Synthesis and Structure of $W_2Cl_4\{\mu\text{-}(iPr_2PCH_2CH_2CH_2PiPr_2)\}_2$: A Tungsten – Tungsten Quadruple Bond Bridged by Bulky Chelating Diphosphines

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The reduction of WCl_4 in THF by two equivalents of Na/Hg in the presence of the bulky chelating diphosphine $iPr_2PCH_2CH_2CH_2PiPr_2$ (dippp) generates the purple, binuclear complex $W_2Cl_4(\mu\text{-dippp})_2$. The quadruply-bonded molecule has a β structure, that is, the chelating diphosphine bridges the two metal centers. ^{1}H-NMR spectral data show downfield shifts for the ligand protons consistent with the β structure. The $^{31}P\{^1H\}$-NMR spectrum consists of a singlet with ^{183}W satellites. The X-ray crystal structure has a twist angle (P – W – W – P torsion angle) of 75.9°, and the W – W bond length is 2.297(1) Å. Using the solid-state data and the observed downfield shifts in the ^{1}H-NMR spectrum, the diamagnetic anisotropy χ has been estimated as $-3000 \pm 300 \times 10^{-36}$ m^3/molecule. The chiral structure observed in the solid phase is retained in solution.

Synthese und Struktur von $W_2Cl_4\{\mu\text{-}(iPr_2PCH_2CH_2CH_2PiPr_2)\}_2$: Eine durch sperrige, chelatisierende Diphosphane überbrückte Wolfram – Wolfram-Vierfachbindung

Die Reduktion von WCl_4 in THF durch zwei Äquivalente Na/Hg in Gegenwart des sperrigen, chelatisierenden Diphosphinopropans $iPr_2PCH_2CH_2CH_2PiPr_2$ (dippp) liefert den violetten, zweikernigen Komplex $W_2Cl_4(\mu\text{-dippp})_2$. Der Komplex besitzt eine W – W-Vierfachbindung und β-Struktur, d.h. die chelatisierenden Diphosphinopropan-Liganden verbrücken die beiden Metall-Zentren. Die ^{1}H-NMR-spektroskopischen Daten zeigen Tieffeldverschiebungen für die dippp-Liganden, die im Einklang mit der β-Struktur stehen. Das $^{31}P\{^1H\}$-NMR-Spektrum besteht aus einem Singulett mit ^{183}W-Satelliten. Die Röntgen-Stukturanalyse ergibt für die β-Struktur einen Torsionswinkel P – W – W – P von 75.9° und eine W – W-Bindungslänge von 2.297(1) Å. Aus den Molekülstruktur-Daten und den ^{1}H-NMR-Tieffeldverschiebungen kann die diamagnetische Anisotropie χ der W – W-Vierfachbindung mit $-3000 \pm 300 \times 10^{-36}$ m^3/Molekül abgeschätzt werden. Die für den festen Zustand beobachtete Chiralität wird auch in Lösung beibehalten.

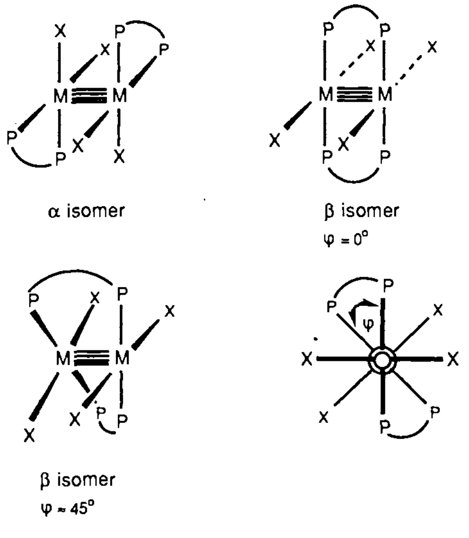
Introduction

One of the major discoveries in modern inorganic chemistry is the class of complexes that contain metal – metal multiple bonds[1]. Of particular interest are those binuclear complexes with formal d^4-d^4 configurations since quadruple bonding between metals can be invoked.

A tremendous amount of work has been published[2–8,11] on complexes of the type $M_2X_4(LL)_2$ where M = Mo and/or W, X = halide or pseudohalide, and LL = chelating diphosphine. The structures of these derivatives can be classified into two main categories: α, having LL chelating to a single metal, or β, having LL bridging the two metals, as shown in Scheme 1. In the latter category, further variation is possible according to the degree of twist in the conformation of the bridging unit. For example, β structures have been structurally characterized[2,3] with twist angles of 0° (eclipsed bridging phosphorus donors) to 56° (staggered bridging phosphorus donors); this is summarized in Scheme 1.

The vast majority of these complexes have M = Mo. In fact, there are only three crystal structures[4,5] of tungsten

Scheme 1



$M_2X_4(LL)_2$ **1**: M = W, X = Cl, LL = dippp complexes having the formula $W_2Cl_4(LL)_2$ with LL as either $Me_2PCH_2CH_2PMe_2$ (dmpe) or $Ph_2PCH_2CH_2PPh_2$ (dppe). The derivative $W_2Cl_4(dmpe)_2$ has the α geometry, while $W_2Cl_4(dppe)_2$ crystallizes in both the α and β forms.

Much of the structural knowledge on these complexes comes from single-crystal X-ray data since studies on solution structures have been hampered by the insolubility[6] of these complexes. Only recently has an effort been made to study the conformational aspects[2,7,8] of these complexes in solution, although this has been confined to molybdenum so far. Given the fact that phosphorus NMR is a proven sensitive structural tool[9], it is somewhat surprising that this nucleus has not been more utilized[10] for these complexes. In addition, it has been shown[11] that soluble tungsten dimers having monodentate phosphine ligands also display a more complex $^{31}P\{^1H\}$-NMR spectrum due to coupling with ^{183}W (spin = 1/2, 14.4% natural abundance) which might also provide information on structural features in solution. In this paper we report our findings on the synthesis and structural characterization of the complex $W_2Cl_4(\mu\text{-dippp})_2$ [dippp: 1,3-bis(diisopropylphosphino)propane]. It is of particular interest that this is the first structurally characterized dimer having a bridging diphosphine with a linear three-carbon backbone[12]. In addition, we show that the solution and the solid-state structures can be correlated to provide information about the configurational stability in solution and the magnitude of the diamagnetic anisotropy (χ) of a tungsten – tungsten quadruple bond.

Results and Discussion

The reaction of two equivalents of Na/Hg with WCl_4 in THF in the presence of one equivalent of dippp generates the binuclear tungsten complex $W_2Cl_4(dippp)_2$ (**1**) in moderate yield. This purple, air-stable (in the solid) crystalline material is soluble in aromatic hydrocarbons and tetrahydrofuran and nearly insoluble in pentane and diethyl ether. Solutions of **1** are mildly air-sensitive and slowly thermally decompose at room temperature over a period of days. In dichloromethane, the complex decomposes in a matter of minutes. It is of interest to note that this synthetic procedure has been reported[11] to fail for other chelating diphosphines such as dmpe and dppe. Indeed, binuclear complexes of tungsten containing dmpe or dppe were prepared[11] by displacement of $PnBu_3$ from $W_2Cl_4(PnBu_3)_4$ at high temperatures. Attempts to utilize this displacement procedure using the bulky chelating diphosphine dippp did not generate any $W_2Cl_4(dippp)_2$; monitoring the reaction of $W_2Cl_4(PnBu_3)_4$ in toluene with dippp from 80 to 140°C by $^{31}P\{^1H\}$-NMR spectroscopy did show the presence of free $PnBu_3$, unchanged $W_2Cl_4(PnBu_3)_4$, and dippp, but none of the expected tungsten (dippp) dimer **1**. Given the thermal instability of the purple dippp dimer **1**, perhaps this last result is not surprising.

The room-temperature ^1H-NMR spectrum of **1** is particularly informative. There are four signals for the isopropyl methyls [$PCH(CH_3)_2$], two widely separated (by 2 ppm) methine signals [$PCH(CH_3)_2$], two multiplets for the α-methylene hydrogens ($PCH_2CH_2CH_2P$), and a broad multiplet for the central methylene protons of the ligand backbone. Moreover, all of these signals are downfield compared to other complexes[13] containing this ligand system. This downfield shift suggests that some of these protons are in close proximity to the diamagnetically anisotropic tungsten – tungsten quadruple bond[14]. Consideration of these data and the known structural types for this class of complexes (Scheme 1) suggest that a twisted β structure is present in **1**. Much of the data can be reconciled with the corresponding α isomer as well, except for the fact that central methylene protons of the ligand backbone are equivalent (same multiplet is observed at 200 MHz and 400 MHz). The $^{13}C\{^1H\}$-NMR spectrum of **1** is consistent with both isomeric forms as might be predicted on symmetry arguments alone.

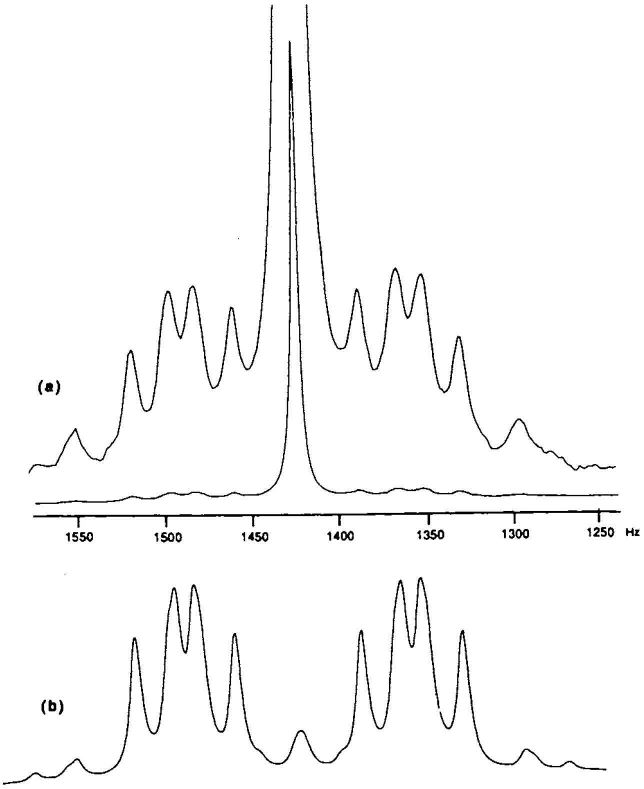


Figure 1. $^{31}P\{^1H\}$-NMR spectrum of $W_2Cl_4\{\mu\text{-}(iPr_2PCH_2CH_2CH_2PiPr_2)\}_2$ (C_6D_6, 161.9 MHz on a Varian XL-400): (a) actual spectrum with ^{183}W satellites blown up for clarity; (b) simulated spectrum (see Experimental for details)

The $^{31}P\{^1H\}$-NMR spectrum of **1** consists of a sharp singlet with ^{183}W satellites. This is shown in Figure 1 along with the simulation. Analysis of this spin system as a AA'BB'X is straightforward[11]: the A and A' ^{31}P nuclei reside on the ^{183}W center, while B and B' reside on the magnetically inactive tungsten center of the molecule. Since the chemical difference between A and B is only due to isotopic substitution of tungsten, the chemical shift difference must be small. Such an analysis generates coupling constants of ^1J_W = 190.5, ^2J_W = 73.3, and ^3J_P = 40 Hz. For comparison[11], similar complexes with monodentate phosphine ligands, $W_2Cl_4(PR_3)_4$, have values of ^1J_W = 230 – 236, ^2J_W = 49 – 51, and $^3J_P = 27-28$ Hz. It is not clear what the differences mean, even if they are significant, since the data base is still too restricted.

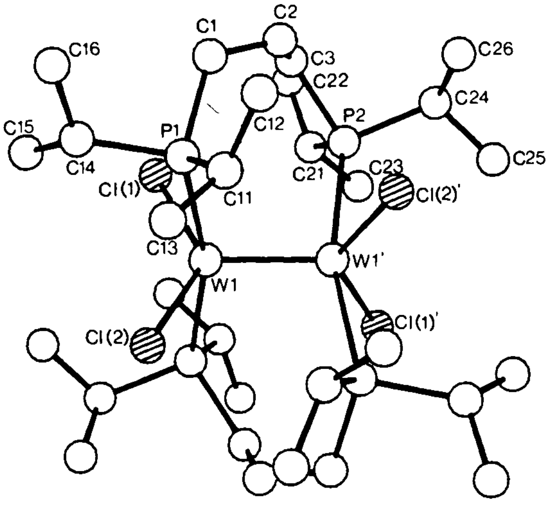


Figure 2. ORTEP plot of $W_2Cl_4\{\mu\text{-}(iPr_2PCH_2CH_2CH_2PiPr_2)\}_2$ with atom labelling scheme

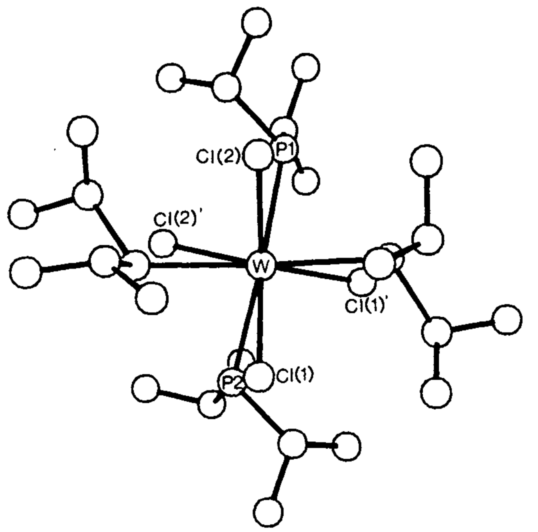


Figure 3. View of $W_2Cl_4\{\mu\text{-}(iPr_2PCH_2CH_2CH_2PiPr_2)\}_2$ along the W–W′ axis with the ligand backbone carbons removed for clarity showing the twist angle of 75.9°

The single-crystal X-ray structure of **1** is shown in Figure 2. The β structure is clearly apparent with a twist angle of 75.9°, the largest such twist angle as yet observed for complexes of the formula $M_2X_4(\mu\text{-}LL)_2$. This large twist angle nearly results in an eclipsed structure similar to that found for binuclear complexes with monodentate phosphines (see Figure 3). The W–W bond distance is 2.297(1) Å and is slightly longer than in $W_2Cl_4(PMe_3)_4$ [2.262(1) Å] and α-$W_2Cl_4(dmpe)_2$ [2.287(1) Å] but shorter than that found in $W_2Cl_4(\mu\text{-}dppe)_2$ [2.314(1) Å]. Other bond distances compare favorably with other similar molecules and are not unusual. The conformation of the seven-membered ditungstadiphospha heterocycle can be described as a twisted chair, although this is, at best, only an approximation since there are no other comparable seven-membered heterocycles, particularly containing a tungsten–tungsten quadruple bond. The molecule is chiral by virtue of the twisted chelate bridge; in the solid state, the molecule has C_2 symmetry, not D_2 as found in solution (vide infra), since the backbone linkages have slightly different conformations and the isopropyl groups are not equivalent.

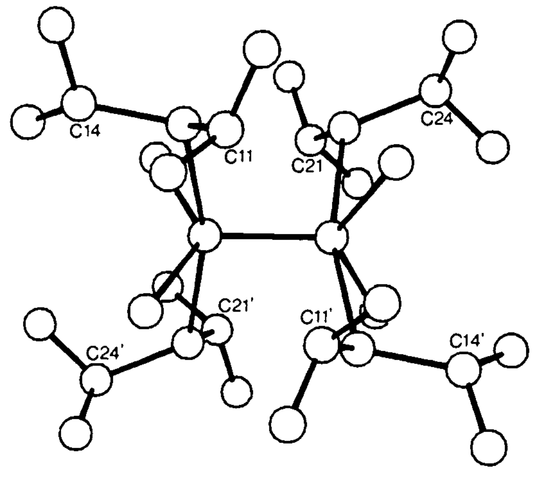


Figure 4. View of $W_2Cl_4\{\mu\text{-}(iPr_2PCH_2CH_2CH_2PiPr_2)\}_2$ with the ligand backbone carbons removed for clarity showing the positions of the labelled methine carbons lying over the quadruple W–W bond (C11, C11′, C21, and C21′) and pointing away from this source of anisotropy (C14, C14′, C24, and C24′)

The solid-state structure contains information that relates to the solution structure. Examination of the view shown in Figure 4 (having the backbone carbons removed) shows that there are four isopropyl groups positioned directly over the quadruple bond while the other four are pointed away. In fact, the hydrogen atoms on the methine carbons $[PCH(CH_3)_2]$ are pointed toward this W–W bond. Is should be noted that the hydrogen atoms were not located during the structure refinement but their positions were assumed[15] using a tetrahedral angle of 109° and a bond length of 0.95 Å. Similar arguments can be made regarding the α-methylene protons on the ligand backbone, in that one hydrogen atom of each methylene pair resides closer to the W–W quadruple bond than the other. Both of these observations are reflected in the ^{1}H-NMR spectrum of **1** wherein there are observed large downfield shifts for the methine and α-methylene protons of the dippp. The symmetry of the molecule in solution at room temperature is D_2 and is higher than the C_2 symmetry observed in the solid because of rotational and conformational averaging of the ligand substituents in solution. This is confirmed to some extent by low-temperature ^{1}H-NMR spectra which show broadening and more complexity as the temperature is lowered. For example, as the temperature is lowered to −90°C, the downfield resonance[16] for the methine protons situated above the quadruple bond broadens, decoalesces and finally appears as two broad multiplets at $\delta = 4.8$ and 4.1; the distal (away from the W–W quadruple bond) methine resonance also broadens and splits as do the distal isopropyl methyl resonances. It is probable that the seven-membered ring is flexible enough, particularly the three-carbon propylene chain, to undergo conformational changes which are frozen out at lower temperatures. In addition, rotation of the isopropyl groups at room temperature also maintains the higher D_2 symmetry.

As already mentioned, this molecule is chiral in the solid, and this is also reflected in the solution state since we observe diastereotopicity in the ^{1}H-NMR spectrum for the appropriate symmetry-related groups. Thus, in solution this molecule exists as a racemic mixture that is configurationally stable on the NMR time scale at ambient temperatures. This contrasts that found for binuclear molybdenum complexes where configurational stability in solution has only been found[2)] for those dimers with chiral diphosphine[7)] ligands as bridges. The origin of the configurational stability of **1** is probably related to the severely twisted, nearly eclipsed ground-state structure in which there is a strong enough δ bond to constrain the two ends of the molecule and prevent racemization.

The combination of the chemical shift difference observed in the ^{1}H-NMR spectrum for certain protons and their positions as calculated[15)] from the X-ray crystal-structure data can be used for estimating the diamagnetic anisotropy[17)] (χ) for the tungsten – tungsten quadruple bond using the McConnell equation (1).

$$\sigma = \frac{4\pi\chi(1 - 3\cos^2\theta)}{3r^3} \qquad (1)$$

σ is the chemical shift (in ppm) of the particular proton, r is the distance from the proton to the center of the quadruple bond, and θ is the angle made by the vector r with the quadruple bond axis. Table 1 lists the various factors calculated for the methine protons situated over (H_{prox}) and away from (H_{dist}) the quadruple bond; using these values and following earlier treatments[18)] of similar systems, a value for $\chi = -3000 \pm 300 \times 10^{-36}$ m^3/molecule can be calculated. Such a value is reasonable for a tungsten – tungsten quadruple bond given that a W – W triple bond has a value of $\chi = -1960 \times 10^{-36}$ m^3/molecule and a Mo – Mo triple bond has $\chi = -1784 \times 10^{-36}$ m^3/molecule. However, for a molybdenum – molybdenum quadruple bond, a value of $\chi = -8800 \pm 250 \times 10^{-36}$ m^3/molecule has been found[6)], and it is clear that such a large difference is unrealistic. It should be emphasized that the ligand systems were different and the α isomer was used for the Mo_2 value. Although these factors should not be influential, further discussion must await more data.

Table 1. Geometric factors for proximal (H_{prox}) and distal (H_{dist}) protons[a)] of $W_2Cl_4(\mu\text{-dippp})_2$

Proton[b)]	r [Å]	θ [°]	10^{-27} G[c)] [m^3]	10^{-27} G_{av}[c)] [m^3]
H_{prox} C(11)	3.51	91.67	7.69	7.42
H_{prox} C(21)	3.60	89.12	7.14	
H_{dist} C(14)	4.78	40.0	−2.32	−1.35
H_{dist} C(24)	5.19	51.65	−0.37	

[a)] The C – H distances is 0.95 Å and the C – C – H bond angle is 109°. – [b)] There are two pairs of proximal and distal protons related by a C_2 axis. Only one of each pair is given along with the attached carbon number. – [c)] $G = \dfrac{(1 - 3\cos^2\theta)}{3r^3}$.

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Experimental

General Procedures: All procedures were performed under prepurified N_2 using standard Schlenck techniques. – Tetrahydrofuran (THF) was predried by refluxing over CaH_2, then distilled freshly from sodium diphenylketyl under N_2. Toluene and pentane were dried over sodium diphenylketyl and stored under N_2 over activated molecular sieves (4 Å). WCl_4 was prepared[11)] from WCl_6 (Aldrich) and $W(CO)_6$ (Merck), dippp was prepared as previously described[19)]. – NMR spectra were run on either a Bruker AM-400 or a Varian XL-400. Simulations were performed on a Bruker WH-200 using PANIC[20)]. – Deuterated solvents were obtained from standard sources and dried over activated molecular sieves (4 Å) prior to use.

$W_2Cl_4\{\mu\text{-}(iPr_2PCH_2CH_2CH_2PiPr_2)\}_2$: Sodium/mercury amalgam (Na/Hg: 0.58 g Na, 25 mmol, in 140 g Hg) was added to THF (100 ml) and dippp (3.30 g, 12 mmol) and cooled to 0°C. Solid WCl_4 (4.00 g, 12 mmol) was added all at once and the mixture shaken at 0°C for 20 min then warmed to room temp. with periodic shaking. Over a period of 1 h, the dark suspension turned brown-orange, then green transiently and finally to a dark brownish blue. The mixture was filtered through Kieselgur (Filter-Cel) and the solvent removed i. vac. The residue was dissolved in toluene (30 ml), filtered, and pentane (30 ml) was added. Cooling at −35°C for ca. 12 h produced purple crystals (2.30 g, 36%). The filtrate contained a brown material that could not be purified further. – ^{1}H NMR [C_6D_6, δ(C_6D_5H, int.) = 7.15]: δ = 4.27, 2.20 [sept, ^3J_H = 7.2 Hz, $PCH(CH_3)_2$]; 3.04 and 2.30 (br. d, $PCH_2CH_2CH_2P$); 2.63 (br. m, $PCH_2CH_2CH_2P$); 1.65, 1.38, 0.99, and 0.80 (q, $^3J_P = {}^3J_H$ = 7.2 Hz). – $^{31}P\{^1H\}$ NMR ⟨C_6D_6, δ[$P(OMe)_3$, ext.] = 141.0⟩: δ = 8.8 (s with AA′BB′X satellite pattern, X = ^{183}W; simulation[20)] gives $^3J_{AB} = {}^3J_{AB'} = {}^3J_{A'B'} = {}^3J_{A'B} = 40$, $^1J_{AX} = {}^1J_{A'X} = 190.5$, $^2J_{BX} = {}^2J_{B'X}$ = 73.3 Hz; the simulated spectra are insensitive to values of $^2J_{AA'}$ and $^2J_{BB'}$ from 0 to 100 Hz.). – $^{13}C\{^1H\}$ NMR [C_6D_6, δ(C_6D_6, int.) = 128.0]: δ = 25.9, 25.5 [br. t, $PCH(CH_3)_2$]; 24.5 (br. t, $PCH_2CH_2CH_2P$); 21.7, 21.1, 20.2, 20.0 [s, $PCH(CH_3)_2$]; 17.4 (s, $PCH_2CH_2CH_2P$).

$C_{15}H_{34}Cl_2P_2W$ (531.1)	Calcd.	C 33.9 H 6.45
	Found	C 34.3 H 6.33

Table 2. Crystallographic and refinement data for $W_2Cl_4(\mu\text{-dippp})_2$

Molecular formula: $C_{30}H_{68}Cl_4P_4W_2$. – Crystal system: monoclinic. – Space group: $C2$. – a = 16.497(4), b = 12.487(4), c = 11.372(3) Å. – β = 119.32(3)°. – V = 2042.5(23) Å^3. – Z = 2. – F(000) = 1048. – Molecular mass: 1062.28. – d_{calcd} = 1.73 g · cm^{-3}. – Crystal size: 0.32 × 0.23 × 0.18 mm. – T = 20°C. – X-ray source: Mo-K_α. – λ = 0.71073 Å. – μ = 61.9 cm^{-1}. – Absorption correction: empirical. – Maximum transmission: 26.18%. – Minimum transmission: 19.33%. – Scan method: ω/2θ. – 2θ range: 3.00 – 50.00°. – $(\sin\theta/\lambda)_{max}$ = 0.594. – *hkl* measurement range: 0,19/0,14/−13,11. – θ – 2θ scan speed: 1.10 – 5.03°/min. – Scan width: 1.00 + 0.35 tanθ. – Reflections measured: 1888. – Reflections observed: 1713. – Rejection criterion: $I_{obs} < 3.00\sigma(I_{obs})$. – Number of parameters: 105. – R = 0.047. – R_w = 0.045. – Instability factor p = 0.014. – Last shift/esd: 0.12. – Residual electron density: 1.33 e$^\ominus$/Å^3.

Table 3. Atom positional parameters with isotropic temperature factors ($Å^2 \times 10^3$)[a]

Atom	x/a	y/b	z/c	U
W(1)	1.0689 (1)	0.0000 (0)	0.9979 (1)	37 (1)
Cl(1)	1.0760 (5)	0.1332 (5)	0.8535 (7)	69 (4)
Cl(2)	1.1757 (4)	-0.1369 (4)	1.1299 (6)	62 (3)
P(1)	1.0251 (5)	-0.1277 (7)	0.8019 (8)	63 (4)
P(2)	0.8430 (4)	0.1209 (5)	0.7970 (6)	57 (3)
C(1)	0.9364 (18)	-0.0861 (26)	0.6279 (20)	108 (10)
C(2)	0.8524 (14)	-0.0284 (13)	0.6051 (21)	62 (6)
C(3)	0.8515 (16)	0.0838 (18)	0.6438 (20)	65 (6)
C(11)	0.9879 (12)	-0.2668 (12)	0.8181 (18)	54 (5)
C(12)	0.9083 (16)	-0.3126 (22)	0.6891 (21)	79 (8)
C(13)	1.0687 (18)	-0.3448 (22)	0.8898 (27)	103 (9)
C(14)	1.1229 (13)	-0.1581 (19)	0.7669 (24)	87 (8)
C(15)	1.1908 (18)	-0.0673 (20)	0.7944 (26)	87 (8)
C(16)	1.1020 (23)	-0.2194 (27)	0.6392 (26)	113 (10)
C(21)	0.8820 (15)	0.2643 (12)	0.8142 (19)	62 (6)
C(22)	0.8630 (22)	0.3242 (24)	0.6862 (23)	95 (9)
C(23)	0.8525 (24)	0.3324 (26)	0.8986 (32)	123 (11)
C(24)	0.7141 (10)	0.1328 (22)	0.7277 (22)	92 (8)
C(25)	0.6891 (22)	0.1123 (28)	0.8371 (27)	109 (10)
C(26)	0.6663 (23)	0.0372 (25)	0.6366 (30)	133 (13)

[a] Equivalent isotropic temperature parameters are given for the W, Cl, and P atoms.

Table 4. Bond lengths [Å] and bond angles [°]

W(1)–W(1)	2.297 (1)	C(1)–C(2)	1.469 (22)
W(1)–Cl(1)	2.381 (5)	C(2)–C(3)	1.471 (22)
W(1)–Cl(2)	2.385 (5)	C(11)–C(12)	1.522 (14)
W(1)–P(1)	2.541 (7)	C(11)–C(13)	1.526 (15)
W(1)–P(2)	2.552 (6)	C(14)–C(15)	1.516 (15)
P(1)–C(1)	1.868 (19)	C(14)–C(16)	1.525 (15)
P(1)–C(11)	1.880 (13)	C(21)–C(22)	1.526 (15)
P(1)–C(14)	1.880 (13)	C(21)–C(23)	1.530 (15)
P(2)–C(3)	1.873 (19)	C(24)–C(25)	1.511 (15)
P(2)–C(21)	1.880 (13)	C(24)–C(26)	1.524 (15)
P(2)–C(24)	1.877 (13)		
Cl(1)–W(1)–Cl(2)	131.6 (2)	C(2)–C(3)–P(2)	122.1 (17)
P(1)–W(1)–Cl(1)	85.5 (2)	C(12)–C(11)–P(1)	114.9 (15)
P(1)–W(1)–Cl(2)	84.7 (2)	C(13)–C(11)–P(1)	113.6 (15)
C(1)–P(1)–W(1)	119.6 (10)	C(13)–C(11)–C(12)	113.0 (19)
C(11)–P(1)–W(1)	117.4 (6)	C(15)–C(14)–P(1)	115.5 (16)
C(11)–P(1)–C(1)	103.7 (12)	C(16)–C(14)–P(1)	119.1 (18)
C(14)–P(1)–W(1)	114.0 (7)	C(16)–C(14)–C(15)	111.8 (21)
C(14)–P(1)–C(1)	98.0 (12)	C(22)–C(21)–P(2)	117.9 (16)
C(14)–P(1)–C(11)	100.9 (10)	C(23)–C(21)–P(2)	113.3 (17)
C(21)–P(2)–C(3)	98.9 (9)	C(23)–C(21)–C(22)	110.2 (22)
C(24)–P(2)–C(3)	102.4 (11)	C(25)–C(24)–P(2)	110.5 (17)
C(24)–P(2)-C(21)	103.2 (11)	C(26)–C(24)–P(2)	109.0 (18)
C(2)–C(1)–P(1)	120.3 (17)	C(26)–C(24)–C(25)	99.6 (23)
C(3)–C(2)–C(1)	124.2 (24)		

X-ray Crystal-Structure Determination: Crystals of **1** suitable for X-ray analysis were obtained from satd. toluene solutions at −35°C. A purple crystal of dimensions 0.32 × 0.23 × 0.18 mm was sealed in epoxy and mounted on an Enraf-Nonius CAD4 diffractometer. Other information relating to the crystal and the collection of the data are given in Table 2. 1888 measured reflections of which 1713 with $F_o^2 > \sigma(F_o^2)$ were considered observed ($2\theta \leqslant 50°$). The structure was solved by Patterson and difference Fourier synthesis and refined to $R = 0.047$, $R_w = 0.045$ with weights given by $w = 1/(\sigma^2(F_o) + 0.0002 \cdot F_o^2)$. The W, Cl, and P atoms were refined anisotropically, the C atoms isotropically. H atoms could not be located in the final difference synthesis and were not included in the final refinement cycles (last shift/esd 0.12, residual electron density 1.33 $e^{\ominus}/Å^3$). A refinement of the enantiomorph yielded $R = 0.050$, $R_w = 0.048$; the deterioration in the R factor is significant at the 0.005 level (Hamilton R-test). The SHELX-76 system (G. M. Sheldrick) and local programs were used. Atom coordinates are given in Table 3[21].

CAS Registry Numbers

1: 118977-81-4 / W: 7440-33-7

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[319/88]