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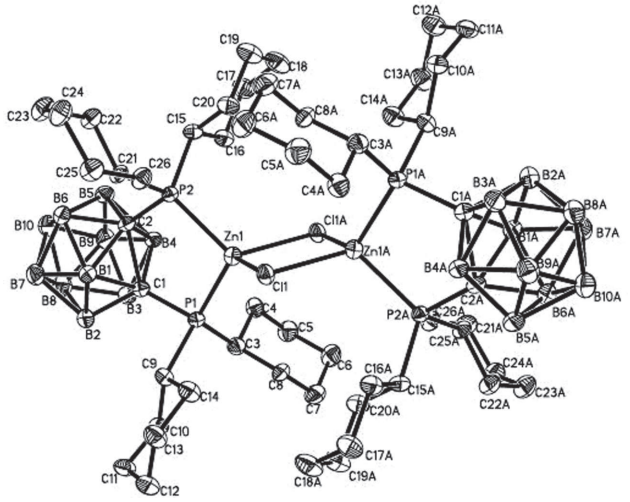
Crystal structure of di-μ-chlorido-bis[1,2-bis (dicyclohexylphosphino)-1,2-dicarba-*closo*-dodecaborane-κ^2P,P']zinc(II), $C_{52}H_{108}B_{20}Cl_2P_4Zn_2$



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Abstract

$C_{52}H_{108}B_{20}Cl_2P_4Zn_2$, monoclinic, $C2/c$ (no. 15), $a = 31.783(3)$ Å, $b = 10.0780(10)$ Å, $c = 24.9326(19)$ Å, $\beta = 109.901(2)°$, $V = 7509.2(11)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0569$, $wR_{ref}(F^2) = 0.0972$, $T = 298$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow blocks
	Size 0.18 × 0.08 × 0.06 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	8.3 cm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω
$2\theta_{max}$, completeness:	50°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	18590, 6558, 0.132
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2649
$N(param)_{refined}$:	362
Programs:	SHELX [7], Bruker programs [8]

Source of material

The ligand 1,2-$(PCy_2)_2$-1,2-$C_2B_{10}H_{10}$, was synthesized according to the literature method [1]. By the reaction of $ZnCl_2$ (1 mmol) and 1,2-$(PCy_2)_2$-1,2-$C_2B_{10}H_{10}$ in chloromethane (10 mL) under N_2 atmosphere. The mixture was refluxed for 4 h, then a colourless solution formed. Single crystals were obtained by slow evaporation of a dichloromethane/n-hexane solution. Yield: (48.9%, m.p. 463–472 K). FTIR (KBr) ν (cm^{-1}): 2989, 2966, 2930, 2872 (C—H); 2614, 2602, 2585, 2556 (B—H); 1071 (C—P).

Experimental details

All H atoms were placed geometrically and treated as riding on their parent atoms, with B—H 1.10, C—H 0.96, with $U_{iso}(H) = 1.2U_{eq}(B)$, $U_{iso}(H) = 1.5U_{eq}(C)$.

Discussion

The title complex shows a crystallographically imposed inversion symmetry (A = $-x$, y, 1/2$-z$. Comparison of the configuration of the free ligand 1,2-$(PCy_2)_2$-1,2-$(C_2B_{10}H_{10})$: the P1—C1—C2—P2 torsion angle is 10.9(4)° in the free ligand [2, 3], whereas coordinated to Zn, this torsion angle is largely altered with the value 0.0(2) in the title complex. The two Cc—Cc—P angles in the free ligand is 113.48(5)° for C(2)—C(1)—P(1) and C(1)—C(2)—P(2), while these two angles in the title complex tend to become equivalent to each other (115.38 and 115.56°) [4, 5]. These data show

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Zn1	0.30463(2)	0.76624(7)	0.53116(3)	0.0388(2)
Cl1	0.25360(4)	0.59301(14)	0.52602(5)	0.0376(4)
P1	0.34466(5)	0.85758(15)	0.61647(6)	0.0319(4)
P2	0.36191(5)	0.73367(16)	0.49798(5)	0.0309(4)
B1	0.4322(2)	0.7336(8)	0.6165(2)	0.0389(18)
H1	0.4193	0.6364	0.6236	0.047*
B2	0.4501(2)	0.8572(7)	0.6712(3)	0.042(2)
H2	0.4503	0.8392	0.7148	0.051*
B3	0.4356(2)	1.0162(8)	0.6366(3)	0.044(2)
H3	0.4265	1.1020	0.6576	0.053*
B4	0.4094(2)	0.9821(7)	0.5629(3)	0.0368(19)
H4	0.3818	1.0436	0.5357	0.044*
B5	0.4500(2)	0.9091(7)	0.5364(3)	0.042(2)
H5	0.4501	0.9255	0.4928	0.050*
B6	0.4646(2)	0.7524(8)	0.5713(3)	0.0431(19)
H6	0.4742	0.6671	0.5505	0.052*
B7	0.4898(2)	0.7796(8)	0.6463(3)	0.048(2)
H7	0.5152	0.7116	0.6736	0.058*
B8	0.4919(2)	0.9561(8)	0.6568(3)	0.051(2)
H8	0.5195	1.0029	0.6911	0.061*
B9	0.4655(2)	1.0377(8)	0.5893(3)	0.049(2)
H9	0.4750	1.1372	0.5793	0.059*
B10	0.5013(2)	0.8937(8)	0.5969(3)	0.051(2)
H10	0.5345	0.9007	0.5927	0.061*
C1	0.40250(18)	0.8793(6)	0.6143(2)	0.0371(16)
C2	0.41169(18)	0.8138(5)	0.5516(2)	0.0362(16)
C3	0.32592(19)	1.0220(6)	0.6342(2)	0.0404(16)
H3A	0.3461	1.0494	0.6719	0.049*
C4	0.32459(19)	1.1325(6)	0.5909(2)	0.0434(16)
H4A	0.3547	1.1500	0.5910	0.052*
H4B	0.3066	1.1039	0.5528	0.052*
C5	0.3049(2)	1.2589(7)	0.6061(2)	0.0554(17)
H5A	0.3244	1.2909	0.6428	0.066*
H5B	0.3036	1.3265	0.5779	0.066*
C6	0.2587(2)	1.2383(7)	0.6087(2)	0.0576(18)
H6A	0.2382	1.2146	0.5712	0.069*
H6B	0.2482	1.3199	0.6204	0.069*
C7	0.2598(2)	1.1282(6)	0.6510(2)	0.0558(19)
H7A	0.2775	1.1570	0.6892	0.067*
H7B	0.2296	1.1111	0.6504	0.067*
C8	0.27955(18)	1.0006(6)	0.6372(2)	0.0418(17)
H8A	0.2812	0.9349	0.6663	0.050*
H8B	0.2600	0.9664	0.6009	0.050*
C9	0.35583(18)	0.7548(6)	0.68182(19)	0.0389(15)
H9A	0.3824	0.7024	0.6846	0.047*
C10	0.36732(19)	0.8267(6)	0.7399(2)	0.0429(17)
H10A	0.3914	0.8896	0.7443	0.052*
H10B	0.3414	0.8755	0.7412	0.052*
C11	0.3814(2)	0.7268(6)	0.7880(2)	0.0465(17)
H11A	0.4083	0.6815	0.7878	0.056*
H11B	0.3883	0.7725	0.8242	0.056*
C12	0.3449(2)	0.6262(6)	0.7820(2)	0.0576(19)
H12A	0.3551	0.5616	0.8125	0.069*
H12B	0.3189	0.6707	0.7854	0.069*
C13	0.3319(2)	0.5559(6)	0.7252(2)	0.0528(19)
H13A	0.3071	0.4966	0.7217	0.063*
H13B	0.3569	0.5026	0.7238	0.063*
C14	0.3186(2)	0.6530(6)	0.6753(2)	0.0486(17)
H14A	0.2913	0.6987	0.6738	0.058*
H14B	0.3127	0.6047	0.6399	0.058*
C15	0.35554(19)	0.8075(5)	0.4272(2)	0.0358(16)
H15	0.3825	0.7889	0.4178	0.043*
C16	0.34621(19)	0.9577(6)	0.4221(2)	0.0416(16)
H16A	0.3204	0.9773	0.4332	0.050*
H16B	0.3718	1.0050	0.4476	0.050*
C17	0.3373(2)	1.0041(6)	0.3611(2)	0.0542(18)
H17A	0.3309	1.0984	0.3585	0.065*
H17B	0.3638	0.9895	0.3509	0.065*
C18	0.2981(2)	0.9297(7)	0.3198(2)	0.062(2)
H18A	0.2935	0.9593	0.2812	0.075*
H18B	0.2711	0.9497	0.3283	0.075*
C19	0.3061(2)	0.7800(7)	0.3237(2)	0.0584(19)
H19A	0.2798	0.7345	0.2987	0.070*
H19B	0.3312	0.7585	0.3116	0.070*
C20	0.31566(18)	0.7349(6)	0.3845(2)	0.0440(16)
H20A	0.3217	0.6403	0.3870	0.053*
H20B	0.2893	0.7497	0.3950	0.053*
C21	0.38465(19)	0.5631(5)	0.4955(2)	0.0349(15)
H21	0.4062	0.5464	0.5337	0.042*
C22	0.41062(19)	0.5435(6)	0.4540(2)	0.0444(17)
H22A	0.3904	0.5525	0.4151	0.053*
H22B	0.4336	0.6111	0.4608	0.053*
C23	0.4321(2)	0.4070(6)	0.4623(3)	0.0569(19)
H23A	0.4545	0.4017	0.5001	0.068*
H23B	0.4471	0.3942	0.4347	0.068*
C24	0.3975(2)	0.2966(6)	0.4555(2)	0.0568(19)
H24A	0.3777	0.2935	0.4161	0.068*
H24B	0.4128	0.2118	0.4645	0.068*
C25	0.3703(2)	0.3189(5)	0.4940(2)	0.0478(18)
H25A	0.3894	0.3086	0.5334	0.057*
H25B	0.3469	0.2523	0.4859	0.057*
C26	0.34870(19)	0.4585(6)	0.4858(2)	0.0411(16)
H26A	0.3272	0.4666	0.4475	0.049*
H26B	0.3329	0.4711	0.5126	0.049*

that the symmetry of the moiety 1,2-$(PCy_2)_2$-1,2-$(C_2B_{10}H_{10})$ in the three complexes has a tendency to approach C_{2v} symmetry. The average bond lengths of C—P in the complexes (1.872(3) Å) are similar with the corresponding distance 1.894(3) Å in 1,2-$(PCy_2)_2$-1,2-$(C_2B_{10}H_{10})$, indicating that the coordinating to the metal atom has no influence on this distance [6].

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