Crystal structure of chlorobis(η^5 -pentamethylcyclopentadienyl)-(η^3 -2-methyl-2-propenyl)zirconium, $\text{Zr}(\text{C}_4\text{H}_7)(\text{C}_{10}\text{H}_{15})_2\text{Cl}$

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Abstract

$\text{C}_{24}\text{H}_{37}\text{ClZr}$, triclinic, $P\bar{1}$ (no. 2), $a = 8.7650(1)$ Å, $b = 9.3278(1)$ Å, $c = 15.3642(2)$ Å, $\alpha = 77.5549(6)^\circ$, $\beta = 80.6252(7)^\circ$, $\gamma = 70.8162(7)^\circ$, $V = 1152.7$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.021$, $wR_{\text{ref}}(F^2) = 0.054$, $T = 150$ K.

Source of material

The compound may be synthesized as described previously [1], or through the direct reaction of bis(pentamethylcyclopentadienyl)-zirconium dichloride with one equivalent of 2-methylallyl magnesium chloride. The compound was crystallized by evaporation of a saturated hexane solution.

Experimental details

Positional parameters for all hydrogen atoms could be refined successfully, as well as their isotropic thermal parameters, except for H19B, whose thermal parameter was fixed at 1.5 times the isotropic equivalent of C19.

Discussion

The structural result is similar to that of a related σ allyl complex [2], although there is a significant difference in the allyl group orientations, as can be seen from the $\text{Zr}-\text{C}21-\text{C}22-\text{C}23$ and $\text{Zr}-\text{C}21-\text{C}22-\text{C}24$ torsion angles, $-65.0(2)^\circ$ and $118.9(2)^\circ$, which can be compared with the value of $-116.1(3)^\circ$ for the σ allyl complex. The $\text{C}22-\text{C}23$ and $\text{C}22-\text{C}24$ distances of $1.504(2)$ Å $1.336(2)$ Å suggest that there is little if any disorder

between the CH_3 (C23) and CH_2 (C24) groups. Possibly this occurs as a result of $\text{C}-\text{H}\cdots\pi$ interactions (e.g., $\text{C}22\cdots\text{H}6\text{b}$, 2.70 Å). Due to the presence of the new methyl substituent, there appears to be some steric influence on the bonding parameters, such as $d(\text{Zr}-\text{Cl}) = 2.4480(3)$ Å, $d(\text{Zr}-\text{C}21) = 2.3421(1)$ Å, and the average tilt of the methyl groups by 8.7° out of the pentamethylcyclopentadienyl ligand plane. For the σ allyl analogue, the respective values were $2.4362(5)$ Å, $2.325(2)$ Å, and 7.6° [2], while for a σ phenyl analogue, the average $\text{Zr}-\text{Cl}$ and $\text{Zr}-\text{C}(\text{phenyl})$ distances were $2.447(1)$ Å and $2.289(3)$ Å, respectively [3].

Table 1. Data collection and handling.

Crystal:	yellow prism, size $0.20 \times 0.23 \times 0.33$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	5.98 cm^{-1}
Diffraction, scan mode:	Nonius KappaCCD, ϕ/ω
$2\theta_{\text{max}}$:	56.04°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	8666, 5485
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 5244
$N(\text{param})_{\text{refined}}$:	383
Programs:	SIR97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(6A)	2i	0.854(4)	0.489(3)	0.248(2)	0.079(9)
H(6B)	2i	0.706(3)	0.517(3)	0.316(2)	0.077(9)
H(6C)	2i	0.708(3)	0.628(3)	0.226(2)	0.058(7)
H(7A)	2i	0.352(4)	0.368(3)	0.355(2)	0.077(9)
H(7B)	2i	0.469(3)	0.430(3)	0.379(2)	0.059(7)
H(7C)	2i	0.340(3)	0.537(3)	0.321(2)	0.061(7)
H(8A)	2i	0.264(3)	0.276(3)	0.235(2)	0.056(7)
H(8B)	2i	0.230(3)	0.426(3)	0.165(2)	0.058(7)
H(8C)	2i	0.305(3)	0.268(3)	0.132(2)	0.063(7)
H(9A)	2i	0.688(3)	0.202(3)	0.002(1)	0.044(6)
H(9B)	2i	0.599(3)	0.376(3)	-0.027(2)	0.051(6)
H(9C)	2i	0.502(3)	0.266(3)	0.014(2)	0.056(7)
H(10A)	2i	0.933(3)	0.425(3)	0.098(2)	0.073(8)
H(10B)	2i	0.806(3)	0.528(3)	0.035(2)	0.059(7)
H(10C)	2i	0.885(3)	0.358(3)	0.024(2)	0.067(8)
H(16A)	2i	1.031(3)	-0.351(3)	0.311(2)	0.074(8)
H(16B)	2i	1.035(3)	-0.204(3)	0.347(2)	0.068(8)
H(16C)	2i	1.089(4)	-0.225(3)	0.243(2)	0.074(8)
H(17A)	2i	0.688(3)	-0.284(3)	0.446(2)	0.049(6)
H(17B)	2i	0.610(3)	-0.113(3)	0.467(2)	0.061(7)
H(17C)	2i	0.794(3)	-0.188(3)	0.451(2)	0.059(7)
H(18A)	2i	0.381(4)	-0.122(4)	0.360(2)	0.082(9)
H(18B)	2i	0.361(3)	0.065(3)	0.368(2)	0.083(9)
H(18C)	2i	0.319(3)	0.009(3)	0.284(2)	0.056(7)
H(19A)	2i	0.566(4)	-0.008(3)	0.065(2)	0.080(9)

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(19B)	2i	0.404(5)	0.034(4)	0.128(3)	0.12
H(19C)	2i	0.513(3)	-0.142(3)	0.120(2)	0.073(8)
H(20A)	2i	0.904(4)	-0.246(4)	0.086(2)	0.09(1)
H(20B)	2i	1.003(3)	-0.152(3)	0.105(2)	0.054(7)
H(20C)	2i	0.858(3)	-0.065(4)	0.049(2)	0.075(9)
H(21A)	2i	0.834(2)	0.035(2)	0.399(1)	0.040(5)

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(21B)	2i	0.654(2)	0.127(2)	0.421(1)	0.029(4)
H(23A)	2i	1.060(3)	0.129(3)	0.425(2)	0.065(7)
H(23B)	2i	1.017(3)	0.313(3)	0.423(2)	0.057(7)
H(23C)	2i	1.012(3)	0.254(2)	0.335(2)	0.046(6)
H(24A)	2i	0.767(3)	0.404(2)	0.505(1)	0.042(5)
H(24B)	2i	0.612(3)	0.341(2)	0.504(1)	0.038(5)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Zr(1)	2i	0.72981(1)	0.13586(1)	0.239700(7)	0.01268(7)	0.01195(7)	0.01410(7)	-0.00379(5)	-0.00194(4)	-0.00328(4)
Cl(1)	2i	1.01485(4)	0.10842(4)	0.18565(3)	0.0146(2)	0.0281(2)	0.0372(2)	-0.0067(1)	0.0014(1)	-0.0069(1)
C(1)	2i	0.6621(2)	0.4311(2)	0.21448(9)	0.0282(7)	0.0120(6)	0.0240(6)	-0.0055(5)	-0.0068(5)	-0.0015(5)
C(2)	2i	0.5155(2)	0.3957(2)	0.24743(9)	0.0208(6)	0.0167(6)	0.0184(6)	0.0016(5)	-0.0010(5)	-0.0021(5)
C(3)	2i	0.4733(2)	0.3344(2)	0.18127(9)	0.0164(6)	0.0183(6)	0.0223(6)	-0.0038(5)	-0.0048(5)	0.0024(5)
C(4)	2i	0.5980(2)	0.3273(2)	0.10824(9)	0.0233(6)	0.0163(6)	0.0164(6)	-0.0039(5)	-0.0042(5)	-0.0001(5)
C(5)	2i	0.7115(2)	0.3903(2)	0.12890(9)	0.0212(6)	0.0159(6)	0.0221(6)	-0.0060(5)	-0.0003(5)	0.0016(5)
C(6)	2i	0.7379(3)	0.5218(2)	0.2543(1)	0.067(1)	0.0229(8)	0.041(1)	-0.0236(8)	-0.0222(9)	0.0009(7)
C(7)	2i	0.4105(2)	0.4376(2)	0.3312(1)	0.0324(8)	0.042(1)	0.0253(8)	0.0122(8)	0.0025(7)	-0.0089(7)
C(8)	2i	0.3076(2)	0.3215(2)	0.1799(1)	0.0199(7)	0.0395(9)	0.047(1)	-0.0105(7)	-0.0106(7)	0.0068(8)
C(9)	2i	0.5974(3)	0.2911(2)	0.0175(1)	0.054(1)	0.0272(8)	0.0185(7)	-0.0096(8)	-0.0098(7)	-0.0019(6)
C(10)	2i	0.8476(2)	0.4275(2)	0.0652(1)	0.0318(8)	0.0349(9)	0.0373(9)	-0.0147(7)	0.0056(7)	0.0085(8)
C(11)	2i	0.8450(2)	-0.1588(2)	0.2709(1)	0.0230(7)	0.0133(6)	0.0413(8)	-0.0037(5)	-0.0018(6)	-0.0043(6)
C(12)	2i	0.7061(2)	-0.1270(2)	0.33266(9)	0.0258(7)	0.0149(6)	0.0220(6)	-0.0084(5)	-0.0077(5)	0.0000(5)
C(13)	2i	0.5676(2)	-0.0596(2)	0.28494(9)	0.0236(7)	0.0173(6)	0.0233(6)	-0.0103(5)	-0.0071(5)	0.0005(5)
C(14)	2i	0.6206(2)	-0.0564(2)	0.19256(9)	0.0435(8)	0.0194(6)	0.0202(6)	-0.0180(6)	-0.0095(6)	-0.0014(5)
C(15)	2i	0.7919(2)	-0.1148(2)	0.1831(1)	0.0473(9)	0.0185(6)	0.0294(7)	-0.0167(6)	0.0105(7)	-0.0125(6)
C(16)	2i	1.0148(2)	-0.2428(2)	0.2948(2)	0.0255(9)	0.0238(9)	0.098(2)	0.0016(7)	-0.009(1)	0.004(1)
C(17)	2i	0.6991(3)	-0.1828(2)	0.4320(1)	0.056(1)	0.0301(8)	0.0240(8)	-0.0229(8)	-0.0154(8)	0.0074(6)
C(18)	2i	0.3955(2)	-0.0277(2)	0.3283(1)	0.0237(8)	0.042(1)	0.050(1)	-0.0160(7)	-0.0018(7)	0.0103(8)
C(19)	2i	0.5128(3)	-0.0390(3)	0.1215(1)	0.094(2)	0.043(1)	0.034(1)	-0.042(1)	-0.035(1)	0.0052(8)
C(20)	2i	0.8957(4)	-0.1453(3)	0.0972(2)	0.091(2)	0.041(1)	0.052(1)	-0.034(1)	0.040(1)	-0.033(1)
C(21)	2i	0.7540(2)	0.1394(2)	0.38872(9)	0.0267(7)	0.0211(6)	0.0173(6)	-0.0078(5)	-0.0050(5)	-0.0040(5)
C(22)	2i	0.8117(2)	0.2447(2)	0.42593(9)	0.0312(7)	0.0245(7)	0.0189(6)	-0.0096(6)	-0.0087(5)	-0.0030(5)
C(23)	2i	0.9872(2)	0.2358(3)	0.3999(1)	0.0319(8)	0.054(1)	0.042(1)	-0.0169(8)	-0.0099(7)	-0.0189(9)
C(24)	2i	0.7216(2)	0.3366(2)	0.4831(1)	0.046(1)	0.0315(8)	0.0214(7)	-0.0147(7)	-0.0042(7)	-0.0086(6)

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