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trans-Dichlorobis[ethane-1,2-diylbis(diphenylphophine)-κ^2P,P']tungsten(II) pentane hemisolvate

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Key indicators

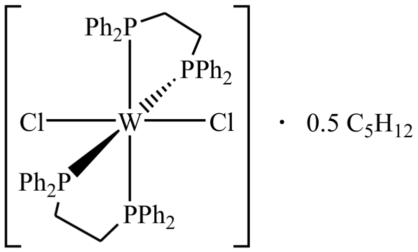
Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.008 Å
Disorder in solvent or counterion
R factor = 0.036
wR factor = 0.084
Data-to-parameter ratio = 15.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

trans-[WCl_2(dppe)$_2$] [dppe is ethane-1,2-diylbis(diphenylphosphine), $C_{26}H_{24}P_2$] was formed as by-product in the reaction of *trans*-[W(dppe)$_2$(N_2)$_2$] with the *m*-terphenyltin(II) chloride, [Sn(Cl)(C_6H_3-2,6-Mes$_2$)]$_2$ (Mes is 2,4,6-trimethylphenyl), which yields mainly the stannylidyne complex *trans*-[Cl(dppe)$_2$W$\equiv$Sn$-$$C_6H_3$-2,6-Mes$_2$]. The crystal structure of the pentane hemisolvate, *trans*-[WCl_2(dppe)$_2$]·0.5C_5H_{12}, has been determined. The geometric parameters of the title compound are compared with those of *trans*-[$MoCl_2$(dppe)$_2$]·0.5C_5H_{12}.

Comment

The synthesis of compounds containing a triple bond to silicon, germanium, tin or lead is one of the most challenging areas in main-group chemistry (Jutzi, 2000; Weidenbruch, 2003). Our recent studies in this field showed that thermal elimination of dinitrogen from the complexes *trans*-[M(dppe)$_2$(N_2)$_2$] (M = Mo, W; dppe is $Ph_2PCH_2CH_2PPh_2$) in the presence of the germanium(II) halides Cp*GeX (Cp* = C_5Me_5; X = Cl, Br, I) provides a convenient route to the germylidyne complexes *trans*-[X(dppe)$_2M$$\equiv$Ge$-$($\eta^1$-Cp*)]. These compounds feature a triple bond to linear-coordinated germanium (Filippou, Philippopoulos *et al.*, 2000; Filippou *et al.*, 2002). The usefulness of the dinitrogen elimination method was recently demonstrated with the selective synthesis and full characterization of the stannylidyne complex *trans*-[Cl(PMe_3)$_4$W$\equiv$Sn$-$$C_6H_3$-2,6-Mes$_2$], which is the first compound featuring a triple bond to linear-coordinated tin (Filippou, Portius *et al.*, 2003).



(4α)

The same methodology was recently applied to the dppe complex *trans*-[W(dppe)$_2$(N_2)$_2$], (1), to elucidate the influence of the ligand sphere on the selectivity of the reaction with the *m*-terphenyltin(II) chloride, [Sn(Cl)(C_6H_3-2,6-Mes$_2$)]$_2$, (2). This yielded mainly the stannylidyne complex *trans*-[Cl(dppe)$_2$W$\equiv$Sn$-$$C_6H_3$-2,6-Mes$_2$], (3) (Filippou, Philippopoulos & Schnakenburg, 2003). A by-product was also formed in this reaction, which by elemental analysis and ^{1}H NMR

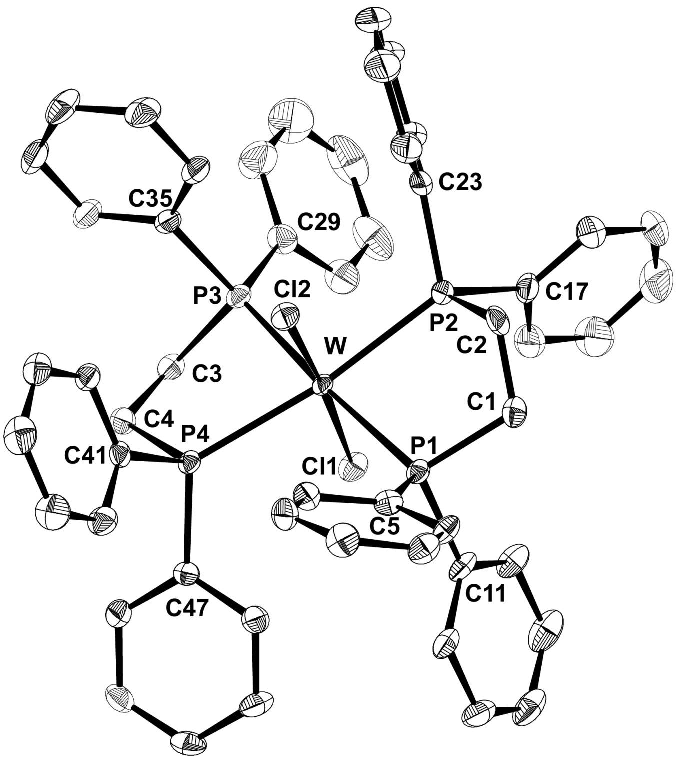


Figure 1
The molecular structure of (4α), showing 50% probability displacement ellipsoids (*DIAMOND*; Brandenburg, 1999). All H atoms and the solvent molecule have been omitted for clarity.

spectroscopy was identified as *trans*-[$WCl_2(dppe)_2$], (4). Complex (4) was previously prepared by ligand exchange of *trans*-[$WCl_2(PMePh_2)_4$] with dppe; however, its molecular structure was not reported (Over *et al.*, 1992). The title compound, (4α), crystallizes in the same space group ($C2/c$) as the isostructural molybdenum complex *trans*-[$MoCl_2(dppe)_2$]·$0.5C_5H_{12}$ (Filippou, Portius *et al.*, 2000). The 16 valence-electron complex reveals a distorted octahedral geometry with the *trans*-arranged chloro ligands forming at tungsten an angle of 173.65 (4)° (Table 1). Distortion results from the small bite of the dppe ligands [P1—W—P2 = 79.37 (4)° and P3—W—P4 = 78.91 (4)°] and is also evidenced in the tilt of the axial chloro ligands with respect to the equatorial plane defined by the four P atoms. The angle between the Cl1···Cl2 axis and the P_4 plane [82.76 (3)°] is similar to that in *trans*-[$MoCl_2(dppe)_2$]·$0.5C_5H_{12}$ [82.38 (7)°]. The W—P and W—Cl distances in (4α) [$(W—P)_{av}$ = 2.501 Å and $(W—Cl)_{av}$ = 2.423 Å] are slightly shorter than the Mo—P and Mo—Cl distances in *trans*-[$MoCl_2(dppe)_2$]·$0.5C_5H_{12}$ [$(Mo—P)_{av}$ = 2.529 Å and $(Mo—Cl)_{av}$ = 2.434 Å, respectively; Filippou, Portius *et al.*, 2000).

Experimental

A Schlenk tube was charged in a glove-box with complex (1) (1.635 g, 1.577 mmol) and a stoichiometric amount of (2) (0.737 g, 0.788 mmol). Toluene (100 ml) was added to the mixture and the orange suspension was gently refluxed for 10–15 min with a heating mantle. The color of the solution changed to dark red–brown. An IR spectrum of the resulting reaction solution was recorded and revealed that the $\nu(N_2)$ absorption bands of (1) at 2010 and 1949 cm^{-1} had disappeared. The warm solution was filtered from some black powder, the filtrate was evaporated to dryness, and the residue dried under high vacuum at 333 K for *ca* 2 h to afford the crude product, which was found by ^{1}H NMR spectroscopy to contain complex (3) contaminated with 4% of *trans*-[$W(dppe)_2Cl_2$], (4). Crude yield: 1.571 g (69%). Suitable yellow single crystals of (4α) were obtained upon diffusion of pentane into a toluene solution of the crude product at 298 K.

Crystal data

[$WCl_2(C_{26}H_{24}P_2)_2$]·$0.5C_5H_{12}$
M_r = 1087.61
Monoclinic, $C2/c$
a = 49.230 (13) Å
b = 10.955 (2) Å
c = 17.937 (4) Å
β = 99.49 (3)°
V = 9542 (4) Å^3
Z = 8

D_x = 1.514 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1723 reflections
θ = 3.0–25.0°
μ = 2.70 mm^{-1}
T = 180 (2) K
Plate, yellow
0.24 × 0.20 × 0.08 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: refined from ΔF (Walker & Stuart, 1983)
T_{min} = 0.563, T_{max} = 0.813
32 126 measured reflections
8465 independent reflections

6743 reflections with $I > 2\sigma(I)$
R_{int} = 0.056
θ_{max} = 25.5°
$h = -59 \rightarrow 59$
$k = -13 \rightarrow 13$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.084
S = 0.95
8465 reflections
553 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.029
$\Delta\rho_{max}$ = 1.39 e Å^{-3}
$\Delta\rho_{min}$ = −2.54 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00009 (2)

Table 1
Selected geometric parameters (Å, °).

Cl1—W	2.4324 (11)	P2—W	2.4847 (14)
Cl2—W	2.4131 (11)	P3—W	2.4803 (13)
P1—W	2.5130 (13)	P4—W	2.5251 (15)
Cl2—W—Cl1	173.65 (4)	P3—W—P1	174.87 (4)
Cl2—W—P3	95.21 (4)	P2—W—P1	79.37 (4)
Cl1—W—P3	87.74 (4)	Cl2—W—P4	91.47 (4)
Cl2—W—P2	81.97 (4)	Cl1—W—P4	83.58 (4)
Cl1—W—P2	103.27 (4)	P3—W—P4	78.91 (4)
P3—W—P2	97.09 (5)	P2—W—P4	172.02 (4)
Cl2—W—P1	88.01 (4)	P1—W—P4	105.05 (4)
Cl1—W—P1	89.45 (4)		

All H atoms were placed in calculated positions, with C—H distances ranging from 0.95 to 0.99 Å, and included in the refinement in riding-motion approximation, with $U_{iso} = 1.2U_{eq}$ of the carrier atom. Geometric restraints were applied to the geometry of the pentane solvent molecule so that the C—C distances were approximately 1.54 Å and the C—C—C angles were 109.5° The highest peak and deepest hole in the difference map are located 0.99 and 0.91 Å, respectively, from the W atom..

Data collection: *IPDS* (Stoe & Cie, 1997); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND*

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(Brandenburg, 1999); software used to prepare material for publication: *SHELXL*97.

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