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Crystal structure of (hydrido)(η^3-butenyl)bis(η^5-pentamethylcyclopentadienyl)zirconium, $Zr(C_4H_7)[C_5(CH_3)_5]_2(H)$

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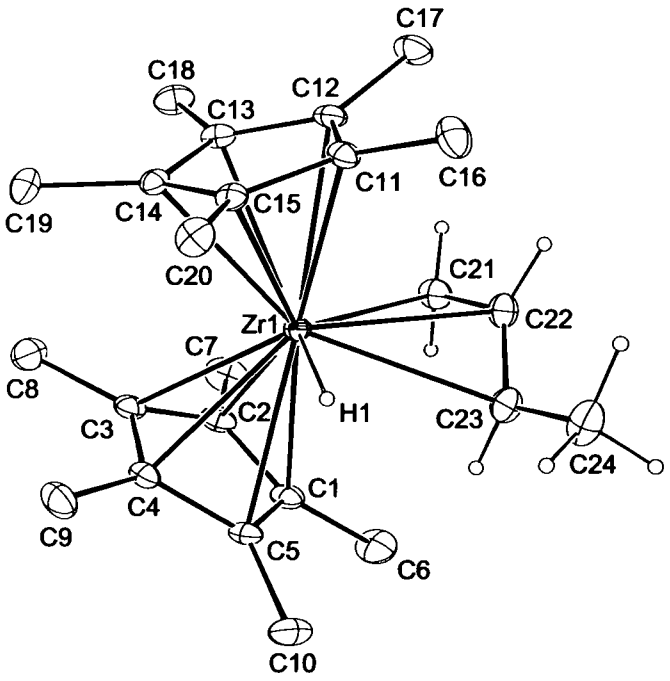

Abstract

$C_{24}H_{38}Zr$, triclinic, $P\bar{1}$ (no. 2), a = 8.6524(3) Å, b = 9.3669(2) Å, c = 14.2269(5) Å, α = 81.977(2)°, β = 88.117(2)°, γ = 72.557(2)°, V = 1089.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.034, $wR_{ref}(F^2)$ = 0.079, T = 150 K.

Source of material

The compound is readily prepared from $Zr(C_5Me_5)_2(n\text{-}C_4H_9)_2$, which loses *n*-butane slowly at room temperature (ca. 12 or more hours) [1], yielding the title compound. Crystallization may then be achieved by cooling concentrated solutions of the compound in pentane to –60 °C.

Experimental details

The identification of the location of the hydride ligand could be supported by the direction of tilting between the two pentamethylcyclopentadienyl ligands, and by the deviations of their carbon atoms from the least-squares planes defined be the five metal-bound atoms, C1 – C5 and C11 – C15. In addition to the hydride ligand, the hydrogen atoms on the methylallyl ligand were subjected to isotropic refinement in order to observe their positional orientations relative to the allyl ligand plane. The remaining hydrogen atoms were placed in fixed locations.

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Discussion

The reaction of $Zr(C_5H_5)_2Cl_2$ with two equivalents of *n*-butyllithium yields the purported compound $Zr(C_5H_5)_2$(1-butene) [2,3], which has found significant application in organic synthesis. However, spectroscopic data have suggested that the butene ligand actually becomes converted to a methylallyl ligand and a hydride ligand, leading to an 18-electron Zr(IV) complex rather than a 16-electron Zr(II) complex. This structural determination of the pentamethylcyclopentadienyl ligand analogue serves to confirm that formulation.

The Zr—C distances for the C_5Me_5 ligand average to 2.565(7) Å. The bonding of the allyl ligand is quite unsymmetric, with the Zr—C(21,22,23) distances being 2.383(2) Å, 2.524(2) Å, and 2.654(3) Å, respectively. Together with C21—C22 and C22—C23 distances of 1.434(4) Å and 1.369(4) Å, this reflects some contribution from a σ coordination mode. However, the apparent hydride position, at a reasonable 1.76(2) Å from the zirconium center, is fairly close to C23 at 2.41 Å (H1–Zr–C23 angle of 62.3(9)°), apparently providing an indication that the hydride and allyl ligands are well-positioned to regenerate a 1-butene ligand. Although the distance of 2.41 Å is substantially shorter than an expected van der Waals separation, it does not appear short enough to be regarded as bearing any significant degree of contribution as a C—H bond engaging in an agostic interaction with an electron deficient metal center.

Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.08 × 0.20 × 0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.09 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, φ/ω
$2\theta_{max}$:	54.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7472, 4918
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4230
$N(param)_{refined}$:	268
Programs:	SIR97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.583(3)	0.372(3)	0.137(2)	0.024(6)
H(6A)	2*i*	0.8710	0.6051	0.2220	0.060
H(6B)	2*i*	0.8916	0.6106	0.3327	0.060
H(6C)	2*i*	0.7502	0.7375	0.2722	0.060
H(7A)	2*i*	0.8323	0.4419	0.5012	0.060
H(7B)	2*i*	0.9542	0.3610	0.4243	0.060
H(7C)	2*i*	0.8517	0.2699	0.4898	0.060
H(8A)	2*i*	0.6055	0.1978	0.4934	0.053

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(8B)	2*i*	0.4185	0.2777	0.4663	0.053
H(8C)	2*i*	0.5106	0.3536	0.5311	0.053
H(9A)	2*i*	0.2232	0.5728	0.3059	0.050
H(9B)	2*i*	0.2661	0.3952	0.3403	0.050
H(9C)	2*i*	0.2824	0.4559	0.2307	0.050
H(10A)	2*i*	0.4302	0.7811	0.2068	0.053
H(10B)	2*i*	0.3907	0.6603	0.1498	0.053
H(10C)	2*i*	0.5605	0.6955	0.1352	0.053
H(16A)	2*i*	0.8846	0.0608	0.0346	0.049
H(16B)	2*i*	0.6972	0.1378	0.0076	0.049
H(16C)	2*i*	0.7682	−0.0422	0.0292	0.049
H(17A)	2*i*	1.0372	−0.1777	0.2040	0.049
H(17B)	2*i*	1.0768	−0.0837	0.2808	0.049
H(17C)	2*i*	1.0720	−0.0201	0.1702	0.049
H(18A)	2*i*	0.8741	−0.1554	0.4147	0.047

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(18B)	2*i*	0.7401	−0.0223	0.4571	0.047
H(18C)	2*i*	0.9096	0.0009	0.4219	0.047
H(19A)	2*i*	0.3562	0.1506	0.3344	0.041
H(19B)	2*i*	0.4794	0.0461	0.4154	0.041
H(19C)	2*i*	0.4143	−0.0290	0.3367	0.041
H(20A)	2*i*	0.4369	0.1977	0.0667	0.041
H(20B)	2*i*	0.3344	0.2091	0.1625	0.041
H(20C)	2*i*	0.3939	0.0524	0.1199	0.041
H(21A)	2*i*	0.993(3)	0.352(3)	0.264(2)	0.027(7)
H(21B)	2*i*	1.071(3)	0.176(3)	0.263(2)	0.028(7)
H(22)	2*i*	0.996(3)	0.207(3)	0.101(2)	0.025(6)
H(23)	2*i*	0.798(3)	0.501(3)	0.120(2)	0.024(6)
H(24A)	2*i*	0.687(4)	0.476(3)	−0.027(2)	0.042(8)
H(24B)	2*i*	0.852(4)	0.336(4)	−0.040(2)	0.050(9)
H(24C)	2*i*	0.858(4)	0.504(4)	−0.047(3)	0.07(1)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr(1)	2*i*	0.70646(2)	0.28770(2)	0.23845(2)	0.0139(1)	0.0149(1)	0.0215(1)	−0.00448(8)	−0.00032(8)	−0.00246(8)
C(1)	2*i*	0.7007(3)	0.5350(2)	0.3041(2)	0.022(1)	0.016(1)	0.037(1)	−0.0053(9)	−0.001(1)	−0.0098(9)
C(2)	2*i*	0.7159(3)	0.4206(2)	0.3831(2)	0.026(1)	0.020(1)	0.028(1)	−0.0020(9)	−0.005(1)	−0.0104(9)
C(3)	2*i*	0.5700(3)	0.3813(2)	0.3905(2)	0.028(1)	0.016(1)	0.024(1)	−0.0019(9)	0.002(1)	−0.0075(9)
C(4)	2*i*	0.4676(3)	0.4659(2)	0.3133(2)	0.021(1)	0.018(1)	0.026(1)	−0.0021(9)	0.0019(9)	−0.0073(9)
C(5)	2*i*	0.5491(3)	0.5622(2)	0.2608(2)	0.024(1)	0.013(1)	0.030(1)	−0.0014(9)	−0.001(1)	−0.0054(9)
C(6)	2*i*	0.8132(3)	0.6304(3)	0.2807(2)	0.039(2)	0.029(1)	0.062(2)	−0.020(1)	−0.001(1)	−0.014(1)
C(7)	2*i*	0.8502(3)	0.3688(3)	0.4559(2)	0.040(2)	0.042(2)	0.037(2)	−0.004(1)	−0.015(1)	−0.013(1)
C(8)	2*i*	0.5219(4)	0.2951(3)	0.4780(2)	0.052(2)	0.028(1)	0.026(1)	−0.011(1)	0.009(1)	−0.006(1)
C(9)	2*i*	0.2948(3)	0.4731(3)	0.2961(2)	0.019(1)	0.034(1)	0.045(2)	−0.004(1)	0.002(1)	−0.011(1)
C(10)	2*i*	0.4763(3)	0.6855(3)	0.1812(2)	0.040(2)	0.020(1)	0.040(2)	−0.001(1)	−0.005(1)	0.002(1)
C(11)	2*i*	0.7355(3)	0.0605(2)	0.1492(2)	0.021(1)	0.017(1)	0.026(1)	−0.0051(9)	0.0010(9)	−0.0082(9)
C(12)	2*i*	0.8456(3)	0.0055(2)	0.2267(2)	0.020(1)	0.013(1)	0.033(1)	−0.0016(9)	−0.0007(9)	−0.0047(9)
C(13)	2*i*	0.7554(3)	0.0154(2)	0.3119(2)	0.023(1)	0.015(1)	0.026(1)	−0.0048(9)	−0.0062(9)	−0.0022(9)
C(14)	2*i*	0.5877(3)	0.0699(2)	0.2863(2)	0.022(1)	0.016(1)	0.023(1)	−0.0079(9)	0.0002(9)	−0.0032(8)
C(15)	2*i*	0.5763(3)	0.1000(2)	0.1859(2)	0.019(1)	0.017(1)	0.023(1)	−0.0078(9)	−0.0022(9)	−0.0042(8)
C(16)	2*i*	0.7748(3)	0.0536(3)	0.0463(2)	0.033(1)	0.040(1)	0.028(1)	−0.012(1)	0.007(1)	−0.014(1)
C(17)	2*i*	1.0234(3)	−0.0761(3)	0.2198(2)	0.020(1)	0.024(1)	0.051(2)	0.000(1)	−0.000(1)	−0.008(1)
C(18)	2*i*	0.8260(3)	−0.0457(3)	0.4100(2)	0.037(1)	0.024(1)	0.031(1)	−0.005(1)	−0.010(1)	0.002(1)
C(19)	2*i*	0.4472(3)	0.0584(3)	0.3486(2)	0.028(1)	0.030(1)	0.028(1)	−0.016(1)	0.003(1)	−0.002(1)
C(20)	2*i*	0.4219(3)	0.1436(3)	0.1288(2)	0.025(1)	0.031(1)	0.029(1)	−0.012(1)	−0.006(1)	−0.003(1)
C(21)	2*i*	0.9875(3)	0.2681(3)	0.2389(2)	0.016(1)	0.025(1)	0.042(2)	−0.007(1)	−0.001(1)	−0.007(1)
C(22)	2*i*	0.9521(3)	0.2938(3)	0.1391(2)	0.019(1)	0.031(1)	0.038(2)	−0.012(1)	0.006(1)	−0.004(1)
C(23)	2*i*	0.8381(3)	0.4153(3)	0.0918(2)	0.028(1)	0.029(1)	0.036(2)	−0.014(1)	0.006(1)	−0.003(1)
C(24)	2*i*	0.8027(4)	0.4355(4)	−0.0126(2)	0.041(2)	0.047(2)	0.032(2)	−0.019(1)	0.002(1)	0.004(1)

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