Crystal structure of 1-bis(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)cyclopentadienyl)-1-trimethylphosphine-2,3-bis(trimethylsilyl)-1-hafnacycloprop-2-ene — hexane (1:0.5), $(HfC_8H_{18}Si_2)(C_{15}H_{22})_2(PC_3H_9) \cdot 0.5C_6H_{14}$

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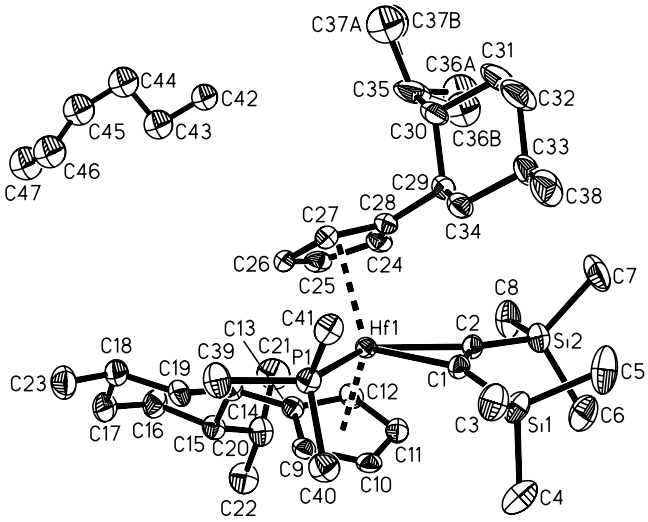

Abstract

$C_{44}H_{78}HfPSi_2$, tetragonal, $P4_12_12$ (no. 92), a = 14.9634(2) Å, c = 44.9270(8) Å, V = 10059.3 Å^3, Z = 8, $R_{gt}(F)$ = 0.026, $wR_{ref}(F^2)$ = 0.073, T = 200 K.

Source of material

(η^5-menthyl-$C_5H_4)_2HfCl_2$ (0.650 g, 0.991 mmol) and magnesium turnings (0.025 g, 1.029 mmol) were dissolved in 15 ml of THF, followed by the addition of bis(trimethylsilyl)acetylene (0.23 ml, 1.015 mmol) and trimethylphosphine (1.0 ml, 1.0 mmol, c = 1 M in THF). The solution was stirred at 50 °C for 24 h, the color of the solution changed from colorless to brown. The solvent was removed under vacuum, and the obtained residue was extracted with 20 ml of *n*-hexane. Leaving the *n*-hexane solution at –78 °C gave fine, yellow crystals, which were dried under vacuum.

Discussion

For stoichiometric and catalytic reactions of organometallic compounds it is necessary to have suitable complex fragments that are coordinatively and electronically unsaturated. In group 4 chemistry such complex fragments are titanocene Cp^*_2Ti, zirconocene Cp^*_2Zr, and hafnocene Cp^*_2Hf (Cp^* = substituted or unsubstituted η^5-cyclopentadienyl), which are considered as generally unstable 14-electron compounds having a d^2 configuration [1]. The aim is to find an adequate precursor that liberates the very reactive core complex under mild conditions. Such suitable systems are metallocene alkyne complexes of the type $Cp^*_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (Cp^* = Cp or substituted cyclopentadienyl; M = Ti, Zr, Hf). Until recently, the hafnocene alkyne complexes have been unknown, as the first examples were reported by our group [2]. In a different paper, we showed the applicability of a chiral modification, namely, the menthyl substituted cyclopentadienyl ligand [3]. Throughout these investigations the new chiral-substituted hafnocene dichloride (η^5-menthyl-$C_5H_4)_2HfCl_2$ was synthesized. The reaction of the titanium and zirconium analogues (η^5-menthyl-$C_5H_4)_2MCl_2$ (M = Ti, Zr) with magnesium in THF in the presence of the bistrimethylsilylacetylene yielded the corresponding alkyne complexes (η^5-menthyl-$C_5H_4)_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (M = Ti, Zr) [4]. Herein, we present the molecular structure of the first hafnocene alkyne complex with the menthyl substituted cyclopentadienyl ligand. Other than the titanium and zirconium analogues, an additional ligand is mandatory to form the title compound.

The molecular structure shows a hafnacyclopropene unit with two bent cyclopentadienyl ligands and the attached phosphine. The alkyne is coordinated unsymmetrically to the hafnium shown by two different C—Hf distances (d(C1—Hf1) = 2.282(5) Å, d(C2—Hf1) = 2.211(5) Å). Also the C–C–Si angles (∠C2–C1–Si1 = 127.9(4)° and ∠C1–C2–Si2 = 158.2(3)°) show a large deviation from each other. These differences are due to the steric influence of the additional ligand. The bond length C1—C2 with 1.312(8) Å is in the range of a double bond. These observations are in agreement with these found for $Cp_2Hf(PMe_3)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ [2].

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.18 × 0.30 × 0.32 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.178 cm^{-1}
Diffractometer, scan mode:	STOE IPDS II, ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	52884, 8440
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7322
$N(param)_{refined}$:	441
Programs:	SHELXS-97 [5], SHELXL-97 [6], SHELXTL [7]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(3A)	8*b*		–0.0244	0.0060	0.5592	0.099
H(3B)	8*b*		–0.0346	–0.0854	0.5411	0.099
H(3C)	8*b*		0.0622	–0.0521	0.5514	0.099
H(4A)	8*b*		0.0836	–0.2364	0.5805	0.119
H(4B)	8*b*		–0.0163	–0.2612	0.5707	0.119
H(4C)	8*b*		0.0131	–0.2694	0.6049	0.119
H(5A)	8*b*		–0.1487	–0.1493	0.6193	0.136
H(5B)	8*b*		–0.1703	–0.1368	0.5847	0.136
H(5C)	8*b*		–0.1539	–0.0511	0.6053	0.136
H(6A)	8*b*		–0.0991	–0.2562	0.6492	0.126
H(6B)	8*b*		–0.1154	–0.2799	0.6835	0.126
H(6C)	8*b*		–0.0180	–0.2912	0.6692	0.126
H(7A)	8*b*		–0.1393	–0.0122	0.6893	0.132
H(7B)	8*b*		–0.1934	–0.1025	0.6955	0.132
H(7C)	8*b*		–0.1792	–0.0685	0.6621	0.132
H(8A)	8*b*		0.0563	–0.1754	0.7183	0.111
H(8B)	8*b*		–0.0436	–0.1744	0.7311	0.111
H(8C)	8*b*		0.0086	–0.0824	0.7259	0.111
H(9)	8*b*		0.3470	–0.1409	0.6270	0.048
H(10)	8*b*		0.2017	–0.2239	0.6232	0.054
H(11)	8*b*		0.1322	–0.2282	0.6741	0.054
H(12)	8*b*		0.2299	–0.1402	0.7088	0.053
H(14)	8*b*		0.3849	–0.0365	0.7000	0.054
H(15)	8*b*		0.4856	–0.1958	0.6868	0.054
H(16A)	8*b*		0.5228	–0.0595	0.7298	0.073
H(16B)	8*b*		0.5816	–0.1482	0.7260	0.073
H(17A)	8*b*		0.6234	–0.1059	0.6786	0.082
H(17B)	8*b*		0.6480	–0.0280	0.7016	0.082
H(18)	8*b*		0.5260	0.0586	0.6859	0.071
H(19A)	8*b*		0.4219	0.0072	0.6511	0.058
H(19B)	8*b*		0.4766	–0.0835	0.6463	0.058
H(20)	8*b*		0.3600	–0.2367	0.7157	0.067
H(21A)	8*b*		0.4318	–0.1376	0.7643	0.118
H(21B)	8*b*		0.3425	–0.1965	0.7649	0.118
H(21C)	8*b*		0.3460	–0.1061	0.7458	0.118
H(22A)	8*b*		0.4891	–0.3249	0.7178	0.105
H(22B)	8*b*		0.4408	–0.3263	0.7495	0.105
H(22C)	8*b*		0.5278	–0.2659	0.7445	0.105
H(23A)	8*b*		0.6512	0.0779	0.6547	0.120
H(23B)	8*b*		0.5623	0.0860	0.6350	0.120
H(23C)	8*b*		0.6201	–0.0039	0.6342	0.120
H(24)	8*b*		0.0881	0.0327	0.7066	0.053
H(25)	8*b*		0.2564	0.0313	0.7080	0.057
H(26)	8*b*		0.3106	0.1066	0.6609	0.057
H(27)	8*b*		0.1747	0.1610	0.6322	0.051
H(29)	8*b*		–0.0381	0.0938	0.6711	0.055
H(30)	8*b*		0.0206	0.2737	0.6621	0.079
H(31A)	8*b*		–0.1523	0.2107	0.6801	0.114
H(31B)	8*b*		–0.1266	0.3141	0.6771	0.114
H(32A)	8*b*		–0.2040	0.2654	0.6344	0.102
H(32B)	8*b*		–0.1055	0.2981	0.6257	0.102
H(33)	8*b*		–0.1584	0.1169	0.6333	0.069
H(34A)	8*b*		–0.0092	0.0795	0.6190	0.058
H(34B)	8*b*		0.0164	0.1833	0.6176	0.058
H(35A)	8*b*		0.0768	0.2179	0.7085	0.114
H(35B)	8*b*		0.0779	0.2204	0.7075	0.114
H(38A)	8*b*		–0.2086	0.1776	0.5885	0.113
H(38B)	8*b*		–0.1325	0.1050	0.5819	0.113
H(38C)	8*b*		–0.1093	0.2093	0.5804	0.113
H(39A)	8*b*		0.3602	0.0571	0.5717	0.092
H(39B)	8*b*		0.3939	–0.0024	0.5991	0.092
H(39C)	8*b*		0.3574	0.0966	0.6048	0.092
H(40A)	8*b*		0.1846	–0.1203	0.5690	0.087
H(40B)	8*b*		0.2840	–0.1407	0.5802	0.087
H(40C)	8*b*		0.2680	–0.0743	0.5528	0.087
H(41A)	8*b*		0.1858	0.0754	0.5556	0.078
H(41B)	8*b*		0.1952	0.1425	0.5832	0.078
H(41C)	8*b*		0.1113	0.0765	0.5812	0.078
C(42)	8*b*	0.50	0.7503(9)	0.256(1)	1.0024(4)	0.085(4)
H(42A)	8*b*	0.50	0.7181	0.1996	1.0045	0.128
H(42B)	8*b*	0.50	0.7289	0.2877	0.9846	0.128
H(42C)	8*b*	0.50	0.7400	0.2933	1.0200	0.128
C(43)	8*b*	0.50	0.8483(9)	0.238(1)	0.9993(5)	0.106(3)
H(43A)	8*b*	0.50	0.8728	0.2048	1.0165	0.128
H(43B)	8*b*	0.50	0.8629	0.2062	0.9806	0.128
C(44)	8*b*	0.50	0.8779(9)	0.334(1)	0.9988(5)	0.114(3)
H(44A)	8*b*	0.50	0.8604	0.3666	1.0170	0.137
H(44B)	8*b*	0.50	0.8572	0.3659	0.9809	0.137
C(45)	8*b*	0.50	0.9758(9)	0.313(2)	0.9979(5)	0.124(3)
H(45A)	8*b*	0.50	0.9856	0.2756	1.0158	0.148
H(45B)	8*b*	0.50	1.0047	0.3708	1.0023	0.148
C(46)	8*b*	0.50	1.036(1)	0.272(2)	0.9750(3)	0.130(4)
H(46A)	8*b*	0.50	1.0544	0.3143	0.9594	0.156
H(46B)	8*b*	0.50	1.0098	0.2172	0.9658	0.156
C(47)	8*b*	0.50	1.109(1)	0.251(2)	0.9967(5)	0.144(5)
H(47A)	8*b*	0.50	1.1536	0.2124	0.9872	0.215
H(47B)	8*b*	0.50	1.0839	0.2202	1.0141	0.215
H(47C)	8*b*	0.50	1.1376	0.3067	1.0031	0.215
C(36A)	8*b*	0.50	–0.042(2)	0.198(1)	0.7315(4)	0.098(4)
H(36A)	8*b*	0.50	–0.0438	0.1336	0.7284	0.147
H(36B)	8*b*	0.50	–0.1023	0.2228	0.7310	0.147
H(36C)	8*b*	0.50	–0.0144	0.2110	0.7509	0.147
C(37A)	8*b*	0.50	0.020(2)	0.3442(5)	0.7104(5)	0.105(5)
H(37A)	8*b*	0.50	0.0560	0.3695	0.6943	0.158
H(37B)	8*b*	0.50	0.0474	0.3586	0.7296	0.158
H(37C)	8*b*	0.50	–0.0405	0.3695	0.7096	0.158
C(36B)	8*b*	0.50	–0.038(2)	0.177(1)	0.7267(4)	0.096(4)
H(36D)	8*b*	0.50	–0.0407	0.1179	0.7171	0.144
H(36E)	8*b*	0.50	–0.0991	0.1994	0.7295	0.144
H(36F)	8*b*	0.50	–0.0086	0.1713	0.7460	0.144
C(37B)	8*b*	0.50	0.017(2)	0.3367(6)	0.7201(5)	0.107(5)
H(37D)	8*b*	0.50	0.0506	0.3764	0.7069	0.160
H(37E)	8*b*	0.50	0.0453	0.3350	0.7397	0.160
H(37F)	8*b*	0.50	–0.0445	0.3592	0.7222	0.160

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)	8*b*	0.0528(4)	–0.0781(4)	0.6248(1)	0.034(3)	0.039(3)	0.043(3)	–0.002(2)	–0.006(3)	–0.001(2)
C(2)	8*b*	0.0371(4)	–0.0900(3)	0.6532(1)	0.032(3)	0.039(3)	0.051(3)	–0.003(2)	–0.003(3)	0.001(3)
C(3)	8*b*	–0.0012(5)	–0.0548(5)	0.5569(2)	0.062(4)	0.081(5)	0.055(4)	–0.009(4)	–0.021(3)	0.002(4)
C(4)	8*b*	0.0207(6)	–0.2350(5)	0.5865(2)	0.105(7)	0.061(5)	0.072(5)	–0.025(4)	–0.017(4)	–0.006(4)
C(5)	8*b*	–0.1363(5)	–0.1132(6)	0.6016(2)	0.062(5)	0.130(7)	0.081(6)	–0.033(5)	–0.026(5)	0.030(6)
C(6)	8*b*	–0.0727(6)	–0.2552(5)	0.6691(2)	0.084(6)	0.073(5)	0.094(6)	–0.033(5)	0.008(5)	0.012(4)
C(7)	8*b*	–0.1520(4)	–0.0725(6)	0.6819(2)	0.040(4)	0.114(7)	0.111(7)	0.007(4)	0.023(4)	0.006(6)
C(8)	8*b*	–0.0007(5)	–0.1432(6)	0.7183(1)	0.060(4)	0.111(7)	0.050(4)	–0.022(4)	0.010(3)	0.015(4)
C(9)	8*b*	0.3069(4)	–0.1518(3)	0.6430(1)	0.037(3)	0.037(3)	0.044(3)	0.007(2)	0.000(2)	–0.002(2)
C(10)	8*b*	0.2258(4)	–0.1981(4)	0.6408(1)	0.044(3)	0.032(3)	0.058(4)	0.013(3)	–0.008(3)	–0.006(3)
C(11)	8*b*	0.1868(4)	–0.1997(3)	0.6690(1)	0.038(3)	0.033(3)	0.064(4)	0.004(3)	–0.005(3)	0.013(3)
C(12)	8*b*	0.2420(4)	–0.1519(4)	0.6884(1)	0.041(3)	0.049(4)	0.043(3)	0.007(3)	–0.004(3)	0.006(3)
C(13)	8*b*	0.3193(4)	–0.1238(3)	0.6726(1)	0.034(3)	0.039(3)	0.041(3)	0.005(3)	–0.006(3)	0.003(2)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(14)	8*b*	0.4031(4)	–0.0833(4)	0.6854(1)	0.043(3)	0.047(3)	0.045(3)	0.001(3)	0.001(3)	–0.001(3)
C(15)	8*b*	0.4622(4)	–0.1536(4)	0.7022(1)	0.039(3)	0.051(4)	0.045(3)	0.006(3)	–0.010(3)	0.003(3)
C(16)	8*b*	0.5436(5)	–0.1047(5)	0.7153(2)	0.049(4)	0.067(4)	0.066(4)	–0.006(4)	–0.018(4)	0.000(3)
C(17)	8*b*	0.5977(4)	–0.0598(5)	0.6919(2)	0.037(4)	0.073(5)	0.095(6)	0.001(3)	–0.021(4)	–0.007(4)
C(18)	8*b*	0.5443(4)	0.0076(4)	0.6729(2)	0.043(3)	0.053(4)	0.082(5)	–0.001(3)	0.000(4)	–0.001(3)
C(19)	8*b*	0.4593(4)	–0.0381(4)	0.6613(1)	0.033(3)	0.056(4)	0.055(3)	0.005(3)	0.000(3)	0.004(3)
C(20)	8*b*	0.4138(4)	–0.2105(5)	0.7256(1)	0.050(4)	0.070(5)	0.049(4)	–0.001(3)	–0.011(3)	0.010(3)
C(21)	8*b*	0.3806(6)	–0.1579(6)	0.7526(2)	0.095(6)	0.095(7)	0.046(4)	0.006(5)	–0.005(4)	0.003(4)
C(22)	8*b*	0.4733(5)	–0.2890(5)	0.7352(2)	0.070(5)	0.074(5)	0.067(4)	0.010(4)	–0.020(4)	0.023(4)
C(23)	8*b*	0.5995(5)	0.0453(5)	0.6468(2)	0.054(4)	0.067(4)	0.118(7)	–0.004(4)	0.013(4)	0.021(5)
C(24)	8*b*	0.1262(4)	0.0591(4)	0.6921(1)	0.050(4)	0.048(4)	0.036(3)	0.006(3)	0.006(3)	–0.011(3)
C(25)	8*b*	0.2201(4)	0.0568(4)	0.6928(1)	0.055(4)	0.049(4)	0.040(3)	0.009(3)	–0.012(3)	–0.018(3)
C(26)	8*b*	0.2501(4)	0.0994(4)	0.6668(2)	0.034(3)	0.040(3)	0.069(4)	–0.004(3)	0.000(3)	–0.018(3)
C(27)	8*b*	0.1737(4)	0.1301(3)	0.6506(1)	0.041(3)	0.037(3)	0.050(3)	–0.003(3)	0.003(3)	–0.004(3)
C(28)	8*b*	0.0970(4)	0.1067(4)	0.6668(1)	0.038(3)	0.039(3)	0.043(3)	0.005(3)	0.004(3)	–0.008(3)
C(29)	8*b*	0.0030(4)	0.1369(4)	0.6610(1)	0.037(3)	0.050(4)	0.051(3)	0.005(2)	0.001(3)	–0.007(3)
C(30)	8*b*	–0.0151(4)	0.2304(5)	0.6741(2)	0.043(4)	0.064(5)	0.091(5)	0.019(3)	–0.004(4)	–0.031(4)
C(31)	8*b*	–0.1145(5)	0.2538(7)	0.6691(2)	0.062(5)	0.113(7)	0.108(7)	0.044(5)	–0.007(5)	–0.048(6)
C(32)	8*b*	–0.1396(5)	0.2516(6)	0.6365(2)	0.058(5)	0.099(7)	0.099(6)	0.043(5)	–0.018(4)	–0.022(5)
C(33)	8*b*	–0.1207(4)	0.1627(5)	0.6231(2)	0.036(3)	0.070(5)	0.067(4)	0.010(3)	–0.008(3)	0.001(4)
C(34)	8*b*	–0.0215(4)	0.1388(4)	0.6279(1)	0.039(3)	0.050(3)	0.055(3)	0.010(3)	–0.003(3)	–0.003(3)
C(35)	8*b*	0.0147(5)	0.2419(4)	0.7068(2)	0.080(6)	0.092(6)	0.114(7)	0.039(5)	–0.027(5)	–0.067(6)
C(38)	8*b*	–0.1449(5)	0.1637(6)	0.5907(2)	0.054(4)	0.094(6)	0.078(5)	0.016(4)	–0.019(4)	0.000(5)
C(39)	8*b*	0.3503(4)	0.0426(5)	0.5927(1)	0.055(4)	0.079(5)	0.049(4)	–0.005(4)	0.005(3)	0.016(4)
C(40)	8*b*	0.2443(5)	–0.0949(5)	0.5719(1)	0.065(4)	0.066(4)	0.044(3)	0.001(3)	0.003(3)	–0.003(3)
C(41)	8*b*	0.1753(4)	0.0829(4)	0.5770(1)	0.058(4)	0.055(3)	0.042(3)	–0.006(3)	–0.005(3)	0.004(3)
Hf(1)	8*b*	0.17726(2)	–0.04329(1)	0.651719(5)	0.0319(1)	0.0341(1)	0.03199(9)	0.0012(1)	–0.0007(1)	–0.0015(1)
P(1)	8*b*	0.2374(1)	–0.0015(1)	0.59749(3)	0.0453(8)	0.0458(8)	0.0359(7)	–0.0034(7)	0.0004(7)	–0.0007(7)
Si(1)	8*b*	–0.0142(1)	–0.1178(1)	0.59292(4)	0.055(1)	0.056(1)	0.051(1)	–0.0146(8)	–0.0168(8)	0.0000(8)
Si(2)	8*b*	–0.0455(1)	–0.1378(1)	0.67954(4)	0.0399(9)	0.063(1)	0.057(1)	–0.0056(9)	0.0048(9)	0.0059(8)

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