structure. The V atom is bonded to three O atoms of the water molecules, and one N and three O donor atoms of the nta ligand, which acts as a tetradentate ligand. The geometry around the V atom can be described as a capped octahedral seven-coordinate structure rather than a capped trigonal prismatic structure as adopted by V^{III} complexes with a capped water molecule and a hexadentate ligand, $[V(L)(H_2O)]^{n-}$ [L: ethylenediaminetetraacetato, edta (Shimoi, Saito & Ogino, 1989); N'-(2-hydroxyethyl)ethylenediamine-N,N,N'-triacetato, hedtra (Ogino, Shimoi & Saito, 1989); and trans-1,2-cyclohexanediamine-N,N,N',N'-tetraacetato, cydta (Shimoi, Miyamoto & Ogino, 1991)]. The triangular faces are the O(1)—O(3)—O(5) and O(7)—O(8)—O(9) planes, and they almost form equilateral triangles [each angle is 58.4 (1)–62.0 (1)°; average 60.0°], although the O(1)—O(3)—O(5) plane [bond distance of O(m)—O(n): m,n = 1,3, 3.466 (5); 1,5, 3.387 (4); and 3,5, 3.346 (4) Å] is larger than the O(7)—O(8)—O(9) plane [m,n = 7,8, 2.767 (5); 7,9, 2.833 (5); and 8,9, 2.811 (4) Å]. The N donor atom is placed on the O(1)—O(3)—O(5) triangular face. Furthermore, two triangular faces are almost parallel [dihedral angles: 2 (1)° for the O(1)—O(3)—O(5) and O(7)—O(8)—O(9) planes], and rotate about 60° around the V—N axis, to which two faces are perpendicular [dihedral angles between the V—N—O(m)—O(n) (m,n = 1,7; 3,8; and 5,9) planes are 57.1 (1), 60.0 (1) and 62.8 (1)° respectively], as shown in Fig. 2. The distances from the O(1)—O(3)—O(5) plane to the V and N atoms are 0.5829 (6) and 1.639 (3) Å, respectively, and that from the V atom to the O(7)—O(8)—O(9) plane is 1.3292 (6) Å. This

indicates that the V atom is pulled from the centre of the octahedron toward the capping N atom. These structural characteristics differ from those of V^{III} complexes with a capped water molecule and a hexadentate ligand, $[V(L)(H_2O)]^{n-}$ (L = hedtra, edta and cydta), in which two triangular faces are formed by two O atoms and one N atom in the hexadentate ligand, and are twisted. The V—O(aqua) distances [average 2.095 (3) Å] are somewhat longer than the V—O(nta) distances [average 2.052 (3) Å]. The V—O(nta), V—O(aqua), and V—N distances are in the range of the corresponding distances which have been found in $[V(L)(H_2O)]^{n-}$. The geometry in the nta complex, however, seems to be more symmetrical than the hedtra, edta and cydta complexes, since the nta complex has a C_3 axis through the N—V axis (Fig. 2).

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cis-Di[bis(dimethylphosphino)methane P-oxide-P']dichloropalladium(II) Monohydrate

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Abstract. $[Pd(C_5H_{14}OP_2)_2Cl_2].H_2O$, $M_r = 499.55$, orthorhombic, *Pbca*, $a = 14.332$ (3), $b = 16.592$ (3), $c = 17.420$ (3) Å, $V = 4142.3$ (2.5) Å^3, $Z = 8$, $D_x = 1.60$ g cm^{-3}, λ(Mo $K\alpha$) = 0.70930 Å, $\mu = 14.5$ cm^{-1}, $F(000) = 2032$, $T = 294$ (1) K, $R = 0.031$ for 3004 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ of 4541 total data. The molecule is a cis-dichlorobisphosphine complex of Pd^{II}. The phosphine is unusual in being a bisphosphine monoxide, the oxide function being nonbonding to palladium. Principal bond lengths and angles are: Pd—Cl 2.357 (1), 2.387 (1); Pd—P 2.254 (1), 2.248 (1); P=O 1.476 (3), 1.467 (4); P—C 1.768 (6)–1.819 (4) Å; P—Pd—P 99.27 (4); cis-P—Pd—Cl 85.31 (4), 86.55 (4); trans-P—Pd—Cl 174.06 (4), 175.23 (4); Cl—Pd—Cl 88.85 (4); P—C—P 114.3 (2), 115.7 (2)°.

Introduction. It is well known (Pringle & Shaw, 1982) that monodentate diphosphine complexes can be used as intermediates in the synthesis of homo- or

heterobimetallic complexes. The underlying interest in heterobimetallic complexes is to obtain different reactivities at both metal sites. One way of accentuating this character would be to incorporate a hard donor atom on the ligand site that accommodates the adjacent metal. This can easily be done by oxidizing the terminal end of the monodentate diphosphine ligand (Langrick, McEwan, Pringle & Shaw, 1983) forming bis(phosphine oxide) complexes, to be used in the synthesis of novel heterobimetallic systems. We have found that the air oxidation of [Pd$_2$Cl$_2$(dmpm)$_2$], dmpm = bis(dimethylphosphino)-methane, leads to the formation of the title complex, [PdCl$_2${Me$_2$PCH$_2$P(=O)Me$_2$}$_2$], whose structure was determined by single-crystal X-ray diffraction methods. Here the oxidation step is not as straightforward as oxidizing the free phosphine, since palladium(I) is concurrently oxidized to palladium-(II). Presumably, oxidation of the metal centers is accompanied by the oxidation of the bisphosphine ligand leading to the fragmentation of the palladium dimer. The only other related complexes whose structures have been determined by X-ray crystallography are of chelating diphosphine monoxide ligands, [RuCl$_2$(MePhPC$_6$H$_4$PPhMe)MePhPC$_6$H$_4$-P(O)MePh] (Hall, Skelton & White, 1983) and [MoOCl$_3${Et$_2$PCH$_2$CH$_2$P(O)Et$_2$}] (Bakar, Hills, Hughes & Leigh, 1989). A single-crystal structure determination of the title compound, reported herein, shows that the diphosphine monoxide ligand provides a pendant functionality and would serve as an intermediate in the synthesis of heterobimetallic systems with a second metal able to coordinate the phosphine oxide (Ng, Rodley & Robinson, 1978).

Experimental. The title compound was prepared by bubbling oxygen for 10 min through a solution of [Pd$_2$Cl$_2$(dmpm)$_2$] dissolved in methylene chloride. Clear rectangular crystals of the title compound suitable for single-crystal X-ray structure determination were obtained by slow evaporation of the methylene chloride. Infrared spectra were measured using a Nicolet 60SX FTIR spectrometer. Crystal 0.20 × 0.20 × 0.15 mm; Enraf–Nonius CAD-4 computer-controlled κ-axis diffractometer, Mo $K\alpha$ radiation, graphite monochromator; cell dimensions from the setting angles of 25 reflections, $13 < \theta < 14°$; ω–2θ scan; intensities and backgrounds from analysis of scan profile (Blessing, Coppens & Becker, 1974); empirical absorption correction, subsequently refined (Walker & Stuart, 1983), relative transmission coefficients 0.8722–0.9993; maximum $2\theta = 52.0°$; hkl range h 0 to 17, k 0 to 20, l 0 to 21; three standard reflections, average decay 1.5%, intensities adjusted accordingly; 4541 data, 4541 unique; structure solved by Patterson heavy-atom and Fourier methods; refined by full-matrix least squares mini-

Table 1. *Positional parameters and equivalent isotropic displacement parameters* (Å^2) *with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}
Pd(1)	0.39587 (2)	0.22741 (2)	0.35150 (1)	2.806 (5)
Cl(1)	0.23868 (7)	0.20258 (8)	0.38343 (6)	4.59 (2)
Cl(2)	0.36333 (8)	0.18350 (8)	0.22378 (6)	4.74 (2)
P(1)	0.54426 (7)	0.24495 (6)	0.31210 (6)	3.21 (2)
P(2)	0.41181 (7)	0.26389 (6)	0.47506 (6)	3.22 (2)
P(3)	0.59204 (8)	0.07279 (7)	0.36083 (7)	4.47 (3)
P(4)	0.34228 (8)	0.43198 (7)	0.43644 (7)	4.70 (3)
O(1)	0.6231 (2)	0.1055 (2)	0.4354 (2)	6.25 (8)
O(2)	0.4328 (3)	0.4358 (2)	0.3973 (3)	9.5 (1)
O(3)	0.4231 (4)	−0.0035 (3)	0.1791 (4)	12.6 (2)
C(1)	0.3787 (3)	0.1805 (3)	0.5365 (2)	4.7 (1)
C(2)	0.3327 (3)	0.3446 (2)	0.4985 (2)	3.92 (8)
C(3)	0.5192 (3)	0.2944 (3)	0.5191 (3)	5.8 (1)
C(4)	0.5468 (3)	0.3077 (3)	0.2265 (2)	5.2 (1)
C(5)	0.5902 (3)	0.1471 (2)	0.2856 (2)	3.79 (8)
C(6)	0.6392 (3)	0.2878 (3)	0.3657 (3)	5.0 (1)
C(7)	0.4793 (3)	0.0287 (3)	0.3683 (3)	5.6 (1)
C(8)	0.6632 (4)	−0.0055 (3)	0.3225 (4)	6.9 (1)
C(9)	0.2470 (4)	0.4255 (4)	0.3722 (4)	9.5 (2)
C(10)	0.3140 (5)	0.5156 (3)	0.4960 (4)	9.8 (2)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Pd(1)—Cl(1)	2.357 (1)	P(2)—C(3)	1.792 (5)
Pd(1)—Cl(2)	2.387 (1)	P(3)—O(1)	1.476 (3)
Pd(1)—P(1)	2.254 (1)	P(3)—C(5)	1.799 (4)
Pd(1)—P(2)	2.248 (1)	P(3)—C(7)	1.778 (5)
P(1)—C(4)	1.819 (4)	P(3)—C(8)	1.781 (6)
P(1)—C(5)	1.813 (4)	P(4)—O(2)	1.467 (4)
P(1)—C(6)	1.797 (5)	P(4)—C(2)	1.814 (4)
P(2)—C(1)	1.812 (4)	P(4)—C(9)	1.768 (6)
P(2)—C(2)	1.801 (4)	P(4)—C(10)	1.779 (6)

Cl(1)—Pd(1)—Cl(2)	88.85 (4)	C(1)—P(2)—C(3)	100.8 (2)
Cl(1)—Pd(1)—P(1)	175.23 (4)	C(2)—P(2)—C(3)	103.5 (2)
Cl(1)—Pd(1)—P(2)	85.31 (4)	O(1)—P(3)—C(5)	113.2 (2)
Cl(2)—Pd(1)—P(1)	86.55 (4)	O(1)—P(3)—C(7)	111.2 (2)
Cl(2)—Pd(1)—P(2)	174.06 (4)	O(1)—P(3)—C(8)	115.2 (2)
P(1)—Pd(1)—P(2)	99.27 (4)	C(5)—P(3)—C(7)	108.8 (2)
Pd(1)—P(1)—C(4)	110.0 (2)	C(5)—P(3)—C(8)	103.6 (2)
Pd(1)—P(1)—C(5)	107.8 (1)	C(7)—P(3)—C(8)	104.3 (2)
Pd(1)—P(1)—C(6)	127.4 (2)	O(2)—P(4)—C(2)	112.2 (2)
C(4)—P(1)—C(5)	107.3 (2)	O(2)—P(4)—C(9)	113.0 (3)
C(4)—P(1)—C(6)	100.7 (2)	O(2)—P(4)—C(10)	116.0 (3)
C(5)—P(1)—C(6)	102.2 (2)	C(2)—P(4)—C(9)	105.7 (3)
Pd(1)—P(2)—C(1)	109.5 (1)	C(2)—P(4)—C(10)	105.0 (2)
Pd(1)—P(2)—C(2)	110.7 (1)	C(9)—P(4)—C(10)	103.9 (3)
Pd(1)—P(2)—C(3)	125.0 (1)	P(2)—C(2)—P(4)	114.3 (2)
C(1)—P(2)—C(2)	105.6 (2)	P(1)—C(5)—P(3)	115.7 (2)

mizing $\Sigma w(|F_o| - |F_c|)^2$, $w = 4F_o^2/\sigma^2(F_o)^2$, 181 parameters; 3004 reflections with $F_o^2 > 3\sigma(F_o^2)$; H atoms refined as riding atoms with fixed isotropic thermal parameters, anisotropic thermal parameters for non-H atoms; H atoms of the solvent water molecule not included owing to a disorder problem with the water molecule itself; final $R = 0.031$, $wR = 0.045$; maximum shift to e.s.d. = 0.01 in final least-squares cycle; maximum and minimum of ΔF synthesis 0.42 (8) and −0.35 (8) e Å^{-3}; e.s.d. of observations of unit weight = 1.45, atomic scattering factors

for neutral Pd, Cl, P, C, O and spherically bonded H atoms and values of f' and f'' for all atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2, pp. 71–102; Table 2.3.1, pp. 149–150); computer programs *SDP/VAX* (Frenz, 1978). Fig. 1 produced with *ORTEP* (Johnson, 1971).

Discussion. Final atomic coordinates for all non-constrained atoms are listed in Table 1.* Bond lengths and bond angles are listed in Table 2. The atom-numbering scheme is shown in Fig. 1.

The asymmetric unit comprises one discrete $[PdCl_2\{Me_2PCH_2P(=O)Me_2\}_2]$ molecule which lies in a general position along with one solvent water molecule, designated in the atom-numbering scheme as O3 (not shown in Fig. 1). The source of the water molecule is presumed to be atmospheric moisture. The infrared spectrum of the crystalline material as a Nujol mull exhibits bands at *ca* 3350 and *ca* 1650 cm^{-1}, as anticipated for a material containing lattice water (Costello, Fanwick, Meyer & Walton, 1990). The Pd atom exhibits approximately square planar coordination with the diphosphine monoxide ligands *cis* to one another. The intramolecular distance between the two O atoms of the terminal phosphine oxides is 6.157 (5) Å. This forms a significant void into which the host intermediate can incorporate a second metal complex in forming heterobimetallic compounds. There are no significant intramolecular distances to suggest chelation of the P ligands to the Pd-metal center. The geometry about the two terminal P atoms is tetrahedral, consistent with that found in trimethylphosphine oxide (Engelhardt, Raston, Whitaker & White, 1986). The P—O distances, 1.476 (3) and 1.467 (4) Å, are comparable with the P—O distance in [P(O)Me$_3$] of 1.489 (6) Å

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54881 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
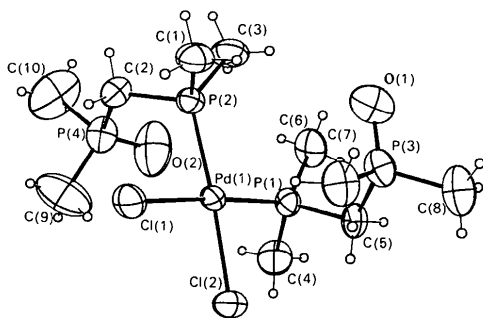
and the range of P—C distances, 1.768 (6)–1.819 (4) Å compares favorably to the P—C distances in [P(O)Me$_3$] of 1.77 (1) Å. The Pd—P distances of 2.254 (1) and 2.248 (1) Å are slightly less than the median Pd—P bond distance of 2.281 (18) Å found in palladium trimethylphosphine complexes (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989). The Pd—Cl bond distances of 2.357 (1) and 2.387 (1) Å are similar to the Pd—Cl bond distance of 2.362 (3) Å observed in [cis-PdCl$_2$\{P(CH$_3$)$_2$C$_6$H$_5$\}$_2$] (Martin & Jacobson, 1971). The large mean-square atomic displacement observed for the O atom of the water molecule probably results from positional disorder although no satisfactory disorder model was found. Attempts to refine the occupancy factor gave no indication of a value lower than one. Not surprisingly we were unable to locate the associated H atoms. Ligand atoms furthest from the metal center, and hence less constrained, show the anticipated higher thermal motion. The shortest intermolecular distance involving the water oxygen [O(3)] is to H(19) of one of the methyl groups bonded to the pendant P=O functionality, *i.e.* O(3)—H(19) 2.546 (6) Å.

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Fig. 1. *ORTEP* (Johnson, 1971) plot of the title complex showing the atom-numbering scheme (50% probability ellipsoids).