C13 | 0.085 (3)   | 0.0400 (18) | 0.0441 (19) | -0.0001 (18)  | 0.0004 (18)  | -0.0052 (15)  |
| C14 | 0.082 (3)   | 0.093 (3)   | 0.083 (3)   | -0.020 (3)    | -0.008 (2)   | -0.007 (3)    |
| C15 | 0.187 (5)   | 0.054 (2)   | 0.064 (3)   | 0.021 (3)     | -0.013 (3)   | -0.025 (2)    |
| C16 | 0.067 (2)   | 0.056 (2)   | 0.064 (2)   | 0.0121 (19)   | 0.0124 (19)  | -0.0068 (18)  |
| C17 | 0.073 (3)   | 0.083 (3)   | 0.098 (3)   | 0.009 (2)     | 0.035 (2)    | 0.004 (3)     |
| C18 | 0.080 (3)   | 0.130 (4)   | 0.094 (4)   | 0.011 (3)     | -0.003 (3)   | 0.013 (3)     |
| C19 | 0.087 (3)   | 0.056 (2)   | 0.072 (3)   | -0.022 (2)    | 0.023 (2)    | 0.004 (2)     |
| C20 | 0.093 (3)   | 0.055 (2)   | 0.051 (2)   | 0.004 (2)     | 0.012 (2)    | 0.0097 (18)   |
| C21 | 0.066 (2)   | 0.0458 (19) | 0.046 (2)   | 0.0012 (17)   | -0.0004 (17) | -0.0013 (15)  |

*Geometric parameters (Å, °)*

|        |           |        |        |
|--------|-----------|--------|--------|
| Ni1—C1 | 1.883 (3) | C8—H8C | 0.9600 |
| Ni1—N1 | 1.925 (2) | C9—H9A | 0.9600 |

|            |             |              |           |
|------------|-------------|--------------|-----------|
| Ni1—P2     | 2.1727 (9)  | C9—H9B       | 0.9600    |
| Ni1—P1     | 2.1779 (9)  | C9—H9C       | 0.9600    |
| P1—O1      | 1.643 (2)   | C10—C11      | 1.525 (5) |
| P1—C10     | 1.814 (4)   | C10—C12      | 1.528 (5) |
| P1—C7      | 1.821 (3)   | C10—H10A     | 0.9800    |
| P2—O2      | 1.639 (2)   | C11—H11A     | 0.9600    |
| P2—C16     | 1.810 (4)   | C11—H11B     | 0.9600    |
| P2—C13     | 1.814 (3)   | C11—H11C     | 0.9600    |
| P3—F6      | 1.571 (2)   | C12—H12A     | 0.9600    |
| P3—F5      | 1.573 (2)   | C12—H12B     | 0.9600    |
| P3—F7      | 1.581 (2)   | C12—H12C     | 0.9600    |
| P3—F4      | 1.587 (2)   | C13—C14      | 1.523 (5) |
| P3—F3      | 1.592 (2)   | C13—C15      | 1.532 (5) |
| P3—F2      | 1.611 (2)   | C13—H13A     | 0.9800    |
| O1—C2      | 1.391 (4)   | C14—H14A     | 0.9600    |
| O2—C6      | 1.380 (4)   | C14—H14B     | 0.9600    |
| N1—C21     | 1.337 (4)   | C14—H14C     | 0.9600    |
| N1—N2      | 1.337 (3)   | C15—H15A     | 0.9600    |
| N2—C19     | 1.336 (4)   | C15—H15B     | 0.9600    |
| N2—H2A     | 0.8600      | C15—H15C     | 0.9600    |
| F1—C4      | 1.355 (4)   | C16—C17      | 1.515 (5) |
| C1—C2      | 1.384 (4)   | C16—C18      | 1.521 (5) |
| C1—C6      | 1.394 (4)   | C16—H16A     | 0.9800    |
| C2—C3      | 1.373 (5)   | C17—H17A     | 0.9600    |
| C3—C4      | 1.373 (5)   | C17—H17B     | 0.9600    |
| C3—H3A     | 0.9300      | C17—H17C     | 0.9600    |
| C4—C5      | 1.370 (5)   | C18—H18A     | 0.9600    |
| C5—C6      | 1.379 (5)   | C18—H18B     | 0.9600    |
| C5—H5A     | 0.9300      | C18—H18C     | 0.9600    |
| C7—C8      | 1.519 (5)   | C19—C20      | 1.344 (5) |
| C7—C9      | 1.530 (5)   | C19—H19A     | 0.9300    |
| C7—H7A     | 0.9800      | C20—C21      | 1.369 (5) |
| C8—H8A     | 0.9600      | C20—H20A     | 0.9300    |
| C8—H8B     | 0.9600      | C21—H21A     | 0.9300    |
|            |             |              |           |
| C1—Ni1—N1  | 178.79 (12) | H8B—C8—H8C   | 109.5     |
| C1—Ni1—P2  | 81.73 (10)  | C7—C9—H9A    | 109.5     |
| N1—Ni1—P2  | 97.11 (8)   | C7—C9—H9B    | 109.5     |
| C1—Ni1—P1  | 81.64 (10)  | H9A—C9—H9B   | 109.5     |
| N1—Ni1—P1  | 99.49 (8)   | C7—C9—H9C    | 109.5     |
| P2—Ni1—P1  | 163.19 (4)  | H9A—C9—H9C   | 109.5     |
| O1—P1—C10  | 103.04 (16) | H9B—C9—H9C   | 109.5     |
| O1—P1—C7   | 101.28 (15) | C11—C10—C12  | 111.9 (4) |
| C10—P1—C7  | 108.00 (18) | C11—C10—P1   | 110.0 (3) |
| O1—P1—Ni1  | 105.77 (9)  | C12—C10—P1   | 109.6 (3) |
| C10—P1—Ni1 | 116.93 (14) | C11—C10—H10A | 108.4     |
| C7—P1—Ni1  | 119.25 (12) | C12—C10—H10A | 108.4     |
| O2—P2—C16  | 101.63 (16) | P1—C10—H10A  | 108.4     |
| O2—P2—C13  | 102.43 (15) | C10—C11—H11A | 109.5     |

|            |             |               |           |
|------------|-------------|---------------|-----------|
| C16—P2—C13 | 108.56 (18) | C10—C11—H11B  | 109.5     |
| O2—P2—Ni1  | 106.24 (9)  | H11A—C11—H11B | 109.5     |
| C16—P2—Ni1 | 119.58 (13) | C10—C11—H11C  | 109.5     |
| C13—P2—Ni1 | 115.87 (12) | H11A—C11—H11C | 109.5     |
| F6—P3—F5   | 91.51 (14)  | H11B—C11—H11C | 109.5     |
| F6—P3—F7   | 90.39 (14)  | C10—C12—H12A  | 109.5     |
| F5—P3—F7   | 90.82 (16)  | C10—C12—H12B  | 109.5     |
| F6—P3—F4   | 91.55 (13)  | H12A—C12—H12B | 109.5     |
| F5—P3—F4   | 90.44 (14)  | C10—C12—H12C  | 109.5     |
| F7—P3—F4   | 177.66 (15) | H12A—C12—H12C | 109.5     |
| F6—P3—F3   | 90.24 (13)  | H12B—C12—H12C | 109.5     |
| F5—P3—F3   | 178.25 (14) | C14—C13—C15   | 111.4 (4) |
| F7—P3—F3   | 89.28 (14)  | C14—C13—P2    | 109.7 (3) |
| F4—P3—F3   | 89.40 (13)  | C15—C13—P2    | 113.2 (3) |
| F6—P3—F2   | 179.49 (15) | C14—C13—H13A  | 107.4     |
| F5—P3—F2   | 88.98 (14)  | C15—C13—H13A  | 107.4     |
| F7—P3—F2   | 89.46 (13)  | P2—C13—H13A   | 107.4     |
| F4—P3—F2   | 88.59 (12)  | C13—C14—H14A  | 109.5     |
| F3—P3—F2   | 89.27 (13)  | C13—C14—H14B  | 109.5     |
| C2—O1—P1   | 112.2 (2)   | H14A—C14—H14B | 109.5     |
| C6—O2—P2   | 111.79 (19) | C13—C14—H14C  | 109.5     |
| C21—N1—N2  | 104.2 (3)   | H14A—C14—H14C | 109.5     |
| C21—N1—Ni1 | 129.7 (2)   | H14B—C14—H14C | 109.5     |
| N2—N1—Ni1  | 126.1 (2)   | C13—C15—H15A  | 109.5     |
| C19—N2—N1  | 111.9 (3)   | C13—C15—H15B  | 109.5     |
| C19—N2—H2A | 124.1       | H15A—C15—H15B | 109.5     |
| N1—N2—H2A  | 124.1       | C13—C15—H15C  | 109.5     |
| C2—C1—C6   | 115.1 (3)   | H15A—C15—H15C | 109.5     |
| C2—C1—Ni1  | 122.9 (2)   | H15B—C15—H15C | 109.5     |
| C6—C1—Ni1  | 121.9 (3)   | C17—C16—C18   | 111.5 (4) |
| C3—C2—C1   | 124.4 (3)   | C17—C16—P2    | 111.9 (3) |
| C3—C2—O1   | 118.4 (3)   | C18—C16—P2    | 109.8 (3) |
| C1—C2—O1   | 117.2 (3)   | C17—C16—H16A  | 107.9     |
| C4—C3—C2   | 116.3 (3)   | C18—C16—H16A  | 107.9     |
| C4—C3—H3A  | 121.9       | P2—C16—H16A   | 107.9     |
| C2—C3—H3A  | 121.9       | C16—C17—H17A  | 109.5     |
| F1—C4—C5   | 118.0 (3)   | C16—C17—H17B  | 109.5     |
| F1—C4—C3   | 117.9 (4)   | H17A—C17—H17B | 109.5     |
| C5—C4—C3   | 124.0 (3)   | C16—C17—H17C  | 109.5     |
| C4—C5—C6   | 116.4 (3)   | H17A—C17—H17C | 109.5     |
| C4—C5—H5A  | 121.8       | H17B—C17—H17C | 109.5     |
| C6—C5—H5A  | 121.8       | C16—C18—H18A  | 109.5     |
| C5—C6—O2   | 118.1 (3)   | C16—C18—H18B  | 109.5     |
| C5—C6—C1   | 123.7 (3)   | H18A—C18—H18B | 109.5     |
| O2—C6—C1   | 118.1 (3)   | C16—C18—H18C  | 109.5     |
| C8—C7—C9   | 111.6 (3)   | H18A—C18—H18C | 109.5     |
| C8—C7—P1   | 107.9 (2)   | H18B—C18—H18C | 109.5     |
| C9—C7—P1   | 113.3 (3)   | N2—C19—C20    | 107.1 (3) |
| C8—C7—H7A  | 107.9       | N2—C19—H19A   | 126.4     |

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|            |       |              |           |
|------------|-------|--------------|-----------|
| C9—C7—H7A  | 107.9 | C20—C19—H19A | 126.4     |
| P1—C7—H7A  | 107.9 | C19—C20—C21  | 105.7 (3) |
| C7—C8—H8A  | 109.5 | C19—C20—H20A | 127.1     |
| C7—C8—H8B  | 109.5 | C21—C20—H20A | 127.1     |
| H8A—C8—H8B | 109.5 | N1—C21—C20   | 111.1 (3) |
| C7—C8—H8C  | 109.5 | N1—C21—H21A  | 124.5     |
| H8A—C8—H8C | 109.5 | C20—C21—H21A | 124.5     |

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