C5	0.2192 (6)	−0.1444 (4)	0.4572 (6)	0.053 (2)
C6	0.0437 (5)	0.3313 (3)	0.6014 (5)	0.037 (1)
C7	0.4685 (5)	0.2546 (4)	0.3574 (5)	0.037 (1)
C10	0.1520 (4)	0.3969 (3)	0.3719 (4)	0.027 (1)
C11	0.2351 (5)	0.4619 (3)	0.3180 (5)	0.032 (1)
C12	0.1670 (5)	0.5119 (3)	0.2087 (5)	0.041 (1)
C13	0.0426 (5)	0.4780 (3)	0.1932 (5)	0.042 (1)
C14	0.0317 (5)	0.4075 (3)	0.2939 (5)	0.032 (1)
C20	0.2518 (4)	0.2441 (3)	0.1591 (4)	0.029 (1)
C21	0.3066 (5)	0.3102 (3)	0.0726 (5)	0.035 (1)
C22	0.2084 (5)	0.3432 (4)	−0.0254 (5)	0.041 (1)
C23	0.0959 (5)	0.2988 (4)	−0.0029 (5)	0.038 (1)
C24	0.1216 (4)	0.2376 (3)	0.1109 (5)	0.032 (1)
C30	0.3085 (5)	0.3664 (3)	0.6270 (4)	0.031 (1)
C31	0.4046 (5)	0.3096 (4)	0.6890 (5)	0.039 (1)
C32	0.4974 (5)	0.3468 (4)	0.7836 (5)	0.049 (2)
C33	0.4956 (5)	0.4406 (4)	0.8158 (5)	0.050 (2)
C34	0.4010 (6)	0.4993 (4)	0.7532 (6)	0.050 (2)
C35	0.3079 (5)	0.4617 (3)	0.6594 (5)	0.038 (1)
C40	0.3901 (4)	0.0772 (3)	0.2384 (5)	0.030 (1)
C41	0.5018 (5)	0.0375 (4)	0.2940 (6)	0.051 (2)
C42	0.5453 (6)	−0.0454 (4)	0.2404 (7)	0.062 (2)
C43	0.4754 (6)	−0.0905 (4)	0.1346 (6)	0.051 (2)
C44	0.3617 (6)	−0.0535 (4)	0.0829 (6)	0.053 (2)
C45	0.3197 (5)	0.0305 (4)	0.1325 (5)	0.042 (1)
B	0.7528 (6)	0.2818 (5)	0.1201 (7)	0.048 (2)

Table 2. *Selected bond lengths (Å) and bond angles (°)*

Pd—P1	2.266 (1)	P2—C(Cp)	1.778 (4)
Pd—P2	2.245 (1)	P2—C(Ph)	1.811 (4)
Pd—O1	2.054 (3)	C—C(Cp)$_{\rm av}$	1.421
Pd—O2	2.031 (3)	C—C(Cp)$_{\rm min}$	1.406 (7)
Fe—C(Cp)$_{\rm av}$	2.035	C—C(Cp)$_{\rm max}$	1.437 (6)
Fe—C(Cp)$_{\rm min}$	2.009 (4)	O1—C2	1.290 (5)
Fe—C(Cp)$_{\rm max}$	2.053 (4)	O2—C4	1.269 (5)
P1—C(Me)	1.813 (4)	C1—C2	1.502 (6)
P1—C(Cp)	1.801 (4)	C2—C3	1.382 (7)
P1—C(Ph)	1.812 (4)	C3—C4	1.388 (7)
P2—C(Me)	1.805 (4)	C4—C5	1.517 (6)
P1—Pd—P2	92.70 (4)	C(Me)—P1—C(Ph)	104.7 (2)
P1—Pd—O1	89.17 (9)	C(Cp)—P1—C(Ph)	105.6 (2)
P1—Pd—O2	177.8 (1)	Pd—P2—C(Me)	114.4 (1)
P2—Pd—O1	174.34 (9)	Pd—P2—C(Cp)	114.0 (1)
P2—Pd—O2	87.97 (9)	Pd—P2—C(Ph)	111.8 (1)
O1—Pd—O2	90.4 (1)	C(Me)—P2—C(Cp)	106.0 (2)
Pd—P1—C(Me)	108.5 (1)	C(Me)—P2—C(Ph)	105.0 (2)
Pd—P1—C(Cp)	120.8 (1)	C(Cp)—P2—C(Ph)	104.8 (2)
Pd—P1—C(Ph)	113.8 (1)	Pd—O1—C2	124.4 (3)
C(Me)—P1—C(Cp)	101.7 (2)	Pd—O2—C4	125.7 (3)

The structure was solved by Patterson and difference Fourier methods. All non-H atoms were refined anisotropically. In the final full-matrix refinement H atoms were included as riding in standard positions (C—H = 0.98 Å).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Software*. Data reduction: *BEGIN* in *SDP* (Frenz, 1978). Program(s) used to solve structure: *FOUR* in *SDP*. Program(s) used to refine structure: *LSFM* in *SDP*. Molecular graphics: *PLATON* (Spek, 1994). Software used to prepare material for publication: *CIF VAX* in *MolEN* (Fair, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1977). *CAD*-4 *Operations Manual*. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4-SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft: Delft University Press.

Gan, K.-S. & Hor, T. S. A. (1995). *1,1'-Bis(diphenylphosphino)-ferrocene - Coordination Chemistry, Organic Syntheses, and Catalysis. Ferrocenes*, edited by A. Togni & T. Hayashi, pp. 3–104. Weinheim: VCH Verlagsgesellschaft.

Herberich, G. E. & Moss, S. (1995). *Chem. Ber.* **128**, 689–93.

Schultz, A. (1994). Dissertation, RWTH Aachen, Germany.

Spek, A. L. (1994). *PLATON. Molecular Graphics Program*. University of Utrecht, The Netherlands.

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A 1:4 Adduct of Tetrachlorobis(μ-phenylimido)dizirconium(IV) and Tetrahydrofuran

MIKA POLAMO,* ILPO MUTIKAINEN AND MARKKU LESKELÄ

Inorganic Chemistry Laboratory, Department of Chemistry, University of Helsinki, PO Box 55 (A. I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland. E-mail: mika.polamo@helsinki.fi

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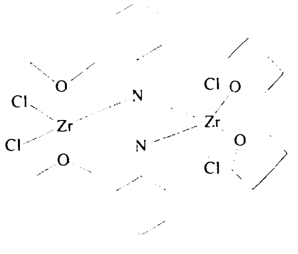
Abstract

The title complex, bis(μ-phenylimido)bis[dichlorobis-(tetrahydrofuran)zinc], [$Zr_2Cl_4(C_6H_5N)_2(C_4H_8O)_4$], contains two octahedral Zr^{IV} ions which are connected by two bridging phenylimido ligands. The Zr coordination polyhedra have significantly different geometries. In one, the chloro ligands are *cis*, while in the other they take up *trans* positions. Both Zr^{IV} ions are situated on a twofold axis.

Comment

Complexes containing Zr—N bonds are predominantly octahedral [ZrX_nL_m] adducts formed by the reaction between a monodentate or polydentate amine and a zirconium halide (Fay, 1987). Various homoleptic dialkylamido complexes involving zirconium and other early transition metals are also known (Bradley & Chisholm, 1976).

The title compound, (I), is a dimer in which two phenylimido ligands bridge two Zr^{IV} ions *via* N atoms (Fig. 1). The N1—Zr1 and N1—Zr2 distances [2.068 (2) and 2.051 (2) Å, respectively] are quite similar to those found in $[(\mu\text{-N}^t\text{Bu})\text{Zr}(\text{NMe}_2)_2]_2$ (Nugent & Harlow, 1979). Both Zr atoms lie on the diad axis at $x = \frac{1}{2}$, $z = \frac{1}{4}$ (Table 1), with a Zr1···Zr2 distance of 3.1466 (8) Å, and each has distorted octahedral coordination. The coordination sphere of Zr1 contains two *cis*-chloro ligands [Cl1—Zr1 2.5141 (10) Å and Cl1—Zr1—Cl1^i 96.56 (6)°; symmetry code: (i) $1 - x, y, \frac{1}{2} - z$], whereas that of Zr2 has two *trans*-chloro ligands [Cl2—Zr2 2.4880 (11) Å and Cl2—Zr2—Cl2^i 165.19 (5)°].



(I)

The octahedral coordination of each metal ion is completed by two tetrahydrofuran O atoms, with Zr1—O1 and Zr2—O2 distances of 2.216 (2) and 2.325 (2) Å, respectively. In the rectangular N1—Zr1—N1^i—Zr2 core, the Zr1—N1—Zr2 angle is 99.61 (10)°, while the N1—Zr1—N1^i and N1—Zr2—N1^i angles are 79.98 (14) and 80.80 (14)°, respectively.

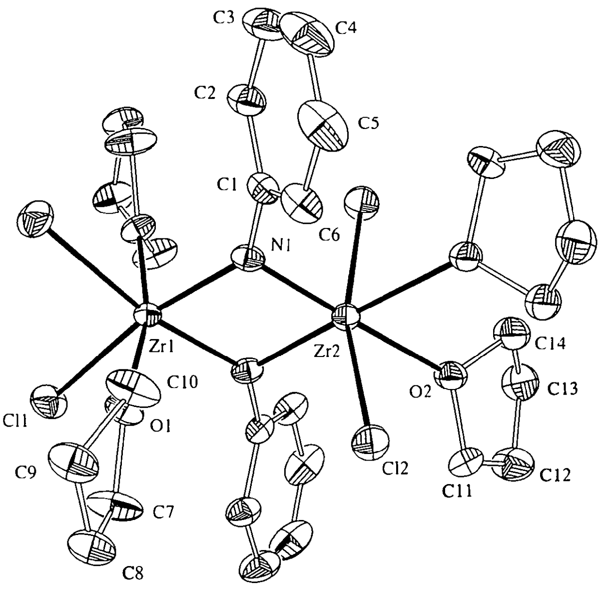


Fig. 1. A view of the title complex with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

N-Allylphenylamine (5.38 g, 43.8 mmol) was dissolved in tetrahydrofuran and the solution was cooled to 198 K. An equimolar amount of butyllithium (2 *M* in hexane) was added and the mixture was warmed slowly to room temperature. After removal of the tetrahydrofuran solvent, the lithium amide was dissolved in toluene (100 ml) and zirconium tetrachloride (4.78 g, 20.5 mmol) was added with vigorous stirring. The solution was refluxed for 60 min and then filtered to remove precipitated LiCl. Pentane (5 ml) was added to the filtrate which was then cooled to 273 K. Yellow prismatic crystals suitable for single-crystal measurements were obtained after 24 h. All reaction steps were carried out under an argon atmosphere using standard Schlenk techniques. The crystal used for the X-ray measurements was mounted on a fibre using the oil-drop method (Kottke & Stalke, 1993).

Crystal data

$[\text{Zr}_2\text{Cl}_4(\text{C}_6\text{H}_5\text{N})_2(\text{C}_4\text{H}_8\text{O})_4]$
$M_r = 794.88$
Monoclinic
$P2/c$
$a = 9.431$ (2) Å
$b = 11.270$ (2) Å
$c = 15.781$ (3) Å
$\beta = 91.13$ (3)°
$V = 1677.0$ (6) Å^3
$Z = 2$
$D_x = 1.574$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 5\text{–}20°$
$\mu = 0.974$ mm^{-1}
$T = 193$ (2) K
Prismatic
0.40 × 0.35 × 0.25 mm
Yellow

Data collection

Rigaku AFC-7*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.874$, $T_{\max} = 1.000$
3292 measured reflections
3292 independent reflections

2974 observed reflections $[I > 2\sigma(I)]$
$\theta_{\max} = 26.51°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 14$
$l = -19 \rightarrow 0$
3 standard reflections monitored every 200 reflections
intensity decay: 0.3%

Refinement

Refinement on F^2
$R(F) = 0.0362$
$wR(F^2) = 0.0896$
$S = 1.037$
3292 reflections
266 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 1.5053P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.08$
$\Delta\rho_{\max} = 0.68$ e Å^{-3}
$\Delta\rho_{\min} = -0.62$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Zr1	1/2	0.89729 (3)	1/4	0.03005 (12)
Zr2	1/2	0.61809 (4)	1/4	0.03371 (12)
Cl1	0.61759 (11)	1.04575 (9)	0.15545 (6)	0.0623 (3)
Cl2	0.32231 (10)	0.58964 (8)	0.13314 (6)	0.0549 (2)
O1	0.3151 (2)	0.9197 (2)	0.16266 (14)	0.0441 (5)
O2	0.6148 (3)	0.4591 (2)	0.18721 (14)	0.0471 (5)

N1	0.4015 (3)	0.7567 (2)	0.3091 (2)	0.0363 (5)
C1	0.3065 (3)	0.7369 (3)	0.3753 (2)	0.0374 (7)
C2	0.3463 (4)	0.7604 (3)	0.4598 (2)	0.0503 (8)
C3	0.2556 (5)	0.7353 (4)	0.5253 (3)	0.0692 (12)
C4	0.1249 (5)	0.6859 (5)	0.5087 (3)	0.079 (2)
C5	0.0832 (4)	0.6649 (5)	0.4271 (3)	0.0704 (13)
C6	0.1725 (4)	0.6887 (4)	0.3598 (3)	0.0514 (9)
C7	0.3110 (4)	0.9320 (6)	0.0714 (2)	0.0698 (13)
C8	0.1585 (4)	0.9520 (5)	0.0456 (2)	0.0579 (10)
C9	0.0827 (4)	0.9704 (5)	0.1270 (3)	0.0627 (11)
C10	0.1688 (4)	0.9006 (5)	0.1893 (3)	0.0647 (12)
C11	0.6223 (4)	0.4341 (4)	0.0962 (2)	0.0496 (8)
C12	0.7460 (6)	0.3513 (6)	0.0864 (3)	0.0768 (14)
C13	0.8101 (5)	0.3348 (5)	0.1727 (3)	0.0683 (11)
C14	0.6901 (6)	0.3618 (4)	0.2300 (3)	0.0684 (12)

Table 2. *Selected geometric parameters (Å, °)*

Zr1—N1	2.068 (2)	Zr2—N1	2.051 (2)
Zr1—O1	2.216 (2)	Zr2—O2	2.325 (2)
Zr1—Cl1	2.5141 (10)	Zr2—Cl2	2.4880 (11)
Zr1···Zr2	3.1466 (8)	N1—C1	1.407 (4)
N1^i—Zr1—N1	79.98 (14)	N1—Zr2—O2	178.14 (9)
N1—Zr1—O1^i	99.31 (9)	O2^i—Zr2—O2	79.19 (12)
N1—Zr1—O1	90.75 (9)	N1—Zr2—Cl2	97.51 (7)
O1^i—Zr1—O1	166.89 (13)	N1^i—Zr2—Cl2	93.75 (7)
N1—Zr1—Cl1^i	92.00 (7)	O2^i—Zr2—Cl2	84.50 (6)
N1—Zr1—Cl1	169.98 (7)	O2—Zr2—Cl2	84.11 (6)
O1^i—Zr1—Cl1	86.69 (7)	Cl2^i—Zr2—Cl2	165.19 (5)
O1—Zr1—Cl1	84.59 (6)	C1—N1—Zr2	121.2 (2)
Cl1^i—Zr1—Cl1	96.56 (6)	C1—N1—Zr1	139.0 (2)
N1—Zr2—N1^i	80.80 (14)	Zr2—N1—Zr1	99.61 (10)
N1—Zr2—O2^i	100.03 (9)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1234). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bradley, D. C. & Chisholm, M. H. (1976). *Acc. Chem. Res.* **9**, 273–280.

Fay, R. C. (1987). *Comprehensive Coordination Chemistry*, edited by G. Wilkinson, R. D. Gillard & J. A. McCleverty, Vol. 3, pp. 371–376. Oxford: Pergamon Press.

Kottke, T. & Stalke, D. (1993). *J. Appl. Cryst.* **26**, 615–619.

Molecular Structure Corporation (1993*a*). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1993*b*). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6c. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Nugent, W. A. & Harlow, R. L. (1979). *Inorg. Chem.* **18**, 2030–2032.

Sheldrick, G. M. (1990). *SHELXTL/PC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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Tricarbonyl(cyclopentadienyl)(selenotriphenylphosphonium)tungsten(I) Perchlorate, $[W(C_5H_5)(C_{18}H_{15}PSe)(CO)_3](ClO_4)$

CARSTEN THÖNE AND PETER G. JONES

Institut für Analytische und Anorganische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: p.jones@tu-bs.de

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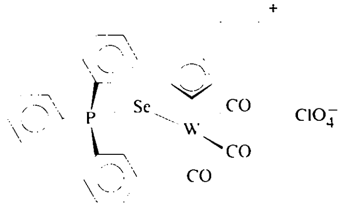
Abstract

The P—Se bond length of 2.194 (1) Å indicates selenophosphonium character, rather than that of a triphenylphosphine selenide complex. The W atom displays 'piano-stool' coordination with a W—Se bond length of 2.658 (1) Å.

Comment

Recently, we reported the first crystal structure of an organoselenophosphonium salt, namely $[Ph_3PSeMe](ClO_4)$ (Jones & Thöne, 1994). This compound was obtained by the reaction of Ph_3PAuCl with Me_2Se_2 in the presence of $AgClO_4$. An analogous reaction employing the organotungsten diselenide $[Cp(CO)_3W]_2Se_2$ (Cp is η^5-cyclopentadienyl) instead of Me_2Se_2 led to the title compound, (I), in low yield.



(I)

The cation is shown in Fig. 1; the structure of the selenophosphonium moiety is very similar to that in $[Ph_3PSeMe]^+$. The Se atom displays slightly distorted pseudo-tetrahedral geometry [P—Se(1)—W(1) 111.43 (4)°], and the P—Se bond length of 2.194 (1) Å is only slightly shorter than that of 2.205 (2) Å observed in $[Ph_3PSeMe]^+$. Corresponding P—Se bond lengths in λ^5-organoselenophosphoranes are considerably longer [2.273 (2) Å in $(MeO)P(Se)C(CF_3)_2N{=}CNMe_2$ (Burger, Ottlinger, Frank & Schubert, 1978), 2.243 (1) Å in (p-O_2NPhO)-(Ph)(p-ClPhSe)P(NMe)C(=O)NMe and 2.239 (2) Å in (PhSe)(Cl)(Me)P(NMe)C(=O)NPh (Pinchuk, Müller, Thönnessen, Shermolovich, Jones & Schmutzler, 1995)].

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