Crystal structure of 1,1-bis(pentamethylcyclopentadienyl)-4,5-bis(trimethylsilyl)-1-hafnafuran-3-one, $Hf(C_{10}H_{15})_2(Me_3SiC_2SiMe_3CO_2)$

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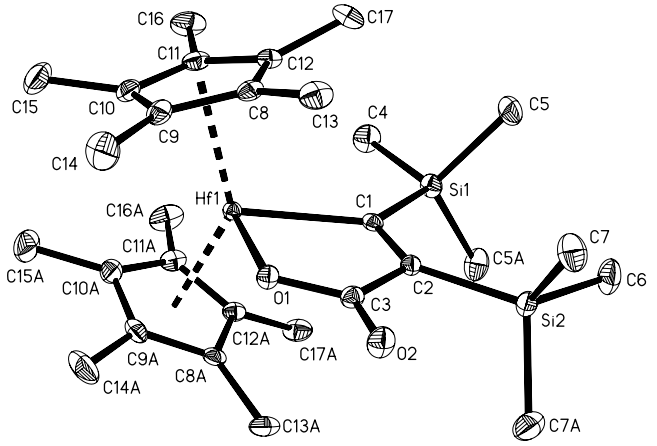

Abstract

$C_{29}H_{48}HfO_2Si_2$, orthorhombic, *Pnma* (no. 62), a = 16.8546(4) Å, b = 14.4139(6) Å, c = 12.1421(3) Å, V = 2949.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.020, $wR_{ref}(F^2)$ = 0.041, T = 200 K.

Source of material

$Cp^*_2Hf(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (0.220 g, 0.35 mmol) was dissolved in 10 ml *n*-hexane and filtered. The argon atmosphere was removed in vacuum and the Schlenk tube was flushed with carbon dioxide. The colour changed immediately from blue to yellow, after two hours at room temperature yellow needles formed which were seperated by decanting of the mother liquor, washed with cold *n*-hexane and dried in vacuum to give 0.136 g (0.21 mmol, 59 %) of the title compound.

Discussion

Titanocene and zirconocene alkyne complexes have been known for several years now, recently we have also accomplished the synthesis of first hafnocene alkyne complexes [1,2]. To investigate the reactivity of such complexes, simple reactions, e.g. with water or carbon dioxide are possible, giving useful information on the reaction behaviour with respect to ligand dissociation or insertion reactions.

The molecular structure of the title compound displays a bent hafnocene fragment with a hafnafuranone unit. The bond length C1—C2 of 1.373(6) Å is in the range of a double bond. Moreover the relevant bond angles of the metallacycle (O1–Hf1–C1 77.0(1)°, Si1–C1–C2 121.1(3)°, Si2–C2–C1 137.6(3)°) are in the expected range and resemble those of the corresponding zirconium complex (O1–Zr–C13 75.5(2)°, Si1–C13–C12 123.0(4)°, Si2–C12–C13 137.2(4)°) [3]. Whereas the reaction of the similar cyclopentadienyl substituted hafnocene alkyne complex $Cp_2Hf(PMe_3)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with carbon dioxide results in the formation of a dinuclear complex [4], the higher steric demand of the pentamethylcyclopentadienyl ligand prevents the dimerization of the product. The described reaction pattern shows the trend of coupling and insertion reactions instead of alkyne dissociation reactions for hafnocene alkyne complexes compared to similar titanium and zirconium species. This is in agreement with the observations made before [2].

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.2 × 0.2 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	36.41 cm^{-1}
Diffractometer, scan mode:	STOE-IPDS II, ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	40712, 3023
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2462
$N(param)_{refined}$:	169
Programs:	SHELXS-97 [5], SHELXL-97 [6]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(4A)	8*d*	0.50	0.5123	0.3039	0.0240	0.059
H(4B)	8*d*	0.50	0.5500	0.2531	–0.0809	0.059
H(4C)	8*d*	0.50	0.5143	0.1930	0.0183	0.059
H(5A)	8*d*		0.3565	0.1402	–0.2244	0.062
H(5B)	8*d*		0.4148	0.0884	–0.1405	0.062
H(5C)	8*d*		0.4506	0.1487	–0.2394	0.062
H(6A)	4*c*		0.2050	¼	–0.3509	0.065
H(6B)	8*d*	0.50	0.2764	0.1945	–0.2942	0.065
H(6C)	8*d*	0.50	0.2764	0.3055	–0.2942	0.065
H(7A)	8*d*		0.0950	0.1422	–0.2300	0.064
H(7B)	8*d*		0.0892	0.1408	–0.0985	0.064
H(7C)	8*d*		0.1602	0.0878	–0.1592	0.064
H(13A)	8*d*		0.2232	–0.0230	0.1579	0.049
H(13B)	8*d*		0.2358	0.0556	0.0666	0.049
H(13C)	8*d*		0.1792	0.0748	0.1700	0.049
H(14A)	8*d*		0.2180	0.0602	0.4315	0.071
H(14B)	8*d*		0.1774	0.1302	0.3461	0.071
H(14C)	8*d*		0.2313	0.1696	0.4441	0.071
H(15A)	8*d*		0.4155	0.0798	0.4963	0.078
H(15B)	8*d*		0.3652	0.1731	0.5113	0.078
H(15C)	8*d*		0.4546	0.1779	0.4672	0.078
H(16A)	8*d*		0.5337	0.0563	0.2830	0.066
H(16B)	8*d*		0.5340	0.1652	0.3082	0.066
H(16C)	8*d*		0.5346	0.1292	0.1836	0.066
H(17A)	8*d*		0.4163	–0.0256	0.0795	0.052
H(17B)	8*d*		0.4513	0.0720	0.0393	0.052
H(17C)	8*d*		0.3617	0.0443	0.0105	0.052

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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}
C(1)	4*c*	0.3254(3)	¼	0.0119(3)	0.021(2)	0.012(2)	0.020(2)	0	0.003(2)	0
C(2)	4*c*	0.2471(2)	¼	–0.0194(3)	0.022(2)	0.016(2)	0.018(2)	0	0.000(2)	0
C(3)	4*c*	0.1864(2)	¼	0.0726(4)	0.021(2)	0.019(2)	0.024(2)	0	–0.002(2)	0
C(4)	4*c*	0.5082(3)	¼	–0.0249(4)	0.025(2)	0.049(3)	0.043(3)	0	0.000(2)	0
C(5)	8*d*	0.4074(2)	0.1441(3)	–0.1856(3)	0.045(2)	0.051(2)	0.028(2)	0.012(2)	0.004(2)	–0.010(2)
C(6)	4*c*	0.2430(3)	¼	–0.2898(4)	0.046(3)	0.063(3)	0.021(2)	0	–0.001(3)	0
C(7)	8*d*	0.1256(2)	0.1424(3)	–0.1614(3)	0.045(2)	0.043(2)	0.039(2)	–0.011(2)	–0.005(2)	–0.009(2)
C(8)	8*d*	0.2972(2)	0.0809(2)	0.2086(3)	0.024(1)	0.014(1)	0.029(2)	–0.003(1)	–0.003(2)	0.006(1)
C(9)	8*d*	0.2967(2)	0.1127(2)	0.3185(3)	0.034(2)	0.024(2)	0.025(2)	–0.001(1)	0.003(1)	0.009(1)
C(10)	8*d*	0.3759(2)	0.1332(2)	0.3497(3)	0.042(2)	0.021(2)	0.026(2)	0.003(2)	–0.009(2)	0.004(1)
C(11)	8*d*	0.4251(2)	0.1176(2)	0.2569(3)	0.023(2)	0.020(1)	0.039(2)	0.004(1)	–0.009(1)	0.001(1)
C(12)	8*d*	0.3765(2)	0.0837(2)	0.1703(3)	0.021(2)	0.016(1)	0.029(2)	0.001(1)	–0.001(1)	0.001(1)
C(13)	8*d*	0.2279(2)	0.0439(2)	0.1453(3)	0.029(2)	0.022(2)	0.046(2)	–0.007(1)	–0.006(2)	0.002(2)
C(14)	8*d*	0.2245(2)	0.1187(3)	0.3914(3)	0.054(2)	0.048(2)	0.039(2)	–0.006(2)	0.023(2)	0.012(2)
C(15)	8*d*	0.4054(3)	0.1418(3)	0.4663(3)	0.082(3)	0.041(2)	0.034(2)	0.001(2)	–0.024(2)	0.007(2)
C(16)	8*d*	0.5147(2)	0.1170(3)	0.2580(4)	0.024(2)	0.038(2)	0.069(3)	0.008(2)	–0.016(2)	–0.006(2)
C(17)	8*d*	0.4038(2)	0.0399(2)	0.0660(3)	0.036(2)	0.023(2)	0.045(2)	0.001(1)	0.008(2)	–0.010(2)
Hf(1)	4*c*	0.33360(1)	¼	0.20230(1)	0.01624(8)	0.01529(8)	0.01617(8)	0	0.00059(9)	0
O(1)	4*c*	0.2143(2)	¼	0.1743(2)	0.015(1)	0.027(2)	0.020(2)	0	–0.000(1)	0
O(2)	4*c*	0.1151(2)	¼	0.0541(3)	0.019(2)	0.044(2)	0.029(2)	0	–0.001(1)	0
Si(1)	4*c*	0.40801(7)	¼	–0.0942(1)	0.0217(6)	0.0314(7)	0.0219(6)	0	0.0063(5)	0
Si(2)	4*c*	0.18724(7)	¼	–0.1545(1)	0.0252(7)	0.0279(6)	0.0196(5)	0	–0.0035(5)	0

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