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Crystal structure of *rac*-[1,2-ethylene-bis(η^5-4,5,6,7-tetrahydroindenyl)]-1-hafna-4,5-bis(trimethylsilyl)furan-3-one-tris(pentafluorophenyl)borane, $(C_{20}H_{24})Hf(Me_3SiC_2SiMe_3CO_2)B(C_6F_5)_3$

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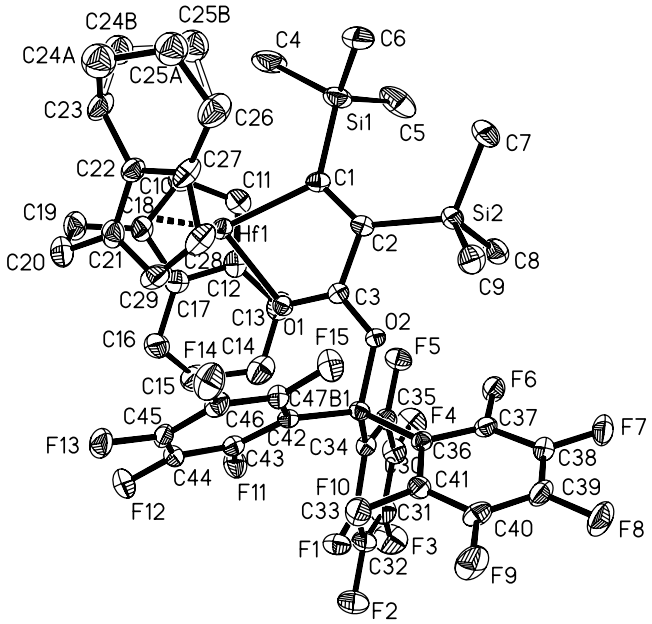

Abstract

$C_{47}H_{42}BF_{15}HfO_2Si_2$, monoclinic, $P12_1/n1$ (no. 14), a = 15.7496(4) Å, b = 20.4074(5) Å, c = 16.3115(5) Å, β = 96.313(2)°, V = 5210.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR_{ref}(F^2)$ = 0.049, T = 200 K.

Source of material

An *n*-hexane solution of $B(C_6F_5)_3$ (0.250 g, 0.49 mmol) was added *via* cannula to an *n*-hexane solution of *rac*-(ebthi)Hf(η^2-$Me_3SiC_2SiMe_3$) (0.300 g, 0.49 mmol), followed by subsequent removal of the argon atmosphere and flushing of the Schlenk tube with carbon dioxide. The colour of the reaction mixture changed from blue green to light green. After one week at −78 °C yellow crystals formed, which were separated by decanting of the mother liquor, washed with cold *n*-hexane and dried in vacuum.

Experimental details

PLATON/SQUEEZE was used to remove the disordered solvent.

Discussion

Until recently, hafnocene alkyne complexes of the type Cp'$_2$Hf(η^2-RC_2R) (Cp' = Cp or substituted cyclopentadienyl, R = $SiMe_3$, Alkyl, Aryl) have been unknown. The first examples were reported by our group and in the synthesis of Cp*$_2$Hf(η^2-$Me_3SiC_2SiMe_3$) unusual Si-C and C-H activations take place [1]. The first *ansa*-bridged hafnocene alkyne complex *rac*-(ebthi)Hf(η^2-$Me_3SiC_2SiMe_3$) was also synthesized throughout these investigations [2]. The corresponding zirconium complex reacts with the borane under formation of a zwitterionic C–H activated species, which eliminated the alkyne at higher temperatures to give a complex in which one pentafluorphenyl group migrated from the boron to the zirconium center [3]. We were interested to investigate the reaction behaviour of the analogous hafnium complex with the borane and carbon dioxide.

The molecular structure of the title compound shows a bent hafnocene unit together with a planar five-membered metallacycle. The borane is coordinated to the exocyclic oxygen atom. This results in a deviation of the C—O bond distances (d(C3—O1) = 1.274(4) Å, d(C3—O2) = 1.279(3) Å) from carbon dioxide insertion products such as Cp*$_2$Hf[–C(Ph)=C($SiMe_3$)C(O)–O–] (d(C3—O1) = 1.332(3) Å; d(C3—O2) = 1.218(3) Å) [4]. In the title compound, both distances are equal due to the delocalization of the bond electrons of the exocyclic C—O bond between O1, C3 and O2. The borane is coordinated weakly to the exocyclic oxygen atom (d(B1—O2) 1.552(4) Å), with a slightly distorted tetrahedral coordination environment at the boron. One annelated six-membered ring of the ebthi ligand was found to be disordered over two positions.

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.15 × 0.30 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	21.36 cm^{-1}
Diffractometer, scan mode:	STOE-IPDS II, ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	66709, 1022
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6746
$N(param)_{refined}$:	611
Programs:	PLATON [5], SIR2004 [6], SHELXL-97 [7]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(4A)	4*e*		0.3203	0.1037	0.5969	0.144
H(4B)	4*e*		0.2943	0.0282	0.5841	0.144
H(4C)	4*e*		0.3928	0.0484	0.6028	0.144
H(5A)	4*e*		0.2027	0.1172	0.7270	0.126
H(5B)	4*e*		0.2028	0.0631	0.7980	0.126
H(5C)	4*e*		0.1753	0.0434	0.7038	0.126

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Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(6A)	4*e*		0.3524	–0.0461	0.8112	0.117
H(6B)	4*e*		0.4129	–0.0468	0.7385	0.117
H(6C)	4*e*		0.3143	–0.0665	0.7197	0.117
H(7A)	4*e*		0.2678	–0.0145	0.9788	0.101
H(7B)	4*e*		0.3402	–0.0284	0.9194	0.101
H(7C)	4*e*		0.2514	0.0040	0.8830	0.101
H(8A)	4*e*		0.2195	0.1174	1.0198	0.083
H(8B)	4*e*		0.2094	0.1428	0.9264	0.083
H(8C)	4*e*		0.2708	0.1809	0.9953	0.083
H(9A)	4*e*		0.3902	0.0475	1.0893	0.081
H(9B)	4*e*		0.4438	0.1105	1.0672	0.081
H(9C)	4*e*		0.4644	0.0403	1.0303	0.081
H(10A)	4*e*		0.4142	0.1733	0.5464	0.056
H(11A)	4*e*		0.3011	0.2024	0.6432	0.058
H(13A)	4*e*		0.3201	0.2914	0.7884	0.069
H(13B)	4*e*		0.2899	0.3395	0.7132	0.069
H(14A)	4*e*		0.3606	0.4074	0.8081	0.082
H(14B)	4*e*		0.4347	0.3551	0.8327	0.082
H(15A)	4*e*		0.4825	0.4430	0.7540	0.099
H(15B)	4*e*		0.4139	0.4225	0.6784	0.099
H(16A)	4*e*		0.5446	0.3765	0.6535	0.075
H(16B)	4*e*		0.5579	0.3450	0.7441	0.075
H(19A)	4*e*		0.5762	0.2958	0.5366	0.073
H(19B)	4*e*		0.5633	0.2195	0.5161	0.073

Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(20A)	4*e*		0.6943	0.2212	0.5889	0.082
H(20B)	4*e*		0.6677	0.2762	0.6511	0.082
H(23A)	4*e*	0.50	0.6224	0.1084	0.5404	0.078
H(23B)	4*e*	0.50	0.5301	0.0819	0.5582	0.078
H(23C)	4*e*	0.50	0.6376	0.0984	0.5484	0.078
H(23D)	4*e*	0.50	0.5360	0.0969	0.5490	0.078
C(24A)	4*e*	0.50	0.6279(7)	0.0167(3)	0.5963(7)	0.082(4)
H(24A)	4*e*	0.50	0.6245	–0.0084	0.5441	0.098
H(24B)	4*e*	0.50	0.6886	0.0197	0.6194	0.098
C(25A)	4*e*	0.50	0.5762(7)	–0.0169(5)	0.6569(4)	0.075(4)
H(25A)	4*e*	0.50	0.5986	–0.062	0.6657	0.091
H(25B)	4*e*	0.50	0.5166	–0.0207	0.6308	0.091
C(24B)	4*e*	0.50	0.5943(6)	0.0110(2)	0.5929(5)	0.059(3)
H(24C)	4*e*	0.50	0.5750	–0.0103	0.5396	0.071
H(24D)	4*e*	0.50	0.6545	–0.002	0.6085	0.071
C(25B)	4*e*	0.50	0.5408(7)	–0.0146(5)	0.6575(3)	0.071(3)
H(25C)	4*e*	0.50	0.5444	–0.063	0.6600	0.085
H(25D)	4*e*	0.50	0.4802	–0.0023	0.6429	0.085
H(26A)	4*e*	0.50	0.5171	0.0071	0.7602	0.092
H(26B)	4*e*	0.50	0.6174	–0.0062	0.7812	0.092
H(26C)	4*e*	0.50	0.5314	0.0064	0.7803	0.092
H(26D)	4*e*	0.50	0.6274	–0.0081	0.7623	0.092
H(28A)	4*e*		0.6220	0.1177	0.8619	0.067
H(29A)	4*e*		0.6705	0.2248	0.8023	0.064

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}
B(1)	4*e*	0.5045(2)	0.2567(2)	1.0219(2)	0.027(2)	0.032(2)	0.031(2)	–0.004(2)	0.000(2)	–0.002(2)
C(1)	4*e*	0.3983(2)	0.1134(2)	0.7878(2)	0.040(2)	0.031(2)	0.033(2)	0.002(2)	–0.004(2)	–0.001(2)
C(2)	4*e*	0.3958(2)	0.1272(2)	0.8696(2)	0.032(2)	0.028(2)	0.036(2)	0.001(2)	–0.003(2)	0.002(2)
C(3)	4*e*	0.4449(2)	0.1874(2)	0.8990(2)	0.028(2)	0.029(2)	0.031(2)	0.006(2)	0.001(1)	0.001(2)
C(4)	4*e*	0.3345(4)	0.0587(2)	0.6144(2)	0.155(5)	0.084(4)	0.046(3)	–0.063(4)	–0.004(3)	–0.017(2)
C(5)	4*e*	0.2135(3)	0.0710(2)	0.7407(3)	0.066(3)	0.078(4)	0.098(4)	–0.027(3)	–0.035(3)	0.021(3)
C(6)	4*e*	0.3550(3)	–0.0378(2)	0.7523(3)	0.115(4)	0.045(3)	0.077(3)	–0.022(3)	0.025(3)	–0.018(2)
C(7)	4*e*	0.2944(3)	0.0016(2)	0.9311(3)	0.093(4)	0.043(3)	0.068(3)	–0.023(2)	0.017(3)	0.007(2)
C(8)	4*e*	0.2492(2)	0.1377(2)	0.9766(2)	0.043(2)	0.055(3)	0.069(3)	–0.010(2)	0.011(2)	–0.006(2)
C(9)	4*e*	0.4190(3)	0.0689(2)	1.0462(2)	0.072(3)	0.045(2)	0.045(2)	0.002(2)	0.006(2)	0.012(2)
C(10)	4*e*	0.4219(2)	0.2062(2)	0.5921(2)	0.050(2)	0.058(3)	0.028(2)	–0.004(2)	–0.010(2)	0.004(2)
C(11)	4*e*	0.3592(2)	0.2224(2)	0.6449(2)	0.044(2)	0.056(3)	0.041(2)	–0.002(2)	–0.011(2)	0.010(2)
C(12)	4*e*	0.3872(2)	0.2787(2)	0.6894(2)	0.045(2)	0.050(2)	0.039(2)	0.009(2)	–0.001(2)	0.016(2)
C(13)	4*e*	0.3405(3)	0.3196(2)	0.7452(2)	0.060(3)	0.061(3)	0.051(2)	0.015(3)	0.004(2)	0.010(2)
C(14)	4*e*	0.3971(3)	0.3737(2)	0.7859(3)	0.095(4)	0.050(3)	0.064(3)	0.020(3)	0.020(3)	0.006(2)
C(15)	4*e*	0.4511(3)	0.4055(2)	0.7266(3)	0.131(5)	0.047(3)	0.070(3)	–0.005(3)	0.017(3)	0.001(2)
C(16)	4*e*	0.5147(3)	0.3566(2)	0.6976(2)	0.086(3)	0.051(3)	0.051(2)	–0.020(2)	0.015(2)	0.004(2)
C(17)	4*e*	0.4682(3)	0.2963(2)	0.6658(2)	0.059(3)	0.042(2)	0.032(2)	–0.001(2)	–0.002(2)	0.008(2)
C(18)	4*e*	0.4886(3)	0.2520(2)	0.6038(2)	0.053(3)	0.054(3)	0.028(2)	–0.003(2)	0.003(2)	0.011(2)
C(19)	4*e*	0.5689(3)	0.2521(2)	0.5613(2)	0.065(3)	0.080(3)	0.039(2)	–0.014(3)	0.013(2)	0.006(2)
C(20)	4*e*	0.6480(3)	0.2360(2)	0.6208(3)	0.057(3)	0.087(4)	0.065(3)	–0.016(3)	0.023(2)	–0.005(3)
C(21)	4*e*	0.6309(2)	0.1842(2)	0.6812(2)	0.032(2)	0.070(3)	0.045(2)	–0.001(2)	0.005(2)	–0.001(2)
C(22)	4*e*	0.5999(2)	0.1202(2)	0.6626(2)	0.044(2)	0.054(3)	0.034(2)	–0.001(2)	0.005(2)	–0.007(2)
C(23)	4*e*	0.5910(3)	0.0847(2)	0.5807(2)	0.071(3)	0.088(4)	0.037(2)	–0.005(3)	0.015(2)	–0.017(2)
C(26)	4*e*	0.5738(4)	0.0146(2)	0.7411(2)	0.112(4)	0.065(3)	0.056(3)	0.019(3)	0.022(3)	0.007(2)
C(27)	4*e*	0.5907(3)	0.0873(2)	0.7375(2)	0.062(3)	0.059(3)	0.039(2)	0.023(2)	0.011(2)	–0.003(2)
C(28)	4*e*	0.6145(3)	0.1299(2)	0.8021(2)	0.050(3)	0.079(3)	0.037(2)	0.027(2)	–0.003(2)	–0.005(2)
C(29)	4*e*	0.6400(2)	0.1888(2)	0.7696(2)	0.031(2)	0.078(3)	0.049(2)	0.006(2)	–0.006(2)	–0.025(2)
C(30)	4*e*	0.4524(2)	0.3261(2)	1.0154(2)	0.035(2)	0.035(2)	0.030(2)	–0.000(2)	0.005(1)	–0.000(2)
C(31)	4*e*	0.4893(2)	0.3808(2)	1.0557(2)	0.040(2)	0.039(2)	0.038(2)	–0.001(2)	0.005(2)	–0.004(2)
C(32)	4*e*	0.4493(3)	0.4403(2)	1.0597(2)	0.057(3)	0.031(2)	0.055(2)	–0.007(2)	0.011(2)	–0.008(2)
C(33)	4*e*	0.3675(3)	0.4480(2)	1.0231(2)	0.060(3)	0.035(2)	0.066(3)	0.013(2)	0.015(2)	0.003(2)
C(34)	4*e*	0.3271(2)	0.3955(2)	0.9834(2)	0.039(2)	0.043(2)	0.056(2)	0.010(2)	0.005(2)	0.007(2)
C(35)	4*e*	0.3693(2)	0.3365(2)	0.9805(2)	0.037(2)	0.036(2)	0.040(2)	–0.002(2)	0.005(2)	–0.000(2)
C(36)	4*e*	0.5074(2)	0.2357(2)	1.1205(2)	0.030(2)	0.029(2)	0.031(2)	0.001(2)	0.004(1)	–0.005(1)
C(37)	4*e*	0.4334(2)	0.2193(2)	1.1536(2)	0.032(2)	0.040(2)	0.031(2)	0.000(2)	0.001(2)	–0.008(2)
C(38)	4*e*	0.4279(2)	0.2006(2)	1.2339(2)	0.043(2)	0.046(3)	0.035(2)	–0.007(2)	0.011(2)	–0.003(2)
C(39)	4*e*	0.5006(3)	0.2002(2)	1.2877(2)	0.064(3)	0.049(3)	0.027(2)	0.002(2)	0.010(2)	–0.001(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(40)	4*e*	0.5759(2)	0.2193(2)	1.2610(2)	0.046(2)	0.056(2)	0.029(2)	0.008(2)	–0.007(2)	–0.006(2)
C(41)	4*e*	0.5787(2)	0.2364(2)	1.1793(2)	0.030(2)	0.042(2)	0.038(2)	–0.002(2)	0.003(2)	–0.003(2)
C(42)	4*e*	0.5988(2)	0.2580(2)	0.9890(2)	0.031(2)	0.034(2)	0.027(2)	–0.004(2)	0.001(1)	–0.006(1)
C(43)	4*e*	0.6346(2)	0.3088(2)	0.9490(2)	0.037(2)	0.039(2)	0.030(2)	–0.002(2)	0.003(1)	–0.005(2)
C(44)	4*e*	0.7174(2)	0.3086(2)	0.9285(2)	0.040(2)	0.051(2)	0.035(2)	–0.018(2)	0.009(2)	–0.006(2)
C(45)	4*e*	0.7677(2)	0.2546(2)	0.9449(2)	0.026(2)	0.073(3)	0.027(2)	–0.011(2)	0.006(2)	–0.014(2)
C(46)	4*e*	0.7351(2)	0.2014(2)	0.9823(2)	0.031(2)	0.054(3)	0.040(2)	0.008(2)	0.003(2)	–0.010(2)
C(47)	4*e*	0.6526(2)	0.2044(2)	1.0026(2)	0.037(2)	0.044(2)	0.035(2)	–0.006(2)	0.009(2)	–0.002(2)
F(1)	4*e*	0.5691(1)	0.3760(1)	1.0945(1)	0.045(1)	0.046(1)	0.050(1)	–0.006(1)	–0.004(1)	–0.010(1)
F(2)	4*e*	0.4903(2)	0.4910(1)	1.0995(1)	0.086(2)	0.036(1)	0.082(2)	–0.010(1)	0.010(1)	–0.015(1)
F(3)	4*e*	0.3274(2)	0.5055(1)	1.0258(2)	0.090(2)	0.041(1)	0.114(2)	0.025(1)	0.011(2)	–0.005(1)
F(4)	4*e*	0.2466(1)	0.4018(1)	0.9465(1)	0.046(1)	0.064(2)	0.086(2)	0.021(1)	–0.002(1)	0.008(1)
F(5)	4*e*	0.3241(1)	0.2877(1)	0.9398(1)	0.035(1)	0.045(1)	0.057(1)	0.000(1)	–0.006(1)	–0.003(1)
F(6)	4*e*	0.3581(1)	0.2212(1)	1.1046(1)	0.030(1)	0.070(1)	0.038(1)	–0.006(1)	0.0038(9)	–0.005(1)
F(7)	4*e*	0.3528(1)	0.1837(1)	1.2591(1)	0.058(1)	0.096(2)	0.044(1)	–0.022(2)	0.021(1)	–0.001(1)
F(8)	4*e*	0.4981(1)	0.1828(1)	1.3672(1)	0.081(2)	0.095(2)	0.028(1)	–0.001(2)	0.010(1)	0.008(1)
F(9)	4*e*	0.6477(1)	0.2209(1)	1.3142(1)	0.053(2)	0.113(2)	0.037(1)	0.005(1)	–0.013(1)	0.000(1)
F(10)	4*e*	0.6561(1)	0.2548(1)	1.1591(1)	0.031(1)	0.080(2)	0.041(1)	–0.006(1)	–0.0013(9)	–0.002(1)
F(11)	4*e*	0.5891(1)	0.3633(1)	0.9268(1)	0.056(1)	0.045(1)	0.056(1)	–0.002(1)	0.014(1)	0.012(1)
F(12)	4*e*	0.7481(2)	0.3606(1)	0.8903(1)	0.061(2)	0.068(2)	0.066(1)	–0.025(1)	0.025(1)	0.001(1)
F(13)	4*e*	0.8472(1)	0.2522(1)	0.9229(1)	0.034(1)	0.106(2)	0.047(1)	–0.013(1)	0.012(1)	–0.019(1)
F(14)	4*e*	0.7832(1)	0.1482(1)	0.9987(1)	0.045(1)	0.078(2)	0.074(2)	0.022(1)	0.015(1)	–0.000(1)
F(15)	4*e*	0.6242(1)	0.1507(1)	1.0393(1)	0.049(1)	0.041(1)	0.069(1)	0.010(1)	0.019(1)	0.011(1)
Hf(1)	4*e*	0.48778(1)	0.184301(8)	0.730278(8)	0.03470(7)	0.04099(8)	0.02361(6)	0.0002(1)	–0.00235(4)	–0.00001(9)
O(1)	4*e*	0.4788(1)	0.2238(1)	0.8482(1)	0.036(1)	0.032(1)	0.026(1)	–0.005(1)	0.001(1)	0.004(1)
O(2)	4*e*	0.4516(1)	0.20095(9)	0.9761(1)	0.031(1)	0.030(1)	0.026(1)	–0.0023(9)	0.0019(9)	–0.0023(9)
Si(2)	4*e*	0.34009(7)	0.08496(5)	0.95440(6)	0.0485(7)	0.0340(6)	0.0409(5)	–0.0063(5)	0.0073(5)	0.0024(4)
Si(1)	4*e*	0.32693(9)	0.05050(6)	0.72822(7)	0.0773(9)	0.0499(7)	0.0420(6)	–0.0257(7)	–0.0077(6)	–0.0054(5)

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