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A Dinuclear Tungsten(III) Complex Containing a Tungsten–Tungsten Triple Bond with an Asymmetric Arrangement of Ligands: $[\text{W}_2\text{Cl}_3(\text{OCMe}_3)_3(\text{HNMe}_2)_2]$

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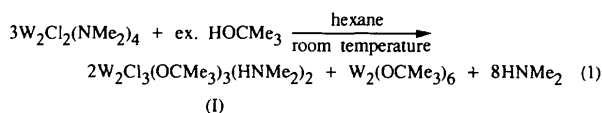
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Abstract

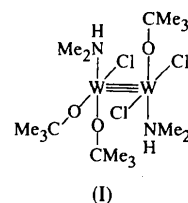
The title complex, tri-*tert*-butoxy- $1\kappa^2\text{O}, 2\kappa\text{O}$ -trichloro- $1\kappa\text{Cl}, 2\kappa^2\text{Cl}$ -bis(*N,N*-dimethylamine)- $1\kappa\text{N}, 2\kappa\text{N}$ -ditungsten(*W*–*W*), $[\text{W}_2\text{Cl}_3(\text{C}_4\text{H}_9\text{O})_3(\text{C}_2\text{H}_7\text{N})_2]$, adopts a dinuclear structure in which two tungsten(III) atoms are united by a $\text{W}\equiv\text{W}$ bond unsupported by bridging ligands. Both *W* atoms are coordinated to four ligand atoms that lie in a roughly square-planar arrangement. The two *W* atoms have different coordination environments: one is ligated by two *cis*-OR groups, one Cl and one HNMe_2 ligand, while the other is ligated by two *trans*-Cl ligands, one OR group and one HNMe_2 ligand.

Comment

There is now an extensive chemistry of ditungsten hexaalkoxides as templates for organometallic chemistry and catalysis (Chisholm, 1996). The $\text{W}_2(\text{OR})_6$ compounds are members of the well known family of so-called d^3 – d^3 ethane-like dimers (Chisholm, 1990), and they are readily prepared from $[\text{W}_2(\text{NMe}_2)_6]$ by an alcoholysis reaction (Akiyama *et al.*, 1979). Our attempt at the alcoholysis of $[\text{W}_2\text{Cl}_2(\text{NMe}_2)_4]$ by *tert*-butyl alcohol resulted in an unusual complex, $[\text{W}_2\text{Cl}_3(\text{OCMe}_3)_3(\text{HNMe}_2)_2]$, (I), by a possible disproportionation reaction as shown in equation (1),



since the $[\text{W}_2\text{Cl}_2(\text{NMe}_2)_4]$ compound is labile towards Cl for an NMe_2 exchange reaction (Akiyama *et al.*, 1977).



The title complex, (I), adopts a dinuclear structure in which two W^{III} atoms are united by a $\text{W}\equiv\text{W}$ bond unsupported by bridging ligands. The W – W distance, 2.3155 (5) Å, differs little from that observed in $[\text{W}_2\text{Cl}_2(\text{NMe}_2)_4]$, 2.301 (1) Å, and the subtle lengthening probably reflects steric interactions across the dinuclear center. Both *W* atoms are coordinated to four ligand atoms that lie in a roughly square-planar arrangement. The largest deviation of W – W –*L* angles from 90° for atoms *W1* and *W2* are O7 –*W1*–*W2* 108.9 (2)° and W1 –*W2*– Cl17 106.43 (6)°, which reflect steric repulsive interactions across the $\text{W}\equiv\text{W}$ bond. The central $\text{W}_2\text{Cl}_3\text{O}_3\text{N}_2$ moiety adopts an eclipsed conformation. The two *W* atoms have different coordination environments: one is ligated by two *cis*-OR groups, one Cl and one HNMe_2 ligand, while the other is ligated by two *trans*-Cl ligands, one OR group and one HNMe_2 ligand. The disposition of two *trans*-Cl ligands in this complex is different from that in $[\text{W}_2\text{Cl}_3(\text{NMe}_2)_3(\text{PMe}_2\text{Ph})_2]$, in which the pair of Cl atoms coordinates one of the tungsten centers in a *cis* configuration (Ahmed *et al.*, 1985*a,b*). The W –O [1.885 (6), 1.911 (6) and 1.903 (6) Å] and W –Cl distances [2.390 (2), 2.358 (2), 2.363 (2) Å] are comparable with those in the $\text{W}_2(\text{OR})_6$ compounds and $[\text{W}_2\text{Cl}_2(\text{NMe}_2)_4]$. However, the W –N distances [2.255 (7) and 2.278 (8) Å] are notably longer than those in $[\text{W}_2(\text{NMe}_2)_6]$ and $[\text{W}_2\text{Cl}_2(\text{NMe}_2)_4]$, indicating that only single W –N bonds are formed, due to the protonation of NMe_2 to HNMe_2 .

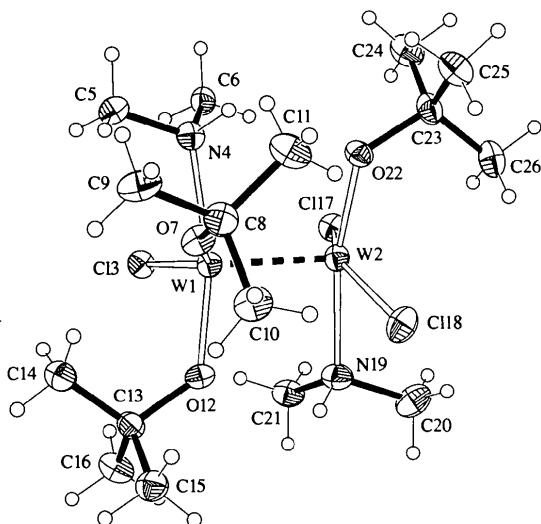


Fig. 1. Perspective view (35% probability ellipsoids) of the title complex with the atom-numbering scheme.

Experimental

$[\text{W}_2\text{Cl}_2(\text{NMe}_2)_4]$ was prepared according to previously described procedures (Akiyama *et al.*, 1977). The title complex was synthesized by a standard Schlenk procedure. To the orange–yellow solution of $[\text{W}_2\text{Cl}_2(\text{NMe}_2)_4]$ (508 mg, 0.83 mmol) dissolved in benzene (10 ml), *tert*-butyl alcohol–benzene azeotrope (2.5 ml), which contains 36.6% by weight *tert*-butyl alcohol, was added. The solution was stirred at room temperature overnight to give a dark-brown solution. The solvent was removed and the black solid was redissolved in hexane. After the dark brown solution was placed in the refrigerator at 253 K for a few days, dark-purple polyhedral crystals suitable for X-ray crystallography were formed, which were isolated by filtration, washed with hexane and dried *in vacuo* (yield: 206 mg, 0.27 mmol, 49%). ^1H NMR (in C_6D_6 , δ): 1.35 (*s*, 9H, CMe_3), 1.40 (*s*, 9H, CMe_3), 1.79 (*s*, 9H, CMe_3), 2.31 (*d*, 3H, NMe), 2.41 (*d*, 3H, NMe), 2.51 (*d*, 3H, NMe), 2.61 (*d*, 3H, NMe), 3.98 (*br.* H, NH), 4.60 (*br.* 1H, NH); ^{13}C NMR (in C_6D_6 , δ): 30.87 (CMe_3), 31.87 (CMe_3), 33.14 (CMe_3), 41.89 (NMe), 41.98 (NMe), 42.23 (NMe), 43.24 (NMe).

Crystal data

| | |
|---|---|
| $[\text{W}_2\text{Cl}_3(\text{C}_4\text{H}_9\text{O})_3(\text{C}_2\text{H}_7\text{N})_2]$ | Mo $K\alpha$ radiation |
| $M_r = 783.56$ | $\lambda = 0.71069 \text{ \AA}$ |
| Orthorhombic | Cell parameters from 25 reflections |
| $Pcab$ | $\theta = 7.5\text{--}15.0^\circ$ |
| $a = 13.705(2) \text{ \AA}$ | $\mu = 9.085 \text{ mm}^{-1}$ |
| $b = 32.939(4) \text{ \AA}$ | $T = 293(2) \text{ K}$ |
| $c = 11.6224(13) \text{ \AA}$ | Polyhedral |
| $V = 5246.6(11) \text{ \AA}^3$ | $0.25 \times 0.25 \times 0.20 \text{ mm}$ |
| $Z = 8$ | Dark purple |
| $D_x = 1.984 \text{ Mg m}^{-3}$ | |
| D_m not measured | |

Data collection

| | |
|--|--|
| Picker four-circle geostat equipped with a Furnas monochromator and a Spellman X-ray generator | 3490 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.043$ |
| | $\theta_{\text{max}} = 25.03^\circ$ |

2 θ scans
Absorption correction:
 ψ scans (XTEL; Chisholm *et al.*, 1984)
 $T_{\text{min}} = 0.043$, $T_{\text{max}} = 0.111$
6990 measured reflections
4622 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.094$
 $S = 1.14$
4620 reflections
236 parameters
H atoms: see below
 $w = 1/\sigma^2(F^2)$
 $(\Delta/\sigma)_{\text{max}} = -0.003$

$h = -16 \rightarrow 0$
 $k = -39 \rightarrow 0$
 $l = -13 \rightarrow 5$
4 standard reflections
every 300 reflections
intensity decay: 1.0%

$\Delta\rho_{\text{max}} = 1.42 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.99 \text{ e \AA}^{-3}$
Extinction correction:
SHELXL93
Extinction coefficient:
0.00013(3)
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|------------|-----------|--------------|-----------|
| W1—O7 | 1.885(6) | W2—O22 | 1.903(6) |
| W1—O12 | 1.911(6) | W2—N19 | 2.278(8) |
| W1—N4 | 2.255(7) | W2—C118 | 2.358(2) |
| W1—W2 | 2.3155(5) | W2—C117 | 2.363(2) |
| W1—C13 | 2.390(2) | | |
| O7—W1—O12 | 98.8(2) | O22—W2—N19 | 167.4(3) |
| O7—W1—N4 | 82.2(2) | O22—W2—W1 | 98.4(2) |
| O12—W1—N4 | 166.4(3) | N19—W2—W1 | 94.2(2) |
| O7—W1—W2 | 108.9(2) | O22—W2—C118 | 97.8(2) |
| O12—W1—W2 | 98.3(2) | N19—W2—C118 | 80.9(2) |
| N4—W1—W2 | 94.1(2) | W1—W2—C118 | 100.14(6) |
| O7—W1—C13 | 141.2(2) | O22—W2—C117 | 93.1(2) |
| O12—W1—C13 | 90.0(2) | N19—W2—C117 | 82.3(2) |
| N4—W1—C13 | 81.1(2) | W1—W2—C117 | 106.43(6) |
| W2—W1—C13 | 106.98(6) | C118—W2—C117 | 149.40(8) |

The structure was solved by a combination of direct methods and difference Fourier techniques. The two W atoms were located in the initial E map and the remainder of the non-H atoms were located in two iterations of least-squares refinement followed by a difference Fourier calculation. All H atoms were included in fixed idealized positions with isotropic displacement parameters equal to 1.0 plus the isotropic equivalent of the parent atom.

Data collection: XTEL (Chisholm *et al.*, 1984). Cell refinement: XTEL. Data reduction: XTEL. Program(s) used to solve structure: MULTAN80 (Main *et al.*, 1980). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP in SHELXL/PC (Sheldrick, 1990). Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1344). Services for accessing these data are described at the back of the journal.

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Ligands with Cycloalkane Backbones. IV. Dichloro{(S,S)-trans-diphenyl[(2-diphenylphosphinyl)cyclohexyl]phosphinic acid ester}palladium(II)†

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Abstract

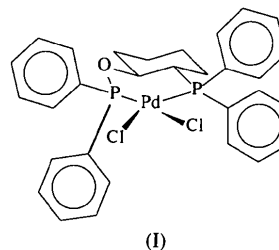
In the title compound, [PdCl₂(C₃₀H₃₀OP₂)], Pd^{II} is square-planar coordinated by two chloro ligands [Pd—Cl 2.340 (1) and 2.372 (1) Å] and the two phosphorus donors [Pd—P 2.263 (1), 2.209 (1) Å] of the asymmetric chelate ligand.

Comment

The application of chiral transition metal complexes as catalysts in enantioselective transformations of organic substrates is one of the most rapidly progressing fields in chemical research. For this purpose, synthetic strategies leading to chiral chelating ligands have been developed over the last two decades. Ligand systems giving high enantiomeric excesses in catalytic reactions usually show a C₂-symmetric arrangement of the donor fragments, forced by a rigid aromatic backbone. Since we are interested in ligands carrying two electronically dif-

† Alternative name: dichloro{diphenyl[2-(diphenylphosphino)cyclohexyloxy]phosphine-*P, P'*}palladium(II).

ferent donor centres linked by a rigid aliphatic backbone, we have developed a synthetic route using the ring opening of epoxides of cyclic olefins by various nitrogen and phosphorus nucleophiles (Barz *et al.*, 1997; Thurner *et al.*, 1997). We recently published the synthesis of new chiral chelate *P, P'*-ligands starting from *rac*-2-(diphenylphosphinyl)cyclohexanol, including structure chemical investigations of racemic dichloro{*trans*-diphenyl[(2-diphenylphosphinyl)cyclohexyl]phosphinic acid ester}palladium(II) (Thurner *et al.*, 1997). Reinvestigation of the crystalline material obtained by slow diffusion of diethyl ether into a solution of the racemic title compound in CH₂Cl₂ showed that, besides the known racemic modification, crystals of a second species are formed. Structural investigations proved that the individual crystal we obtained occupies the chiral space group *P2*₁ and resulted in the structure determination of the (*S, S*)-enantiomer, (I), which we present here. Since we started from a racemic mixture [(*S, S*)- and (*R, R*)-] of the chelate ligand, crystals with the (*R, R*)-configuration must be formed in equimolar amounts.



All bond lengths and angles concerning the slightly distorted square-planar Pd centre are similar to those in the racemic modification, which includes one additional molecule of CH₂Cl₂ per formula unit. Owing to the electronegative O atom at the phosphinite group, the

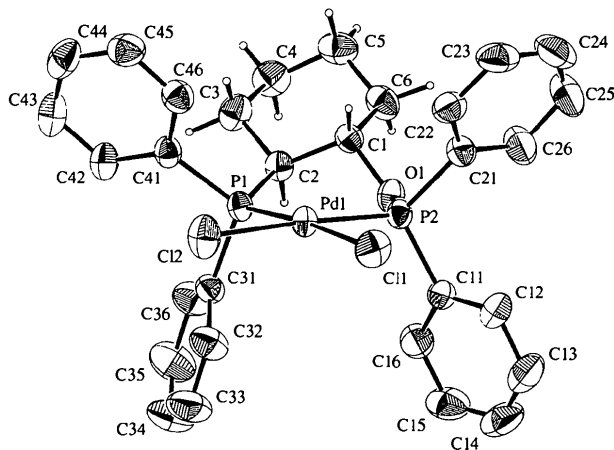


Fig. 1. PLATON (Spek, 1990) plot of the molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level. The H atoms of the phenyl rings have been omitted for clarity.