Crystal structure of μ-oxo-bis(σ-1,2-bis(trimethylsilyl)vinylhafnocene) benzene solvate, $[C_2H\{Si(CH_3)_3\}_2Hf(C_5H_5)_2]_2O \cdot C_6H_6$

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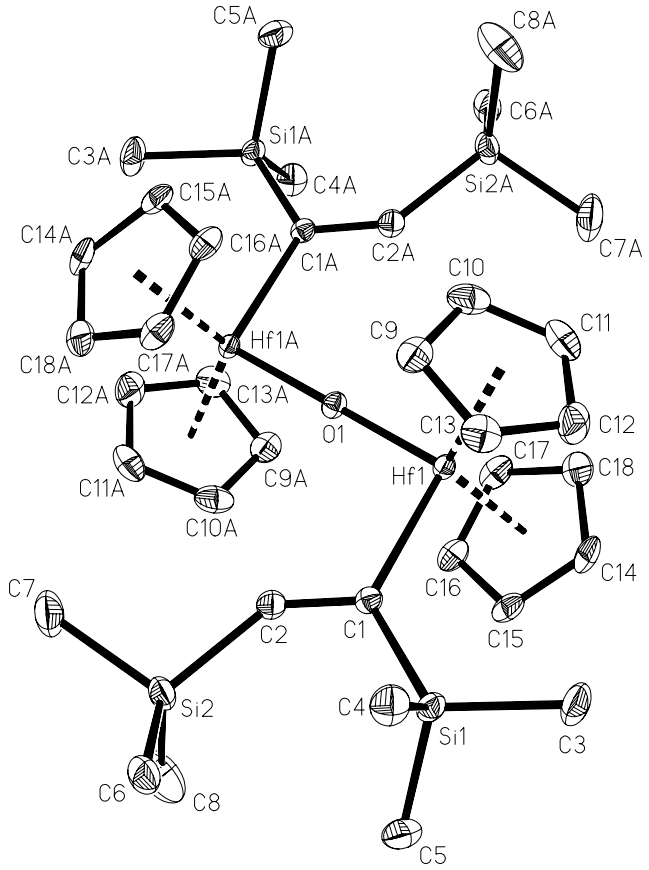

Abstract

$C_{42}H_{64}Hf_2OSi_4$, monoclinic, $P12_1/c1$ (no. 14), a = 11.442(1) Å, b = 9.7998(6) Å, c = 19.827(2) Å, β = 95.229(7)°, V = 2213.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.017, $wR_{ref}(F^2)$ = 0.037, T = 200 K.

Source of material

To a solution of $Cp_2Hf(PMe_3)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (0.160 g, 0.29 mmol) in 5 ml of benzene 2.6 μl of water were added. The solution was stirred and stored at room temperature. After 3 weeks colorless crystals (0.155 g, 55 %) had formed which were separated from the mother liquor by decanting, washed with cold benzene and dried in an argon atmosphere.

Experimental details

The H atoms were added geometrically and refined using riding rigid body approximation, except the H atom associated with C2 which was refined without restraints.

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Discussion

Titanocene and zirconocene alkyne complexes are known for several years and show a broad chemistry [1]. Very recently we reported the synthesis of the first hafnocene alkyne complexes containing the intact starting alkyne: $Cp^*_2Hf(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and $Cp_2Hf(PMe_3)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ [2]. To investigate the reactivity of the latter complex, it was reacted with water to give the bimetallic oxygen bridged title compound.

The dimeric structure was confirmed by X-ray structure analysis. Each hafnium atom is surrounded by two Cp ligands, the alkenyl group and the oxygen which bridges both parts of the molecule. A similar zirconocene complex $((Me_3Si)HCC(SiMe_3)(C_5H_5)_2Zr)_2O$ [3,4] is known, where additional agostic interactions of the alkenyl hydrogens with the zirconium atoms were observed. The Hf—O distance (1.9537(2) Å) is comparable with those in the complexes μ-oxo-bis(methylhafnocene) (1.941(3) Å) [5] and μ-oxo-bis-(chlorohafnocene) (1.945(1) Å) [6]. Additionally, benzene as a solvent molecule was observed in the crystal structure.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.3 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	48.24 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω/φ
$2\theta_{max}$:	49.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7900, 3797
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3295
$N(param)_{refined}$:	227
Programs:	SHELXS-97 [7], SHELXL-97 [8]

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

Atom	Site	x	y	z	U_{iso}
H(3A)	4*e*	0.4741	0.1518	0.5891	0.072
H(3B)	4*e*	0.5184	0.2136	0.6616	0.072
H(3C)	4*e*	0.4052	0.2764	0.6194	0.072
H(4A)	4*e*	0.2620	0.2360	0.7377	0.062
H(4B)	4*e*	0.3858	0.1930	0.7759	0.062
H(4C)	4*e*	0.2743	0.0952	0.7787	0.062
H(5A)	4*e*	0.4738	–0.1230	0.6524	0.072
H(5B)	4*e*	0.4143	–0.1438	0.7216	0.072
H(5C)	4*e*	0.5256	–0.0455	0.7196	0.072
H(6A)	4*e*	0.3000	–0.1322	0.7970	0.065
H(6B)	4*e*	0.2118	–0.2334	0.8304	0.065
H(6C)	4*e*	0.1724	–0.0801	0.8121	0.065
H(7A)	4*e*	–0.0344	–0.2945	0.6767	0.123
H(7B)	4*e*	–0.0403	–0.1843	0.7359	0.123
H(7C)	4*e*	0.0002	–0.3374	0.7538	0.123
H(8A)	4*e*	0.2075	–0.4040	0.6450	0.115

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(8B)	4*e*	0.2269	–0.4435	0.7235	0.115
H(8C)	4*e*	0.3217	–0.3515	0.6901	0.115
H(9)	4*e*	–0.0338	0.2449	0.6023	0.044
H(10)	4*e*	–0.0669	0.2974	0.4779	0.051
H(11)	4*e*	0.1224	0.3769	0.4385	0.057
H(12)	4*e*	0.2743	0.3806	0.5391	0.054
H(13)	4*e*	0.1773	0.2997	0.6400	0.046
H(14)	4*e*	0.3916	0.1889	0.4783	0.045

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(15)	4*e*	0.3840	–0.0463	0.5280	0.040
H(16)	4*e*	0.2184	–0.1748	0.4643	0.040
H(17)	4*e*	0.1262	–0.0202	0.3733	0.045
H(18)	4*e*	0.2309	0.2050	0.3822	0.050
H(19)	4*e*	0.5413	0.9418	0.1120	0.094
H(20)	4*e*	0.3866	0.8337	0.0468	0.088
H(21)	4*e*	0.3466	0.8938	–0.0654	0.089
H(2)	4*e*	0.085(4)	–0.120(4)	0.612(2)	0.05(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}
C(1)	4*e*	0.2164(3)	0.0149(3)	0.6187(1)	0.021(2)	0.028(2)	0.019(1)	0.001(1)	0.004(1)	–0.002(1)
C(2)	4*e*	0.1516(3)	–0.0884(3)	0.6402(1)	0.026(2)	0.036(2)	0.024(1)	–0.005(1)	–0.003(1)	0.001(1)
C(3)	4*e*	0.4492(3)	0.1924(4)	0.6306(2)	0.035(2)	0.068(3)	0.040(2)	–0.028(2)	–0.002(1)	0.006(2)
C(4)	4*e*	0.3142(3)	0.1591(4)	0.7504(2)	0.042(2)	0.047(2)	0.032(2)	–0.009(2)	–0.003(1)	–0.005(2)
C(5)	4*e*	0.4537(3)	–0.0784(4)	0.6940(2)	0.029(2)	0.063(3)	0.052(2)	0.008(2)	–0.001(2)	0.011(2)
C(6)	4*e*	0.2175(3)	–0.1585(4)	0.7981(2)	0.045(2)	0.057(2)	0.028(2)	–0.010(2)	0.001(1)	0.012(2)
C(7)	4*e*	0.0024(4)	–0.2636(6)	0.7206(2)	0.053(3)	0.125(5)	0.063(3)	–0.047(3)	–0.016(2)	0.054(3)
C(8)	4*e*	0.2379(6)	–0.3722(4)	0.6900(2)	0.127(5)	0.037(2)	0.065(3)	0.002(3)	0.010(3)	0.006(2)
C(9)	4*e*	0.0231(3)	0.2785(3)	0.5745(2)	0.035(2)	0.027(2)	0.048(2)	0.002(2)	0.008(2)	–0.009(2)
C(10)	4*e*	0.0052(3)	0.3070(4)	0.5053(2)	0.046(2)	0.030(2)	0.049(2)	0.010(2)	–0.009(2)	–0.005(2)
C(11)	4*e*	0.1098(4)	0.3517(4)	0.4836(2)	0.067(3)	0.030(2)	0.047(2)	0.001(2)	0.008(2)	0.011(2)
C(12)	4*e*	0.1946(4)	0.3535(3)	0.5395(2)	0.042(2)	0.029(2)	0.065(2)	–0.012(2)	0.007(2)	–0.003(2)
C(13)	4*e*	0.1407(3)	0.3086(3)	0.5953(2)	0.048(2)	0.026(2)	0.040(2)	0.001(2)	–0.001(2)	–0.011(2)
C(14)	4*e*	0.3379(3)	0.1187(4)	0.4637(2)	0.024(2)	0.054(2)	0.038(2)	–0.012(2)	0.014(1)	–0.003(2)
C(15)	4*e*	0.3333(3)	–0.0119(4)	0.4912(2)	0.020(2)	0.050(2)	0.031(2)	0.003(2)	0.008(1)	–0.005(2)
C(16)	4*e*	0.2415(3)	–0.0838(4)	0.4557(2)	0.026(2)	0.039(2)	0.037(2)	0.001(2)	0.011(1)	–0.012(1)
C(17)	4*e*	0.1900(3)	0.0024(4)	0.4054(1)	0.029(2)	0.062(2)	0.022(1)	–0.004(2)	0.006(1)	–0.010(2)
C(18)	4*e*	0.2484(3)	0.1275(4)	0.4102(2)	0.040(2)	0.061(3)	0.026(2)	0.002(2)	0.015(1)	0.010(2)
C(19)	4*e*	0.5246(5)	0.9662(6)	0.0657(2)	0.105(5)	0.086(4)	0.039(2)	0.058(4)	–0.014(3)	–0.015(2)
C(20)	4*e*	0.4322(5)	0.9014(5)	0.0271(2)	0.093(4)	0.058(3)	0.070(3)	0.034(3)	0.008(3)	–0.016(2)
C(21)	4*e*	0.4090(5)	0.9366(6)	–0.0384(3)	0.077(4)	0.078(4)	0.064(3)	0.028(3)	–0.012(3)	–0.030(3)
Hf(1)	4*e*	0.14457(1)	0.10560(1)	0.516700(5)	0.01683(6)	0.02296(6)	0.01825(6)	–0.00307(6)	0.00197(4)	0.00001(5)
O(1)	2*b*	0	0	½	0.021(2)	0.027(1)	0.020(1)	–0.004(1)	0.001(1)	–0.002(1)
Si(1)	4*e*	0.35372(7)	0.06922(9)	0.67194(4)	0.0212(4)	0.0390(5)	0.0241(4)	–0.0062(4)	–0.0016(3)	0.0020(4)
Si(2)	4*e*	0.15736(9)	–0.2153(1)	0.71198(4)	0.0382(5)	0.0406(5)	0.0270(4)	–0.0119(4)	–0.0023(4)	0.0119(4)

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