Crystal structure of dimeric bis(tetrahydroindenyl)-2-trimethylsilyl-3-trimethylsiloxacarbonyl-zirconafuran-4-one, $C_{56}H_{80}O_8Si_4Zr_2$

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Abstract

$C_{56}H_{80}O_8Si_4Zr_2$, monoclinic, $P12_1/n1$ (No. 14), $a = 12.381(2)$ Å, $b = 11.994(2)$ Å, $c = 19.029(4)$ Å, $\beta = 98.99(3)^\circ$, $V = 2791.1$ Å³, $Z = 2$, $R_{gt}(F) = 0.035$, $wR_{obs}(F^2) = 0.078$, $T = 200$ K.

Source of material

In an argon atmosphere, methyl vinyl ketone (23 µL, 271 µmol) was added dropwise to a solution of $(\text{thi})_2\text{Zr}(\text{THF})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ (155 mg, 271 µmol) in THF (ca. 10 mL). The green solution changed to yellow immediately. All volatiles were removed in vacuo. The residue was dissolved in 3 mL n-pentane and the Schlenk tube was put in a Dewar (dry ice) for a week, then it was kept three weeks at room temperature to form slightly yellow crystals. Yield = 51 mg (32%).

Discussion

Zirconocene-alkyne complexes are considered to be important reagents for selective carbon-carbon bond forming and for a variety of synthetic transformations [1]. In recent years, we are interested in zirconocene-alkyne complexes for their rich and varied chemistry towards unsaturated $C=X$ ($X = C, N$, and O) substrates, diynes/polynes, and functionalized alkynes [2,3]. The title compound, an unusual carbon dioxide insertion product comparing to those of previously prepared [4–6], was obtained accidentally from the reaction of $(\text{thi})_2\text{Zr}(\text{THF})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with methyl vinyl ketone. The similar insertion reactions were found

for those of alkynylsilanes in presence of activators [7], but the insertion of carbon dioxide into $C-Si$ of zirconocene-alkyne complexes was not found so far.

Table 1. Data collection and handling.

Crystal:	light yellow prism, size $0.3 \times 0.4 \times 0.5$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	5.11 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 100 exposures, $\Delta\varphi = 2^\circ$
$2\theta_{\text{max}}$:	48.72°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	8220, 4398
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3320
$N(\text{param})_{\text{refined}}$:	316
Programs:	SHELXS-96 [8], SHELXL-93 [9]

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

Atom	Site	x	y	z	U_{iso}
H(6)	4e	0.8134(3)	0.2348(2)	0.3027(2)	0.036
H(7)	4e	0.9473(3)	0.1611(3)	0.2263(2)	0.040
H(8)	4e	1.1361(3)	0.1707(3)	0.2976(2)	0.041
H(10A)	4e	1.2138(3)	0.3151(3)	0.4159(2)	0.046
H(10B)	4e	1.1845(3)	0.2122(3)	0.4632(2)	0.046
H(11A)	4e	1.1670(4)	0.3641(3)	0.5331(2)	0.061
H(11B)	4e	1.1072(4)	0.4359(3)	0.4674(2)	0.061
H(12A)	4e	1.0077(3)	0.2505(3)	0.5279(2)	0.055
H(12B)	4e	0.9818(3)	0.3781(3)	0.5434(2)	0.055
H(13A)	4e	0.8471(3)	0.2910(3)	0.4534(2)	0.045
H(13B)	4e	0.8950(3)	0.4059(3)	0.4283(2)	0.045
H(14)	4e	0.9450(3)	−0.0805(2)	0.2287(2)	0.035
H(15)	4e	0.9759(3)	−0.1983(3)	0.3409(2)	0.035
H(16)	4e	0.8305(3)	−0.1477(2)	0.4137(2)	0.032
H(19A)	4e	0.7444(3)	0.0085(3)	0.1585(2)	0.046
H(19B)	4e	0.7660(3)	0.1217(3)	0.2034(2)	0.046
H(20A)	4e	0.5769(3)	0.0988(3)	0.1793(2)	0.054
H(20B)	4e	0.5858(3)	−0.0281(3)	0.2058(2)	0.054
H(21A)	4e	0.5274(3)	0.0934(3)	0.2924(2)	0.055
H(21B)	4e	0.6413(3)	0.1586(3)	0.2984(2)	0.055
H(22A)	4e	0.6687(3)	0.0392(3)	0.3927(2)	0.046
H(22B)	4e	0.6074(3)	−0.0614(3)	0.3476(2)	0.046
H(23A)	4e	0.9317(3)	−0.0030(3)	0.8174(2)	0.065
H(23B)	4e	0.8258(3)	−0.0781(3)	0.7922(2)	0.065
H(23C)	4e	0.8186(3)	0.0257(3)	0.8441(2)	0.065
H(24A)	4e	0.9378(3)	0.2376(3)	0.7638(2)	0.060
H(24B)	4e	0.8283(3)	0.2537(3)	0.7975(2)	0.060
H(24C)	4e	0.8307(3)	0.2878(3)	0.7165(2)	0.060
H(25A)	4e	0.6383(3)	0.0080(3)	0.6914(2)	0.066
H(25B)	4e	0.6336(3)	0.1366(3)	0.6688(2)	0.066
H(25C)	4e	0.6312(3)	0.1026(3)	0.7498(2)	0.066
H(26A)	4e	0.4607(4)	0.2270(4)	0.5983(2)	0.084
H(26B)	4e	0.4225(4)	0.3347(4)	0.5512(2)	0.084
H(26C)	4e	0.5409(4)	0.3317(4)	0.5989(2)	0.084

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(27A)	4e	0.4197(3)	0.0760(4)	0.4773(2)	0.087
H(27B)	4e	0.4737(3)	0.0950(4)	0.4071(2)	0.087
H(27C)	4e	0.3772(3)	0.1749(4)	0.4235(2)	0.087

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(28A)	4e	0.6427(4)	0.3826(4)	0.4679(2)	0.095
H(28B)	4e	0.5266(4)	0.3803(4)	0.4174(2)	0.095
H(28C)	4e	0.6232(4)	0.3004(4)	0.4009(2)	0.095

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
C(1)	4e	0.8721(3)	0.0365(3)	0.5166(2)	0.024(2)	0.027(2)	0.024(2)	-0.002(2)	0.004(1)	-0.001(1)
C(2)	4e	0.8266(3)	0.0821(2)	0.5788(2)	0.021(2)	0.027(2)	0.029(2)	0.000(1)	0.003(2)	-0.001(1)
C(3)	4e	0.7405(3)	0.1716(3)	0.5634(2)	0.030(2)	0.041(2)	0.023(2)	0.001(2)	0.007(2)	-0.003(2)
C(4)	4e	0.8732(3)	0.0450(3)	0.6437(2)	0.022(2)	0.026(2)	0.030(2)	-0.002(1)	0.003(2)	-0.001(1)
C(5)	4e	0.9521(3)	0.2685(2)	0.3809(2)	0.038(2)	0.020(2)	0.026(2)	0.002(1)	0.005(2)	0.005(1)
C(6)	4e	0.8906(3)	0.2315(2)	0.3156(2)	0.039(2)	0.022(2)	0.027(2)	0.003(1)	-0.002(2)	0.006(1)
C(7)	4e	0.9653(3)	0.1893(3)	0.2734(2)	0.053(3)	0.026(2)	0.022(2)	-0.005(2)	0.008(2)	0.008(1)
C(8)	4e	1.0708(3)	0.1959(3)	0.3128(2)	0.045(3)	0.028(2)	0.035(2)	-0.005(2)	0.018(2)	0.004(2)
C(9)	4e	1.0630(3)	0.2466(3)	0.3790(2)	0.037(2)	0.021(2)	0.032(2)	-0.003(2)	0.006(2)	0.005(1)
C(10)	4e	1.1544(3)	0.2796(3)	0.4372(2)	0.038(2)	0.032(2)	0.042(2)	-0.007(2)	0.002(2)	0.004(2)
C(11)	4e	1.1131(4)	0.3605(3)	0.4888(2)	0.061(3)	0.037(2)	0.048(2)	0.000(2)	-0.013(2)	-0.008(2)
C(12)	4e	1.0023(3)	0.3264(3)	0.5072(2)	0.066(3)	0.037(2)	0.031(2)	0.014(2)	0.000(2)	-0.008(2)
C(13)	4e	0.9138(3)	0.3278(3)	0.4420(2)	0.052(3)	0.027(2)	0.036(2)	0.011(2)	0.008(2)	0.001(2)
C(14)	4e	0.8998(3)	-0.0814(2)	0.2648(2)	0.029(2)	0.033(2)	0.027(2)	-0.002(1)	0.007(2)	-0.010(1)
C(15)	4e	0.9185(3)	-0.1460(3)	0.3282(2)	0.029(2)	0.023(2)	0.032(2)	0.001(1)	-0.003(2)	-0.008(1)
C(16)	4e	0.8371(3)	-0.1185(2)	0.3682(2)	0.029(2)	0.024(2)	0.026(2)	-0.005(1)	0.003(2)	0.003(1)
C(17)	4e	0.7651(3)	-0.0392(3)	0.3293(2)	0.026(2)	0.030(2)	0.026(2)	-0.002(2)	0.001(2)	-0.001(1)
C(18)	4e	0.8030(3)	-0.0189(3)	0.2643(2)	0.031(2)	0.027(2)	0.025(2)	-0.001(1)	-0.002(2)	-0.005(1)
C(19)	4e	0.7376(3)	0.0447(3)	0.2043(2)	0.047(3)	0.039(2)	0.026(2)	-0.001(2)	-0.006(2)	-0.003(2)
C(20)	4e	0.6177(3)	0.0472(3)	0.2145(2)	0.043(3)	0.042(2)	0.045(2)	0.010(2)	-0.012(2)	0.000(2)
C(21)	4e	0.6060(3)	0.0848(3)	0.2891(2)	0.035(3)	0.045(2)	0.055(3)	0.011(2)	0.001(2)	-0.003(2)
C(22)	4e	0.6575(3)	0.0024(3)	0.3456(2)	0.025(2)	0.051(2)	0.037(2)	0.003(2)	0.003(2)	-0.008(2)
C(23)	4e	0.8519(3)	-0.0022(3)	0.8041(2)	0.050(3)	0.056(2)	0.027(2)	-0.004(2)	0.012(2)	-0.005(2)
C(24)	4e	0.8578(3)	0.2345(3)	0.7542(2)	0.035(2)	0.047(2)	0.039(2)	0.007(2)	0.006(2)	-0.010(2)
C(25)	4e	0.6610(3)	0.0836(3)	0.7066(2)	0.033(2)	0.062(3)	0.039(2)	-0.005(2)	0.013(2)	-0.010(2)
C(26)	4e	0.4849(4)	0.2870(4)	0.5695(2)	0.046(3)	0.069(3)	0.053(3)	0.016(2)	0.010(2)	-0.008(2)
C(27)	4e	0.4415(3)	0.1321(4)	0.4448(2)	0.034(3)	0.082(3)	0.053(3)	0.015(2)	-0.005(2)	-0.006(2)
C(28)	4e	0.5892(4)	0.3350(4)	0.4387(2)	0.057(3)	0.076(3)	0.058(3)	0.021(2)	0.005(2)	0.020(2)
O(1)	4e	0.8565(2)	0.0828(2)	0.4564(1)	0.029(1)	0.031(1)	0.019(1)	0.0056(9)	0.005(1)	0.0013(9)
O(2)	4e	0.9310(2)	-0.0506(2)	0.5301(1)	0.029(1)	0.027(1)	0.025(1)	0.005(1)	0.005(1)	0.001(1)
O(3)	4e	0.7525(2)	0.2654(2)	0.5859(1)	0.048(2)	0.039(2)	0.053(2)	0.013(1)	-0.003(1)	-0.011(1)
O(4)	4e	0.6491(2)	0.1387(2)	0.5219(1)	0.034(2)	0.047(2)	0.031(1)	0.009(1)	-0.002(1)	-0.007(1)
Si(1)	4e	0.81315(8)	0.09074(8)	0.72510(5)	0.0282(6)	0.0381(5)	0.0249(5)	0.0005(4)	0.0070(4)	-0.0061(4)
Si(2)	4e	0.54251(9)	0.22653(9)	0.49428(5)	0.0353(7)	0.0514(7)	0.0331(6)	0.0135(5)	0.0022(5)	-0.0008(5)
Zr	4e	0.96002(3)	0.05157(2)	0.36790(2)	0.0249(2)	0.0218(2)	0.0195(2)	0.0012(1)	0.0044(1)	0.0007(1)

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