

[*N,N*-Bis(diphenylphosphino)isopropyl-amine]dibromidonickel(II)

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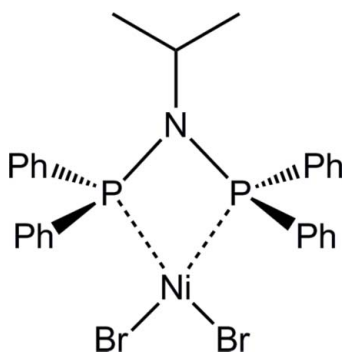
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.036; wR factor = 0.064; data-to-parameter ratio = 23.2.

The title compound, $[\text{NiBr}_2(\text{C}_{27}\text{H}_{27}\text{NP}_2)]$, was synthesized by the reaction of $\text{NiBr}_2(\text{dme})$ (dme is 1,2-dimethoxyethane) with *N,N*-bis(diphenylphosphino)isopropylamine in methanol/tetrahydrofuran. The nickel(II) center is coordinated by two P atoms of the chelating *PNP* ligand, $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, and two bromide ions in a distorted square-planar geometry.

Related literature

For derivatives of the title compound and their structural details, see: Cooley *et al.* (2001); Sushev *et al.* (2005); Sun *et al.* (2006). For structural features of a nickel complex with an arene-bridged bis-*PNP* ligand, see: Majoumo-Mbe *et al.* (2005). For catalytic features of the *PNP* ligand, see: Wöhl *et al.* (2009).



Experimental

Crystal data

| | |
|--|-----------------------------------|
| $[\text{NiBr}_2(\text{C}_{27}\text{H}_{27}\text{NP}_2)]$ | $V = 5153.44$ (19) Å ³ |
| $M_r = 645.97$ | $Z = 8$ |
| Orthorhombic, <i>Pbca</i> | Mo $K\alpha$ radiation |
| $a = 16.6720$ (3) Å | $\mu = 4.00$ mm ⁻¹ |
| $b = 15.1689$ (4) Å | $T = 200$ (2) K |
| $c = 20.3777$ (4) Å | $0.17 \times 0.14 \times 0.04$ mm |

Data collection

| | |
|---|--|
| Stoe IPDS-II diffractometer | 73587 measured reflections |
| Absorption correction: numerical (<i>X-SHAPE</i> ; Stoe & Cie, 2005) | 6956 independent reflections |
| $T_{\min} = 0.484$, $T_{\max} = 0.884$ | 4725 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.080$ |

Refinement

| | |
|---------------------------------|---|
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | 300 parameters |
| $wR(F^2) = 0.064$ | H-atom parameters constrained |
| $S = 0.89$ | $\Delta\rho_{\max} = 0.57$ e Å ⁻³ |
| 6956 reflections | $\Delta\rho_{\min} = -0.43$ e Å ⁻³ |

Data collection: *X-AREA* (Stoe & Cie, 2005); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2764).

References

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supplementary materials

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[*N,N*-Bis(diphenylphosphino)isopropylamine]dibromidonickel(II)

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Comment

Ligands containing the "PNP" moiety as the structural motif of the coordination unit have been used for different purposes in coordination chemistry. During the recent period, they were used with different metals including nickel for investigations into oligomerizations, polymerizations (Cooley *et al.*, 2001) or copolymerizations (Majoumo-Mbe *et al.*, 2005) with ethene or other alkenes (Sun *et al.*, 2006). The Ni(PNP) core was also used for investigations into the reactivity behaviour of the nickel-coordinated HN(PPh₂)₂ ligand (Sushev *et al.*, 2005). During these studies allylation of the N—H yielded a comparable nickel complex to the one that is described here. Dinuclear Ni(PNP)-complexes with arene-bridged PNP units have been prepared that have two independent and structurally identical Ni(PNP) moieties (Majoumo-Mbe *et al.*, 2005).

We became interested in nickel complexes during our studies on the selective oligomerization of ethene *via* transition metal-catalyzed tri- or tetramerization, yielding 1-hexene or 1-octene (Wöhl *et al.*, 2009). Our initial experimental work was focusing on a chromium-based catalyst system (CrCl₃(THF)₃/Ph₂PN(*i*Pr)PPh₂/MAO) and we recently became interested in the kinetic behaviour of this catalyst system, to gain a better understanding of the underlying catalytic mechanism in dependence from different metal/ligand ratios. However, for reasons of comparison we wanted to examine the corresponding nickel complex containing the same simple isopropyl-substituted PNP ligand. We deployed a simple preparation procedure, that is described here, to obtain the complex in high yields for our screening experiments.

The molecular structure of the title compound shows that the Ni^{II} center is coordinated by two P atoms of the chelating Ph₂PN(*i*Pr)PPh₂ ligand and two bromide ions (Fig. 1). Its coordination geometry can be best described as distorted square-planar (P2—Ni1—P1 73.22 (3)°, P1—Ni1—Br1 94.39 (2)°, P2—Ni1—Br2 94.74 (2)°, Br1—Ni1—Br2 98.213 (16)°). Furthermore, the chelating ligand and the metal form a four-membered Ni(PNP) ring which is nearly planar (mean deviation from the best plane defined by Ni1, P1, N1 and P2 atoms is 0.0481 Å).

Experimental

NiBr₂(1,2-dimethoxyethane) (334 mg, 1.08 mmol) was dissolved in dry methanol and heated to 333 K. *N,N*-bis(diphenylphosphino)isopropylamine (462 mg, 1.08 mmol) was dissolved in dry THF and the solution was cannulated into the nickel complex solution under argon. The red solution obtained was stirred for an hour at 333 K and after cooling, the red solid obtained was collected on a glas frit and washed twice with methanol and three times with water and finally with ether. The red solid was dried in high vacuo to yield 645 mg of pure red complex. The identity of the product was proven by ¹H, ¹³C and ³¹P NMR (solvent: CD₂Cl₂). Single crystals suitable for X-ray analysis were grown from a chloroform-diethyl ether solution (2:1).

Refinement

All H atoms were placed in idealized positions with $d(\text{C}-\text{H}) = 0.98$ (CH₃) and $0.95-1.00$ Å (CH) and refined using a riding model with $U_{\text{iso}}(\text{H})$ fixed at $1.5 U_{\text{eq}}(\text{C})$ for CH₃ and $1.2 U_{\text{eq}}(\text{C})$ for CH.

Figures

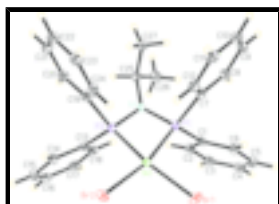


Fig. 1. The molecular structure of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

[*N,N*-Bis(diphenylphosphino)isopropylamine]dibromidonickel(II)

Crystal data

[NiBr₂(C₂₇H₂₇NP₂)]

$M_r = 645.97$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 16.6720$ (3) Å

$b = 15.1689$ (4) Å

$c = 20.3777$ (4) Å

$V = 5153.44$ (19) Å³

$Z = 8$

$F_{000} = 2592$

$D_x = 1.665$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 33195 reflections

$\theta = 2.1-29.5^\circ$

$\mu = 4.00$ mm⁻¹

$T = 200$ K

Prism, red-brown

$0.17 \times 0.14 \times 0.04$ mm

Data collection

Stoe IPDS-II
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 200$ K

rotation method scans

Absorption correction: numerical
(X-SHAPE; Stoe & Cie, 2005)

$T_{\text{min}} = 0.484$, $T_{\text{max}} = 0.884$

73587 measured reflections

6956 independent reflections

4725 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.080$

$\theta_{\text{max}} = 29.3^\circ$

$\theta_{\text{min}} = 2.0^\circ$

$h = -22 \rightarrow 22$

$k = -20 \rightarrow 20$

$l = -27 \rightarrow 27$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.036$$

$$wR(F^2) = 0.064$$

$$S = 0.89$$

6956 reflections

300 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0281P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.57 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| C1 | 0.90625 (17) | 0.87979 (17) | 0.23217 (13) | 0.0230 (5) |
| C2 | 0.88616 (18) | 0.96307 (18) | 0.20951 (14) | 0.0274 (6) |
| H2 | 0.8694 | 0.9707 | 0.1653 | 0.033* |
| C3 | 0.89045 (19) | 1.03524 (19) | 0.25112 (16) | 0.0337 (7) |
| H3 | 0.8760 | 1.0921 | 0.2357 | 0.040* |
| C4 | 0.91578 (19) | 1.0242 (2) | 0.31503 (15) | 0.0354 (7) |
| H4 | 0.9175 | 1.0733 | 0.3439 | 0.043* |
| C5 | 0.9386 (2) | 0.9421 (2) | 0.33713 (15) | 0.0334 (7) |
| H5 | 0.9575 | 0.9353 | 0.3808 | 0.040* |
| C6 | 0.93436 (18) | 0.86966 (19) | 0.29619 (14) | 0.0292 (6) |
| H6 | 0.9505 | 0.8133 | 0.3116 | 0.035* |
| C7 | 0.87114 (17) | 0.69391 (17) | 0.22892 (13) | 0.0227 (5) |
| C8 | 0.81317 (17) | 0.70629 (18) | 0.27757 (13) | 0.0266 (6) |
| H8 | 0.7957 | 0.7640 | 0.2886 | 0.032* |
| C9 | 0.78135 (19) | 0.6339 (2) | 0.30950 (14) | 0.0322 (7) |
| H9 | 0.7416 | 0.6418 | 0.3424 | 0.039* |
| C10 | 0.8074 (2) | 0.5497 (2) | 0.29349 (15) | 0.0366 (7) |
| H10 | 0.7850 | 0.5001 | 0.3153 | 0.044* |
| C11 | 0.8656 (2) | 0.53756 (19) | 0.24623 (16) | 0.0342 (7) |
| H11 | 0.8838 | 0.4798 | 0.2359 | 0.041* |
| C12 | 0.89720 (18) | 0.60961 (17) | 0.21390 (14) | 0.0264 (6) |
| H12 | 0.9371 | 0.6013 | 0.1812 | 0.032* |

supplementary materials

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|------|---------------|---------------|---------------|--------------|
| C13 | 0.92171 (17) | 0.85623 (17) | -0.00596 (13) | 0.0231 (5) |
| C14 | 0.96284 (19) | 0.8386 (2) | -0.06458 (13) | 0.0301 (6) |
| H14 | 0.9826 | 0.7811 | -0.0734 | 0.036* |
| C15 | 0.9743 (2) | 0.9060 (2) | -0.10958 (14) | 0.0377 (7) |
| H15 | 1.0014 | 0.8945 | -0.1497 | 0.045* |
| C16 | 0.9466 (2) | 0.9895 (2) | -0.09623 (15) | 0.0383 (8) |
| H16 | 0.9554 | 1.0354 | -0.1272 | 0.046* |
| C17 | 0.90638 (19) | 1.00777 (19) | -0.03885 (15) | 0.0347 (7) |
| H17 | 0.8876 | 1.0657 | -0.0302 | 0.042* |
| C18 | 0.89349 (18) | 0.94077 (18) | 0.00636 (15) | 0.0274 (6) |
| H18 | 0.8653 | 0.9528 | 0.0459 | 0.033* |
| C19 | 0.88235 (17) | 0.67305 (17) | 0.01232 (13) | 0.0239 (6) |
| C20 | 0.82043 (18) | 0.67961 (19) | -0.03337 (14) | 0.0297 (6) |
| H20 | 0.8025 | 0.7359 | -0.0477 | 0.036* |
| C21 | 0.7852 (2) | 0.6040 (2) | -0.05781 (16) | 0.0362 (7) |
| H21 | 0.7427 | 0.6081 | -0.0887 | 0.043* |
| C22 | 0.8119 (2) | 0.5222 (2) | -0.03737 (16) | 0.0409 (8) |
| H22 | 0.7867 | 0.4705 | -0.0535 | 0.049* |
| C23 | 0.8747 (2) | 0.51497 (19) | 0.00613 (15) | 0.0368 (8) |
| H23 | 0.8935 | 0.4584 | 0.0189 | 0.044* |
| C24 | 0.9107 (2) | 0.59054 (17) | 0.03148 (14) | 0.0295 (6) |
| H24 | 0.9542 | 0.5859 | 0.0615 | 0.035* |
| C25 | 0.75815 (16) | 0.79720 (19) | 0.10263 (13) | 0.0269 (6) |
| H25 | 0.7481 | 0.8093 | 0.0551 | 0.032* |
| C26 | 0.71793 (19) | 0.8703 (2) | 0.14099 (16) | 0.0382 (7) |
| H26A | 0.7308 | 0.8640 | 0.1877 | 0.057* |
| H26B | 0.6597 | 0.8668 | 0.1349 | 0.057* |
| H26C | 0.7373 | 0.9275 | 0.1252 | 0.057* |
| C27 | 0.72121 (18) | 0.7077 (2) | 0.11777 (15) | 0.0355 (7) |
| H27A | 0.7526 | 0.6613 | 0.0963 | 0.053* |
| H27B | 0.6659 | 0.7061 | 0.1015 | 0.053* |
| H27C | 0.7213 | 0.6980 | 0.1653 | 0.053* |
| N1 | 0.84753 (13) | 0.79808 (13) | 0.11239 (10) | 0.0206 (4) |
| P1 | 0.90770 (4) | 0.78459 (4) | 0.17912 (3) | 0.01915 (13) |
| P2 | 0.91702 (4) | 0.77028 (5) | 0.05515 (3) | 0.01925 (12) |
| Ni1 | 1.013681 (19) | 0.761785 (18) | 0.122690 (17) | 0.01868 (7) |
| Br1 | 1.100033 (18) | 0.77856 (2) | 0.211279 (14) | 0.03435 (8) |
| Br2 | 1.108991 (17) | 0.72404 (2) | 0.043377 (14) | 0.03133 (7) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|--------------|-------------|--------------|
| C1 | 0.0219 (14) | 0.0241 (12) | 0.0231 (12) | -0.0011 (11) | 0.0044 (11) | -0.0029 (10) |
| C2 | 0.0303 (16) | 0.0250 (13) | 0.0270 (14) | -0.0001 (11) | 0.0045 (12) | -0.0021 (11) |
| C3 | 0.0303 (16) | 0.0259 (13) | 0.0449 (17) | -0.0008 (12) | 0.0109 (14) | -0.0037 (12) |
| C4 | 0.0292 (17) | 0.0357 (16) | 0.0414 (17) | -0.0099 (13) | 0.0115 (14) | -0.0182 (13) |
| C5 | 0.0347 (18) | 0.0394 (17) | 0.0262 (14) | -0.0058 (13) | 0.0022 (12) | -0.0094 (12) |
| C6 | 0.0306 (16) | 0.0311 (15) | 0.0258 (14) | -0.0013 (12) | 0.0012 (12) | -0.0011 (11) |

| | | | | | | |
|-----|--------------|--------------|--------------|--------------|---------------|---------------|
| C7 | 0.0241 (14) | 0.0227 (12) | 0.0213 (12) | -0.0011 (10) | -0.0034 (10) | 0.0042 (10) |
| C8 | 0.0259 (14) | 0.0289 (14) | 0.0250 (13) | 0.0011 (11) | 0.0007 (11) | 0.0023 (10) |
| C9 | 0.0250 (16) | 0.0439 (17) | 0.0277 (15) | -0.0039 (13) | 0.0029 (12) | 0.0095 (12) |
| C10 | 0.0344 (18) | 0.0400 (17) | 0.0354 (16) | -0.0123 (14) | -0.0077 (14) | 0.0151 (13) |
| C11 | 0.0381 (18) | 0.0251 (13) | 0.0394 (17) | -0.0028 (13) | -0.0101 (15) | 0.0030 (13) |
| C12 | 0.0302 (16) | 0.0229 (12) | 0.0262 (13) | -0.0005 (11) | -0.0015 (13) | 0.0016 (10) |
| C13 | 0.0204 (14) | 0.0257 (13) | 0.0231 (12) | -0.0043 (10) | -0.0036 (11) | 0.0051 (10) |
| C14 | 0.0333 (17) | 0.0350 (15) | 0.0219 (13) | -0.0046 (12) | 0.0019 (12) | 0.0024 (11) |
| C15 | 0.0383 (19) | 0.0511 (18) | 0.0238 (15) | -0.0095 (14) | -0.0015 (13) | 0.0090 (12) |
| C16 | 0.0344 (18) | 0.0447 (18) | 0.0357 (16) | -0.0137 (14) | -0.0132 (14) | 0.0201 (14) |
| C17 | 0.0291 (16) | 0.0302 (14) | 0.0450 (18) | -0.0040 (12) | -0.0141 (15) | 0.0112 (13) |
| C18 | 0.0218 (15) | 0.0293 (14) | 0.0313 (15) | 0.0000 (11) | -0.0055 (12) | 0.0017 (11) |
| C19 | 0.0256 (15) | 0.0248 (13) | 0.0214 (12) | -0.0031 (10) | 0.0052 (11) | -0.0032 (10) |
| C20 | 0.0270 (15) | 0.0336 (14) | 0.0285 (14) | -0.0015 (12) | 0.0010 (12) | -0.0080 (11) |
| C21 | 0.0280 (17) | 0.0457 (18) | 0.0349 (16) | -0.0097 (13) | 0.0010 (13) | -0.0152 (14) |
| C22 | 0.042 (2) | 0.0386 (17) | 0.0425 (18) | -0.0196 (15) | 0.0107 (16) | -0.0170 (14) |
| C23 | 0.051 (2) | 0.0252 (15) | 0.0342 (16) | -0.0063 (13) | 0.0137 (15) | -0.0042 (12) |
| C24 | 0.0395 (18) | 0.0235 (13) | 0.0256 (13) | 0.0011 (12) | 0.0028 (13) | -0.0013 (11) |
| C25 | 0.0169 (13) | 0.0370 (15) | 0.0269 (13) | 0.0022 (11) | -0.0018 (10) | 0.0029 (11) |
| C26 | 0.0249 (16) | 0.0482 (18) | 0.0414 (18) | 0.0097 (13) | 0.0035 (13) | -0.0029 (14) |
| C27 | 0.0255 (15) | 0.0466 (17) | 0.0345 (15) | -0.0115 (12) | -0.0005 (13) | 0.0015 (14) |
| N1 | 0.0174 (11) | 0.0243 (10) | 0.0200 (11) | 0.0023 (8) | -0.0007 (8) | 0.0002 (8) |
| P1 | 0.0200 (3) | 0.0191 (3) | 0.0183 (3) | 0.0005 (3) | 0.0009 (2) | -0.0003 (2) |
| P2 | 0.0198 (3) | 0.0197 (3) | 0.0183 (3) | -0.0001 (3) | -0.0003 (2) | -0.0003 (2) |
| Ni1 | 0.01720 (14) | 0.01814 (14) | 0.02069 (13) | 0.00026 (11) | 0.00008 (15) | 0.00020 (13) |
| Br1 | 0.03006 (16) | 0.03626 (16) | 0.03674 (15) | 0.00651 (14) | -0.01348 (13) | -0.00788 (13) |
| Br2 | 0.02687 (15) | 0.03284 (14) | 0.03429 (14) | 0.00272 (13) | 0.00987 (12) | -0.00076 (12) |

Geometric parameters (Å, °)

| | | | |
|--------|-----------|---------|-----------|
| C1—C2 | 1.386 (4) | C17—C18 | 1.389 (4) |
| C1—C6 | 1.395 (4) | C17—H17 | 0.95 |
| C1—P1 | 1.804 (3) | C18—H18 | 0.95 |
| C2—C3 | 1.387 (4) | C19—C20 | 1.394 (4) |
| C2—H2 | 0.95 | C19—C24 | 1.394 (4) |
| C3—C4 | 1.379 (5) | C19—P2 | 1.809 (3) |
| C3—H3 | 0.95 | C20—C21 | 1.382 (4) |
| C4—C5 | 1.378 (5) | C20—H20 | 0.95 |
| C4—H4 | 0.95 | C21—C22 | 1.381 (5) |
| C5—C6 | 1.381 (4) | C21—H21 | 0.95 |
| C5—H5 | 0.95 | C22—C23 | 1.376 (5) |
| C6—H6 | 0.95 | C22—H22 | 0.95 |
| C7—C12 | 1.385 (4) | C23—C24 | 1.393 (4) |
| C7—C8 | 1.397 (4) | C23—H23 | 0.95 |
| C7—P1 | 1.815 (3) | C24—H24 | 0.95 |
| C8—C9 | 1.382 (4) | C25—N1 | 1.504 (3) |
| C8—H8 | 0.95 | C25—C26 | 1.514 (4) |
| C9—C10 | 1.388 (5) | C25—C27 | 1.522 (4) |
| C9—H9 | 0.95 | C25—H25 | 1.00 |

supplementary materials

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|-------------|-----------|---------------|-------------|
| C10—C11 | 1.379 (5) | C26—H26A | 0.98 |
| C10—H10 | 0.95 | C26—H26B | 0.98 |
| C11—C12 | 1.381 (4) | C26—H26C | 0.98 |
| C11—H11 | 0.95 | C27—H27A | 0.98 |
| C12—H12 | 0.95 | C27—H27B | 0.98 |
| C13—C18 | 1.389 (4) | C27—H27C | 0.98 |
| C13—C14 | 1.403 (4) | N1—P2 | 1.697 (2) |
| C13—P2 | 1.805 (3) | N1—P1 | 1.702 (2) |
| C14—C15 | 1.387 (4) | P1—Ni1 | 2.1364 (7) |
| C14—H14 | 0.95 | P1—P2 | 2.5402 (9) |
| C15—C16 | 1.376 (5) | P2—Ni1 | 2.1231 (7) |
| C15—H15 | 0.95 | Ni1—Br1 | 2.3230 (4) |
| C16—C17 | 1.376 (5) | Ni1—Br2 | 2.3377 (4) |
| C16—H16 | 0.95 | | |
| C2—C1—C6 | 119.6 (3) | C19—C20—H20 | 120.1 |
| C2—C1—P1 | 122.2 (2) | C22—C21—C20 | 120.0 (3) |
| C6—C1—P1 | 117.9 (2) | C22—C21—H21 | 120.0 |
| C1—C2—C3 | 120.2 (3) | C20—C21—H21 | 120.0 |
| C1—C2—H2 | 119.9 | C23—C22—C21 | 120.7 (3) |
| C3—C2—H2 | 119.9 | C23—C22—H22 | 119.6 |
| C4—C3—C2 | 119.8 (3) | C21—C22—H22 | 119.6 |
| C4—C3—H3 | 120.1 | C22—C23—C24 | 120.1 (3) |
| C2—C3—H3 | 120.1 | C22—C23—H23 | 120.0 |
| C5—C4—C3 | 120.2 (3) | C24—C23—H23 | 120.0 |
| C5—C4—H4 | 119.9 | C23—C24—C19 | 119.2 (3) |
| C3—C4—H4 | 119.9 | C23—C24—H24 | 120.4 |
| C4—C5—C6 | 120.5 (3) | C19—C24—H24 | 120.4 |
| C4—C5—H5 | 119.8 | N1—C25—C26 | 111.4 (2) |
| C6—C5—H5 | 119.8 | N1—C25—C27 | 112.5 (2) |
| C5—C6—C1 | 119.6 (3) | C26—C25—C27 | 111.7 (3) |
| C5—C6—H6 | 120.2 | N1—C25—H25 | 107.0 |
| C1—C6—H6 | 120.2 | C26—C25—H25 | 107.0 |
| C12—C7—C8 | 119.9 (2) | C27—C25—H25 | 107.0 |
| C12—C7—P1 | 118.1 (2) | C25—C26—H26A | 109.5 |
| C8—C7—P1 | 121.8 (2) | C25—C26—H26B | 109.5 |
| C9—C8—C7 | 119.5 (3) | H26A—C26—H26B | 109.5 |
| C9—C8—H8 | 120.2 | C25—C26—H26C | 109.5 |
| C7—C8—H8 | 120.2 | H26A—C26—H26C | 109.5 |
| C8—C9—C10 | 120.0 (3) | H26B—C26—H26C | 109.5 |
| C8—C9—H9 | 120.0 | C25—C27—H27A | 109.5 |
| C10—C9—H9 | 120.0 | C25—C27—H27B | 109.5 |
| C11—C10—C9 | 120.5 (3) | H27A—C27—H27B | 109.5 |
| C11—C10—H10 | 119.7 | C25—C27—H27C | 109.5 |
| C9—C10—H10 | 119.7 | H27A—C27—H27C | 109.5 |
| C10—C11—C12 | 119.7 (3) | H27B—C27—H27C | 109.5 |
| C10—C11—H11 | 120.1 | C25—N1—P2 | 125.69 (17) |
| C12—C11—H11 | 120.1 | C25—N1—P1 | 133.53 (17) |
| C11—C12—C7 | 120.4 (3) | P2—N1—P1 | 96.71 (11) |
| C11—C12—H12 | 119.8 | N1—P1—C1 | 112.00 (12) |

| | | | |
|-----------------|------------|----------------|--------------|
| C7—C12—H12 | 119.8 | N1—P1—C7 | 109.87 (12) |
| C18—C13—C14 | 119.7 (3) | C1—P1—C7 | 105.49 (12) |
| C18—C13—P2 | 121.8 (2) | N1—P1—Ni1 | 94.41 (8) |
| C14—C13—P2 | 118.1 (2) | C1—P1—Ni1 | 117.60 (9) |
| C15—C14—C13 | 119.3 (3) | C7—P1—Ni1 | 117.13 (9) |
| C15—C14—H14 | 120.3 | C1—P1—P2 | 131.69 (9) |
| C13—C14—H14 | 120.3 | C7—P1—P2 | 120.79 (9) |
| C16—C15—C14 | 120.1 (3) | Ni1—P1—P2 | 53.15 (2) |
| C16—C15—H15 | 119.9 | N1—P2—C13 | 108.92 (12) |
| C14—C15—H15 | 119.9 | N1—P2—C19 | 108.43 (12) |
| C15—C16—C17 | 121.1 (3) | C13—P2—C19 | 105.66 (13) |
| C15—C16—H16 | 119.4 | N1—P2—Ni1 | 95.03 (8) |
| C17—C16—H16 | 119.4 | C13—P2—Ni1 | 117.27 (9) |
| C16—C17—C18 | 119.5 (3) | C19—P2—Ni1 | 120.40 (10) |
| C16—C17—H17 | 120.3 | C13—P2—P1 | 128.84 (9) |
| C18—C17—H17 | 120.3 | C19—P2—P1 | 122.01 (9) |
| C17—C18—C13 | 120.2 (3) | Ni1—P2—P1 | 53.63 (2) |
| C17—C18—H18 | 119.9 | P2—Ni1—P1 | 73.22 (3) |
| C13—C18—H18 | 119.9 | P2—Ni1—Br1 | 165.35 (2) |
| C20—C19—C24 | 120.2 (3) | P1—Ni1—Br1 | 94.39 (2) |
| C20—C19—P2 | 120.1 (2) | P2—Ni1—Br2 | 94.74 (2) |
| C24—C19—P2 | 119.2 (2) | P1—Ni1—Br2 | 166.90 (3) |
| C21—C20—C19 | 119.7 (3) | Br1—Ni1—Br2 | 98.213 (16) |
| C21—C20—H20 | 120.1 | | |
| C6—C1—C2—C3 | -3.0 (4) | C25—N1—P2—C13 | 72.5 (2) |
| P1—C1—C2—C3 | -176.2 (2) | P1—N1—P2—C13 | -127.71 (12) |
| C1—C2—C3—C4 | 0.8 (4) | C25—N1—P2—C19 | -42.0 (2) |
| C2—C3—C4—C5 | 1.6 (5) | P1—N1—P2—C19 | 117.77 (12) |
| C3—C4—C5—C6 | -1.8 (5) | C25—N1—P2—Ni1 | -166.4 (2) |
| C4—C5—C6—C1 | -0.4 (5) | P1—N1—P2—Ni1 | -6.62 (9) |
| C2—C1—C6—C5 | 2.7 (4) | C25—N1—P2—P1 | -159.8 (3) |
| P1—C1—C6—C5 | 176.2 (2) | C18—C13—P2—N1 | 19.8 (3) |
| C12—C7—C8—C9 | -1.1 (4) | C14—C13—P2—N1 | -167.1 (2) |
| P1—C7—C8—C9 | 173.4 (2) | C18—C13—P2—C19 | 136.1 (2) |
| C7—C8—C9—C10 | 0.4 (4) | C14—C13—P2—C19 | -50.8 (3) |
| C8—C9—C10—C11 | 0.6 (5) | C18—C13—P2—Ni1 | -86.5 (2) |
| C9—C10—C11—C12 | -1.0 (5) | C14—C13—P2—Ni1 | 86.6 (2) |
| C10—C11—C12—C7 | 0.3 (5) | C18—C13—P2—P1 | -22.7 (3) |
| C8—C7—C12—C11 | 0.7 (4) | C14—C13—P2—P1 | 150.41 (18) |
| P1—C7—C12—C11 | -174.0 (2) | C20—C19—P2—N1 | 74.3 (2) |
| C18—C13—C14—C15 | -0.3 (4) | C24—C19—P2—N1 | -97.5 (2) |
| P2—C13—C14—C15 | -173.6 (2) | C20—C19—P2—C13 | -42.4 (3) |
| C13—C14—C15—C16 | 0.9 (5) | C24—C19—P2—C13 | 145.9 (2) |
| C14—C15—C16—C17 | -0.8 (5) | C20—C19—P2—Ni1 | -178.12 (19) |
| C15—C16—C17—C18 | 0.0 (5) | C24—C19—P2—Ni1 | 10.1 (3) |
| C16—C17—C18—C13 | 0.7 (4) | C20—C19—P2—P1 | 118.2 (2) |
| C14—C13—C18—C17 | -0.5 (4) | C24—C19—P2—P1 | -53.5 (3) |
| P2—C13—C18—C17 | 172.5 (2) | C1—P1—P2—N1 | -75.63 (17) |
| C24—C19—C20—C21 | 2.4 (4) | C7—P1—P2—N1 | 85.67 (15) |

supplementary materials

| | | | |
|-----------------|--------------|----------------|--------------|
| P2—C19—C20—C21 | -169.3 (2) | Ni1—P1—P2—N1 | -171.81 (11) |
| C19—C20—C21—C22 | -0.6 (5) | N1—P1—P2—C13 | 73.89 (16) |
| C20—C21—C22—C23 | -1.5 (5) | C1—P1—P2—C13 | -1.73 (18) |
| C21—C22—C23—C24 | 1.8 (5) | C7—P1—P2—C13 | 159.56 (16) |
| C22—C23—C24—C19 | 0.1 (5) | Ni1—P1—P2—C13 | -97.92 (12) |
| C20—C19—C24—C23 | -2.2 (4) | N1—P1—P2—C19 | -81.89 (16) |
| P2—C19—C24—C23 | 169.6 (2) | C1—P1—P2—C19 | -157.52 (17) |
| C26—C25—N1—P2 | -146.0 (2) | C7—P1—P2—C19 | 3.78 (16) |
| C27—C25—N1—P2 | 87.8 (3) | Ni1—P1—P2—C19 | 106.30 (12) |
| C26—C25—N1—P1 | 62.3 (3) | N1—P1—P2—Ni1 | 171.81 (11) |
| C27—C25—N1—P1 | -64.0 (3) | C1—P1—P2—Ni1 | 96.18 (13) |
| C25—N1—P1—C1 | -74.0 (3) | C7—P1—P2—Ni1 | -102.52 (11) |
| P2—N1—P1—C1 | 128.73 (12) | N1—P2—Ni1—P1 | 5.46 (7) |
| C25—N1—P1—C7 | 42.9 (3) | C13—P2—Ni1—P1 | 119.77 (11) |
| P2—N1—P1—C7 | -114.38 (12) | C19—P2—Ni1—P1 | -109.35 (10) |
| C25—N1—P1—Ni1 | 163.8 (2) | N1—P2—Ni1—Br1 | -27.65 (13) |
| P2—N1—P1—Ni1 | 6.57 (9) | C13—P2—Ni1—Br1 | 86.66 (14) |
| C25—N1—P1—P2 | 157.2 (3) | C19—P2—Ni1—Br1 | -142.46 (12) |
| C2—C1—P1—N1 | -23.8 (3) | P1—P2—Ni1—Br1 | -33.12 (10) |
| C6—C1—P1—N1 | 162.9 (2) | N1—P2—Ni1—Br2 | -179.80 (7) |
| C2—C1—P1—C7 | -143.3 (2) | C13—P2—Ni1—Br2 | -65.49 (11) |
| C6—C1—P1—C7 | 43.4 (3) | C19—P2—Ni1—Br2 | 65.39 (10) |
| C2—C1—P1—Ni1 | 84.0 (3) | P1—P2—Ni1—Br2 | 174.74 (2) |
| C6—C1—P1—Ni1 | -89.3 (2) | N1—P1—Ni1—P2 | -5.44 (7) |
| C2—C1—P1—P2 | 20.1 (3) | C1—P1—Ni1—P2 | -123.10 (10) |
| C6—C1—P1—P2 | -153.19 (18) | C7—P1—Ni1—P2 | 109.55 (10) |
| C12—C7—P1—N1 | 87.2 (2) | N1—P1—Ni1—Br1 | 166.59 (7) |
| C8—C7—P1—N1 | -87.4 (2) | C1—P1—Ni1—Br1 | 48.93 (10) |
| C12—C7—P1—C1 | -151.9 (2) | C7—P1—Ni1—Br1 | -78.41 (10) |
| C8—C7—P1—C1 | 33.5 (3) | P2—P1—Ni1—Br1 | 172.04 (2) |
| C12—C7—P1—Ni1 | -18.9 (3) | N1—P1—Ni1—Br2 | -29.24 (14) |
| C8—C7—P1—Ni1 | 166.51 (19) | C1—P1—Ni1—Br2 | -146.90 (13) |
| C12—C7—P1—P2 | 42.5 (3) | C7—P1—Ni1—Br2 | 85.76 (14) |
| C8—C7—P1—P2 | -132.1 (2) | P2—P1—Ni1—Br2 | -23.79 (11) |

Fig. 1

