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Dichlorobis(triphenylphosphine oxide)zinc(II) tetrahydrofuran disolvate

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.033
wR factor = 0.087
Data-to-parameter ratio = 11.5

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

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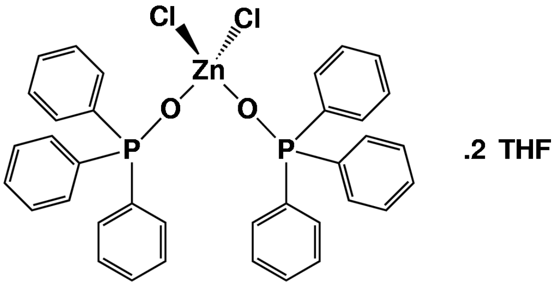
In the crystal structure of the title compound, $[ZnCl_2\{(C_6H_5)_3PO\}_2]\cdot2THF$ (THF is tetrahydrofuran, C_4H_8O), the Zn^{II} ion is four-coordinated by two Cl atoms and two O atoms in a distorted tetrahedral geometry. Additionally, two solvent THF molecules occupy the open space in the unit cell, not bonding to the Zn atom. The Zn—Cl distances are 2.2108 (6) and 2.2165 (6) Å, and the Zn—O distances are 1.9851 (15) and 1.9751 (15) Å. Within the tetrahedral coordination sphere around the central Zn atom, the bond angles are O1—Zn—O2 98.16 (6)° and Cl1—Zn—Cl2 120.55 (2)°; the four Cl—Zn—O bond angles range from 107.43 (4) to 110.55 (4)°.

Comment

Recently Mayer (1998) introduced the bond-strength concept, *i.e.* the importance of the thermodynamics of broken and formed bonds. Because of the importance of phosphine ligands in organometallic chemistry we decided to investigate, structurally and computationally, a series of metal complexes with triphenylphosphine and triphenylphosphine oxide ligands. In the course of our investigation of the coordination strength of triphenylphosphine and triphenylphosphine oxide, we have been able to redetermine the crystal structure of the title complex, (I). It has originally been reported without solvent molecules by Rose *et al.* (1980) and Kosky *et al.* (1982). Structures of the type $[M\{(C_6H_5)_3PO\}_2Cl_2]$ with M = Co^{II} (Mangion *et al.*, 1976) and M = Cu^{II} (Bertrand & Kalyanaraman, 1971) had previously been investigated. Studies on the IR spectra of compounds with M = Zn^{II} by Deacon & Green (1968, 1969), as well as the thermochemistry of M = Zn^{II}, Cd^{II}, Hg^{II} investigated by Jorge *et al.* (1978) give us valuable information as to whether the calculated bond strengths are in good agreement with experimental data.



(I)

As can be seen in Fig. 1, the Zn^{II} ion in the title compound has a slightly distorted tetrahedral coordination, where the metal is ligated by two O atoms and two Cl atoms. Compared to the C_2-symmetrical structure, (II), reported by Rose *et al.*

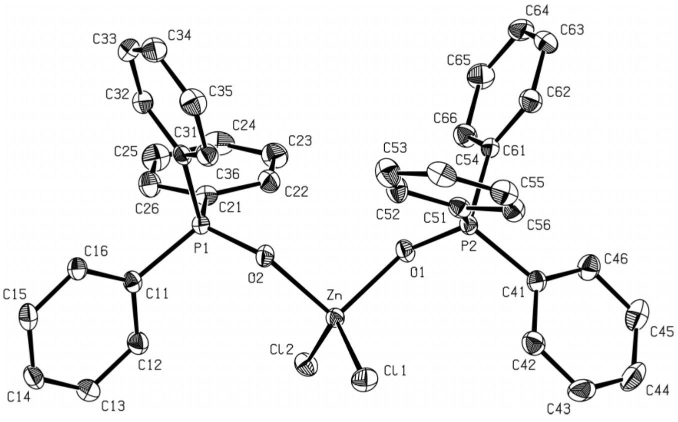


Figure 1
View of the title compound with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. The H atoms and THF molecules have been omitted for clarity.

(1980), (I) shows no point symmetry, and there are two solvent molecules present in the asymmetric unit. The THF molecules occupy the open space in the structure and are not bound to the central atom. Their incorporation also results in a slight flattening of the molecule in (I), as can seen by the larger Cl1—Zn—Cl2 angle of 120.55 (2)° and O1—Zn—O2 angle of 98.16 (6)° compared to 116.3 and 96.8° in (II). The biggest change in bond angles can be seen in the decrease of the Zn—O—P angle from 153.4° in (II) to 139.20 (9) and 141.01 (9)° in (I), whereas the effect on the O—P—C angles is negligible.

Furthermore the Cl—Zn—O—P torsion angles change from −38.9° in (II) to −8.3 (2)° and −8.8 (2)° in (I). A comparison of the corresponding Zn—O—P—C torsion angles indicates a rotation of the triphenylphosphine group of about 20° in the present compound, induced by the THF molecules in the structure, *e.g.* 78.3 (2) and 76.0 (2)° in (I) *versus* 54.7° in the earlier structure (II).

Experimental

The title compound was prepared by adding oxygen to a suspension of $Ni[P(C_6H_5)_3]_4$ and two equivalents of $ZnCl_2$ in toluene at 333 K. After filtration and removal of the solvent, colorless crystals were obtained by slowly cooling a saturated solution in tetrahydrofuran from 313 K to room temperature. NMR data confirm the presence of two THF molecules in the crystal. The crystal was fixed in a capillary with perfluorinated ether and transferred to the diffractometer.

Crystal data

$[ZnCl_2(C_{18}H_{15}OP)_2]\cdot 2C_4H_8O$
$M_r = 837.04$
Triclinic, $P\overline{1}$
$a = 11.6758$ (1) Å
$b = 12.9704$ (1) Å
$c = 15.2874$ (2) Å
$\alpha = 110.2721$ (4)°
$\beta = 109.8102$ (5)°
$\gamma = 92.8572$ (4)°
$V = 2006.16$ (4) Å^3
$Z = 2$
$D_x = 1.386$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7093 reflections
$\theta = 1.5$–25.4°
$\mu = 0.87$ mm^{-1}
$T = 123$ (1) K
Fragment, colorless
0.69 × 0.61 × 0.45 mm

Data collection

Nonius κ-CCD diffractometer
φ and ω-rotation scans
Absorption correction: multi-scan applied during the scaling procedure (Nonius, 2000)
$T_{min} = 0.559$, $T_{max} = 0.677$
30 256 measured reflections
7358 independent reflections
6793 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 25.4°$
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.087$
$S = 1.05$
7357 reflections
640 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 1.6738P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—Cl1	2.2108 (6)	P1—C21	1.789 (2)
Zn—Cl2	2.2165 (6)	P1—C31	1.791 (2)
Zn—O1	1.9851 (15)	P2—O1	1.5031 (15)
Zn—O2	1.9751 (15)	P2—C41	1.792 (2)
P1—O2	1.5039 (15)	P2—C51	1.789 (2)
P1—C11	1.794 (2)	P2—C61	1.794 (2)
Cl1—Zn—Cl2	120.55 (2)	C41—P2—C61	107.94 (11)
Cl1—Zn—O1	110.09 (4)	C51—P2—C61	107.43 (10)
Cl1—Zn—O2	107.43 (4)	Zn—O1—P2	139.20 (9)
Cl2—Zn—O1	107.77 (4)	Zn—O2—P1	141.01 (9)
Cl2—Zn—O2	110.55 (4)	P1—C11—C16	121.95 (17)
O1—Zn—O2	98.16 (6)	P1—C11—C12	118.43 (17)
O2—P1—C11	111.29 (9)	P1—C21—C26	121.67 (17)
O2—P1—C21	111.85 (9)	P1—C21—C22	118.35 (16)
O2—P1—C31	109.09 (9)	P1—C31—C36	118.36 (17)
C11—P1—C21	108.60 (10)	P1—C31—C32	121.80 (16)
C11—P1—C31	107.51 (10)	P2—C41—C46	121.51 (17)
C21—P1—C31	108.36 (10)	P2—C41—C42	118.48 (18)
O1—P2—C41	111.83 (9)	P2—C51—C52	117.87 (16)
O1—P2—C51	112.21 (9)	P2—C51—C56	122.11 (17)
O1—P2—C61	108.73 (9)	P2—C61—C66	118.62 (17)
C41—P2—C51	108.52 (10)	P2—C61—C62	121.53 (16)

All H atoms were located in the difference Fourier maps and refined freely except for those of the disordered THF solvent molecule. These were calculated in ideal positions and refined as a riding model.

Data collection: *Kappa-CCD Control Software* (Nonius, 2000); cell refinement: *DENZO* (Nonius, 2000); data reduction: *DENZO*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *PLATON*.

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References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

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Bertrand, J. A. & Kalyanaraman, A. R. (1971). *Inorg. Chim. Acta*, **5**, 341–345.

Deacon, G. B. & Green, J. H. S. (1968). *Spectrochim. Acta Part A*, **24**, 845–852.

Deacon, G. B. & Green, J. H. S. (1969). *Spectrochim. Acta Part A*, **25**, 355–364.

Jorge, R. A., Airoldi, C. & Chagas, A. P. (1978). *J. Chem. Soc. Dalton Trans.* pp. 1102–1104.

Kosky, C. A., Gayda, J.-P., Gibson, J. F., Jones S. F. & Williams D. J. (1982). *Inorg. Chem.* **21**, 3173–3179.

Mangion, M. M., Smith, R. & Shore, S. G. (1976). *Cryst. Struct. Commun.* **5**, 493–500.

Mayer, J. M. (1998). *Acc. Chem. Res.* **31**, 441–450.

Nonius (2000). *Kappa-CCD Control Software* and *DENZO*. Nonius BV, Delft, The Netherlands.

Rose, J. P., Lalancette, R. A., Potenza, J. A. & Schugar, H. J. (1980). *Acta Cryst.* B**36**, 2409–2411.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2000). *PLATON*. Utrecht University, The Netherlands.

m482 A. Zeller *et al.* • $[ZnCl_2(C_{18}H_{15}OP)_2]\cdot 2C_4H_8O$ *Acta Cryst.* (2001). E**57**, m480–m482