In the final refinement there were no correlations between structural parameters above 35%. Refined atomic parameters are given in Table 1 with selected interatomic contact distances and angles in Table 2. The final difference profile is shown in Fig. 1* with views of the structure shown in Fig. 2.

Related literature. The structure determination of stoichiometric $KCuO_2$ has been reported previously (Hestermann & Hoppe, 1969; Brese, O'Keeffe, von Dreele & Young, 1989). Electrical and magnetic data for the title compound are presented elsewhere (Pienkowski *et al.*, 1992).

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* A list of primary diffraction data, *i.e.* the numerical intensity of each measured point on the profile as a function of scattering angle, has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54711 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0076]

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Structure of Orthorhombic $NbPO_5$

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Abstract. Niobium phosphate, $M_r = 203.88$, orthorhombic, *Pnma*, $a = 11.304\,(2)$, $b = 5.316\,(2)$, $c = 6.640\,(2)$ Å, $V = 399.0\,(3)$ Å^3, $Z = 4$, $D_x = 3.39$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0.71069$ Å, $\mu = 31.8$ cm^{-1}, $F(000) = 384$, $T = 296$ K, $R = 0.030$, $wR = 0.043$ for 462 unique reflections ($R_{\text{int}} = 0.017$) with $F_o^2 > 3\sigma(F_o^2)$. The framework is built up from NbO_6 octahedra and PO_4 tetrahedra. The NbO_6 octahedra share opposite corners to form infinite zigzag chains along the *b* axis. These parallel octahedral chains are interconnected to each other *via* corner-sharing PO_4 tetrahedra.

Experimental. Gem-shaped crystals of $NbPO_5$ were obtained from a reaction in the K–Nb–P–O system. The single crystals were grown at 1375 K from a reaction with the target composition $KNb_{12}P_6O_{33}$. A crystal, with average dimensions $0.15 \times 0.1 \times 0.05$ mm, was selected for indexing and intensity data collection. Diffraction data were collected by an ω scan ($4°\omega$ min^{-1}, $\pm 0.45°$ in ω) at room temperature on a Rigaku AFC5S four-circle diffractometer equipped with a graphite monochromator. The unit-cell parameters and the orientation matrix for data collection were determined by the least-squares fit of 25 peak maxima with $7 < 2\theta < 27°$. There was no detectable decay during the data collection according to the intensities of three standard reflections ($\bar{1}\bar{2}\bar{1}$, $\bar{1}\bar{1}\bar{1}$, $\bar{3}\bar{3}\bar{1}$) measured every 100 reflections. Total of 1043 reflections ($0 \le h \le 14$, $-6 \le k \le 6$, $0 \le l \le 8$; $2\theta_{\max} = 55°$) were measured, of which 839 reflections were observed. The *TEXSAN* (Molecular Structure Corporation, 1989) software package was used for the crystal structure solution and refinement. The systematic extinction conditions, ($0kl$): $k + l \ne 2n$ and ($hk0$): $h \ne 2n$, led to two possible space groups, $Pn2_1a$ (No. 33) and *Pnma* (No. 62). The final space group, *Pnma*, was determined by successful structure refinement using the program *PROCESS*. Lorentz–polarization and empirical absorption corrections (transmission range 0.94–1.00) based on three azimuthal scans ($2\theta = 16.37$, 23.09, 23.90°) were

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applied to the intensity data. The atomic coordinates were found using the direct Patterson method and are listed in Table 1.† A correction for secondary extinction was applied [9(1) × 10^{-7}]; $|F_c| = K^{-1}|F_\sigma|[x^* + (1 + x^{*2})^{1/2}]^{1/2}$, x^* is the value of x corresponding to a replacement of $|F_c|$ by $K^{-1}|F_\sigma|$ (Zachariasen, 1968). The structure and thermal parameters were then refined by full-matrix least-squares methods based on F^2 of a unique data set to $R = 0.030$, $wR = 0.043$ and $S = 1.90$ for 41 variables, $w = [\sigma^2(F_o)]^{-1}$, $(\Delta/\sigma)_{max} = 0.02$. The maximum and minimum residual electron densities in the final difference Fourier map were 1.45 and −2.63 e Å^{-3} respectively. Scattering factors from Cromer & Waber (1974).

The title compound $NbPO_5$ crystallizes in the orthorhombic crystal system and axial photographs of the single crystal showed no sign of a superlattice. A projection onto the *ab* plane of the structure of $NbPO_5$ is shown in Fig. 1. The structure is built up of NbO_6 octahedra and PO_4 tetrahedra. The four oxygen atoms, O(2), 2 × O(3), O(4), of a PO_4 tetrahedron corner share with four NbO_6 octahedra. The remaining two oxygen atoms, 2 × O(1), are oxo oxygens, and are available for Nb—O—Nb bonding between neighboring NbO_6 octahedra. A resultant zigzag chain of NbO_6 octahedra can be observed running along the *b* axis. The parallel corner-sharing NbO_6 octahedral chains are interconnected through the PO_4 tetrahedra to form a three-dimensional framework with an Nb:P ratio of 1:1.

Related literature. The orthorhombic cell of $NbPO_5$ was first indexed by Levin & Roth (1970) using powder X-ray diffraction methods. The present study reports the single-crystal structure and details of the bond distances for orthorhombic $NbPO_5$. A monoclinic cell for $NbPO_5$ was first proposed by Chahboun, Groult, Hervieu & Raveau (1986) using electron diffraction. A single-crystal structure analysis by LeClaire, Chahboun, Groult & Raveau (1986) confirmed the monoclinic cell based on the space group $P2_1/c$ (No. 14). The structure reported here and the monoclinic form are very similar. These two unit cells are related to each other by the following transformation matrix (o = orthorhombic, m = monoclinic):

$$\begin{pmatrix} 101 \\ 010 \\ 002 \end{pmatrix} \begin{pmatrix} a_o \\ b_o \\ c_o \end{pmatrix} = \begin{pmatrix} a_m \\ a_m \\ a_m \end{pmatrix}.$$

Table 1. *Positional and isotropic thermal parameters for* $NbPO_5$

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $B_{eq} = (8\pi^2/3)$ trace **U**.

	Wyckoff notation	x	y	z	B_{eq}(Å^2)
Nb	4(*c*)	0.43757 (5)	$\frac{1}{4}$	0.33111 (9)	0.58 (3)
P	4(*c*)	0.1544 (2)	$\frac{1}{4}$	0.5282 (2)	0.59 (6)
O(1)	4(*a*)	0	0	0	2.5 (3)
O(2)	4(*c*)	0.0818 (5)	$\frac{1}{4}$	0.3353 (8)	1.7 (2)
O(3)	8(*d*)	0.1287 (4)	0.018 (1)	0.6477 (7)	3.9 (2)
O(4)	4(*c*)	0.2852 (4)	$\frac{1}{4}$	0.4719 (8)	1.1 (2)

Table 2. *Selected bond distances* (Å) *for* NbO_6 *and* PO_4 *in* $NbPO_5$

NbO_6 octahedron		PO_4 tetrahedron	
Nb—O($1^{i,ii}$)	1.8764 (4) (2×)	P—O(2)	1.519 (4)
Nb—O(2^{i})	1.973 (4)	P—O(3^{v})	1.499 (3) (2×)
Nb—O($3^{iii,iv}$)	2.015 (3) (2×)	P—O(4)	1.523 (4)
Nb—O(4)	1.959 (4)		

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (iii) $\frac{1}{2}-x, -y, z-\frac{1}{2}$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (v) $x, \frac{1}{2}-y, z$.

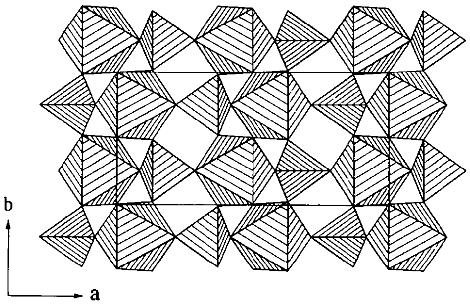

Fig. 1. Projection onto the *ab* plane of the structure of orthorhombic $NbPO_5$.

The bond distances (Table 2) are comparable to those observed in the monoclinic cell except for the P—O(3) bonds which are significantly shorter.

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Structure of an Iridium Bis(phosphine)diene Complex, a Catalyst for Homogeneous Hydrogenation

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Abstract. (η^4-1,5-Cyclooctadiene)bis(triphenylphosphine)iridium(I) hexafluorophosphate, $[Ir(C_8H_{12})(PPh_3)_2][PF_6]$, $C_{44}H_{42}F_6IrP_3.0.5CH_2Cl_2$, $M_r = 1012.4$, monoclinic, $P2_1/c$, $a = 11.666\,(1)$, $b = 18.885\,(3)$, $c = 19.492\,(2)$ Å, $\beta = 97.07\,(1)°$, $V = 4261.7$ Å^3, $Z = 4$, $D_x = 1.58$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 33.5$ cm^{-1}, $F(000) = 2012$, $T = 295$ K, $R = 0.050$, $wR = 0.070$ for 5438 observed reflections with $|F^2| > 2\sigma(F^2)$. The geometry at iridium is approximately square planar, but the iridium—phosphorus bond lengths are significantly different: Ir—P1 2.367 (2), Ir—P2 2.326 (3) Å, P1—Ir—P2 = 94.3 (1), $M1$—Ir—P1 = 90.5, $M1$—Ir—$M2$ = 83.3, $M2$—Ir—P2 = 93.2° ($M1$ and $M2$ are the mid-points of the C1—C2 and C5—C6 bonds).

Experimental. The complex was prepared by the addition of triphenylphosphine to $[Ir(cod)(py)_2][PF_6]$ (Crabtree & Moorehouse, 1986) and well formed prismatic crystals obtained by diffusion of ether into a solution in dichloromethane (cod = 1,5-cyclooctadiene, py = pyridine). Lattice parameters were derived from the setting angles for 25 reflections with $7.5 < \theta < 9.7°$. Data collected using a crystal *ca* 0.25 × 0.25 × 0.25 mm, on an Enraf–Nonius CAD-4 diffractometer, monochromated Mo $K\alpha$ radiation in the θ—2θ mode, with $\Delta\theta = (0.8 + 0.35\tan\theta)°$ and a maximum scan time of 1 min. A total of 8119 measured reflections for $2 < \theta < 25°$ and h 0→13, k 0→22, l −23→23, 7737 unique reflections, $R_{int} = 0.017$, and 5438 observed reflections with $|F^2| > 2\sigma(F^2)$, where $\sigma(F^2) = \{\sigma^2(I) + (0.041I)^2\}^{1/2}/\text{Lp}$, were used in the refinement. Two reference reflections remeasured every hour showed 14% decay, for which a correction was made. An absorption correction was applied using *DIFABS* (Walker & Stuart, 1983), after isotropic refinement, and gave maximum and minimum corrections of 1.14 and 0.81. Lorentz and polarization corrections were made. The structure was solved by routine heavy-atom methods and non-H atoms refined anisotropically by full-matrix least squares. H atoms were held fixed at calculated positions with $U_{iso} = 1.3\,U_{eq}$ for the atoms to which they are bonded. Solvent CH_2Cl_2 at half occupancy and disordered, modelled with two Cl atoms disordered over three sites and H atoms omitted. With a weighting scheme of $w = 1/\sigma^2(F)$, $\sum w(|F_o| - |F_c|)^2$ minimized, the final residuals were $R = 0.050$ and $wR = 0.070$, 5438 observed reflections, 503 variables, $S = 2.0$, $(\Delta/\sigma)_{max} = 0.01$, $\Delta\rho_{max} = 1.9$, $\Delta\rho_{min} = -0.9$ e Å^{-3} near the disordered solvent molecule. Programs from the Enraf–Nonius *SDP-Plus* (Frenz, 1984) package were run on a MicroVAX computer, drawing by *ORTEP*II (Johnson, 1976). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Atomic parameters are given in Table 1,* selected intramolecular bond distances and angles in Table 2. Fig. 1 shows the molecular structure and the numbering scheme. A packing diagram is given in Fig. 2.

Related literature. This complex has proved to be useful as a hydrogenation catalyst (Abbassioun

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* Lists of structure factors, anisotropic temperature factors, H-atom parameters, complete intramolecular distances and angles, least-squares planes and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54634 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0495]

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