Crystal structure of bis(pentamethylcyclopentadienyl)-(4,4′-di-*tert*-butylbipyridyl)hafnium(IV) — hexane (1:0.5), $Hf(C_{10}H_{15})_2(C_{18}H_{24}N_2) \cdot 0.5C_6H_{14}$

Torsten Beweries*, Anke Spannenberg and Uwe Rosenthal

Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany

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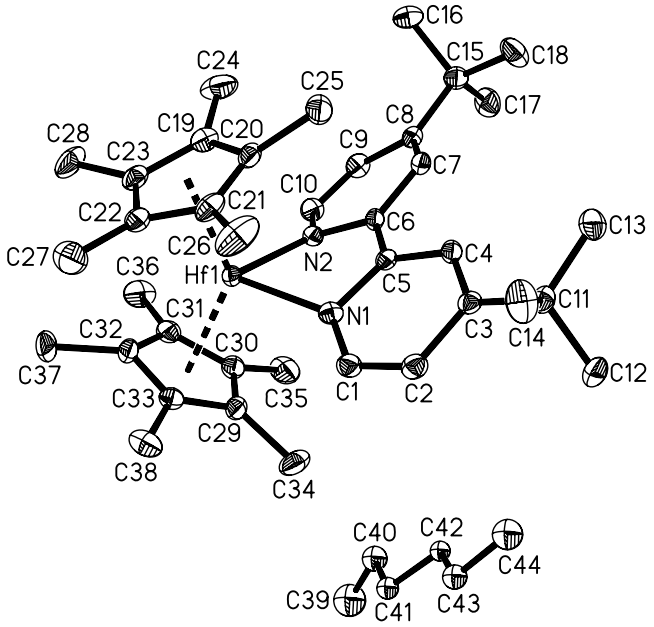

Abstract

$C_{41}H_{61}HfN_2$, monoclinic, $P2_1/n$ (no. 14), a = 13.4410(4) Å, b = 13.9983(6) Å, c = 21.1996(8) Å, β = 98.144(3)°, V = 3948.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.051, $wR_{ref}(F^2)$ = 0.121, T = 200 K.

Source of material

$Cp^*_2HfCl_2$ (1.198 g, 2.31 mmol), finely cut lithium (0.064 g, 9.22 mmol) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (0.619 g, 2.31 mmol) were suspended in 20 mL toluene. The mixture was stirred at 60 °C for two days, resulting in a purple solution. The volatiles were removed in vacuum, followed by extraction of the residue with 2 × 10 mL *n*-hexane. The dark blue filtrate was stored at –78 °C, after 24 hours dark blue crystals had formed which were isolated, washed with cold *n*-hexane and dried in vacuum to give 0.748 g (45 %) of the title compound.

Discussion

Recently we reported on the synthesis of hafnocene alkyne complexes and found the alkyne to be coordinated strongly to the metal resulting in a hafnacyclopropene structure [1]. We were interested to investigate the influence of the Lewis acidic metallocene center on other substrates such as THF [2] and bipyridines. Upon reaction of decamethylhafnocene dichloride with lithium and 4,4′-di-*tert*-butyl-2,2′-bipyridine the deep blue, highly air- and moisture sensitive title compound is formed.

The bipyridine coordinates the metal with both N atoms. Structural data suggest the existence of a σ,σ complex rather than a π,π coordination mode. The bond distance C5—C6 of 1.387(8) Å is indicative of a double bond, this value is at 1.494 Å in free 4,4′-di-*tert*-butylbipyridine [3]. This significantly shorter bond distance and the existence of a bent metallacycle (angle between the planes N1,Hf1,N2 and N1,C5,C6,N2: 33.6(2)°) allow the interpretation of this complex as a 2,5-diazametallacyclopent-3-ene. The aromaticity of the ring system is reduced due to the donation of electron density from the hafnocene center into the antibonding π^* orbitals of the ligand.

Additionally, half a molecule of *n*-hexane as a solvent molecule was found in the asymmetric unit of the title compound.

Table 1. Data collection and handling.

Crystal:	dark-blue prism, size 0.2 × 0.3 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	26.69 cm^{-1}
Diffractometer, scan mode:	STOE IPDS II, ω
$2\theta_{max}$:	53.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	55798, 8368
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6265
$N(param)_{refined}$:	404
Programs:	SHELXS-97 [4], SHELXL-97 [5], SHELXTL [6]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(1A)	4*e*		0.4688	0.5865	0.0881	0.040
H(2A)	4*e*		0.4308	0.4314	0.0721	0.041
H(4A)	4*e*		0.4999	0.3839	0.2620	0.033
H(7A)	4*e*		0.5816	0.4408	0.3506	0.036
H(9A)	4*e*		0.7817	0.6440	0.4186	0.042
H(10A)	4*e*		0.7280	0.7373	0.3337	0.041
H(12A)	4*e*		0.4820	0.2706	0.0732	0.075
H(12B)	4*e*		0.4577	0.1707	0.1043	0.075
H(12C)	4*e*		0.5527	0.2321	0.1351	0.075
H(13A)	4*e*		0.4885	0.2240	0.2390	0.066
H(13B)	4*e*		0.3911	0.1662	0.2079	0.066
H(13C)	4*e*		0.3787	0.2629	0.2463	0.066
H(14A)	4*e*		0.2662	0.3255	0.1492	0.083
H(14B)	4*e*		0.2821	0.2247	0.1166	0.083
H(14C)	4*e*		0.3051	0.3216	0.0814	0.083
H(16A)	4*e*		0.5983	0.5562	0.5016	0.085
H(16B)	4*e*		0.7078	0.6033	0.5139	0.085
H(16C)	4*e*		0.6837	0.5102	0.5529	0.085

* Correspondence author (e-mail: torsten.beweries@catalysis.de)

Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(17A)	4*e*		0.8328	0.4267	0.5153	0.079
H(17B)	4*e*		0.8543	0.5210	0.4767	0.079
H(17C)	4*e*		0.8393	0.4205	0.4406	0.079
H(18A)	4*e*		0.5773	0.3959	0.4540	0.081
H(18B)	4*e*		0.6701	0.3531	0.5012	0.081
H(18C)	4*e*		0.6676	0.3444	0.4257	0.081
H(24A)	4*e*		0.4310	0.7583	0.4133	0.097
H(24B)	4*e*		0.5300	0.7998	0.3892	0.097
H(24C)	4*e*		0.5157	0.6869	0.3955	0.097
H(25A)	4*e*		0.3052	0.5729	0.3353	0.095
H(25B)	4*e*		0.4237	0.5533	0.3467	0.095
H(25C)	4*e*		0.3573	0.5188	0.2820	0.095
H(26A)	4*e*		0.2005	0.6417	0.1818	0.106
H(26B)	4*e*		0.2898	0.5656	0.1842	0.106
H(26C)	4*e*		0.2811	0.6508	0.1334	0.106
H(27A)	4*e*		0.2932	0.8304	0.1278	0.107
H(27B)	4*e*		0.3087	0.9209	0.1743	0.107
H(27C)	4*e*		0.2143	0.8517	0.1760	0.107
H(28A)	4*e*		0.3922	0.9715	0.2679	0.095
H(28B)	4*e*		0.4925	0.9397	0.3129	0.095
H(28C)	4*e*		0.3866	0.9362	0.3391	0.095
H(34A)	4*e*		0.6006	0.6581	0.0516	0.080
H(34B)	4*e*		0.6667	0.6072	0.1108	0.080
H(34C)	4*e*		0.7165	0.6858	0.0703	0.080
H(35A)	4*e*		0.7828	0.6639	0.2154	0.081
H(35B)	4*e*		0.8166	0.7626	0.2501	0.081
H(35C)	4*e*		0.8354	0.7447	0.1781	0.081
H(36A)	4*e*		0.7473	0.8901	0.2874	0.082
H(36B)	4*e*		0.6416	0.9427	0.2874	0.082
H(36C)	4*e*		0.7184	0.9798	0.2416	0.082
H(37A)	4*e*		0.5376	1.0131	0.1283	0.092
H(37B)	4*e*		0.5193	1.0090	0.2012	0.092
H(37C)	4*e*		0.4352	0.9696	0.1464	0.092
H(38A)	4*e*		0.4949	0.8398	0.0250	0.079
H(38B)	4*e*		0.4063	0.8409	0.0681	0.079
H(38C)	4*e*		0.4492	0.7414	0.0464	0.079
C(39)	4*e*	0.50	1.069(1)	0.703(1)	0.0519(9)	0.076
H(39A)	4*e*	0.50	1.1161	0.7266	0.0880	0.114
H(39B)	4*e*	0.50	1.0379	0.7566	0.0272	0.114
H(39C)	4*e*	0.50	1.1056	0.6629	0.0247	0.114
C(40)	4*e*	0.50	0.9913(9)	0.645(1)	0.0756(6)	0.044
H(40A)	4*e*	0.50	0.9584	0.6863	0.1046	0.053
H(40B)	4*e*	0.50	1.0254	0.5931	0.1018	0.053
C(41)	4*e*	0.50	0.9118(8)	0.6020(7)	0.0303(5)	0.032
H(41A)	4*e*	0.50	0.9400	0.5845	–0.0088	0.038
H(41B)	4*e*	0.50	0.8585	0.6501	0.0183	0.038
C(42)	4*e*	0.50	0.8663(7)	0.5169(7)	0.0544(5)	0.026
H(42A)	4*e*	0.50	0.8428	0.5338	0.0952	0.031
H(42B)	4*e*	0.50	0.9193	0.4678	0.0639	0.031
C(43)	4*e*	0.50	0.7821(8)	0.4743(8)	0.0125(5)	0.036
H(43A)	4*e*	0.50	0.7311	0.5246	0.0005	0.043
H(43B)	4*e*	0.50	0.8067	0.4532	–0.0271	0.043
C(44)	4*e*	0.50	0.733(1)	0.3933(9)	0.0386(7)	0.054
H(44A)	4*e*	0.50	0.6776	0.3704	0.0069	0.081
H(44B)	4*e*	0.50	0.7056	0.4134	0.0771	0.081
H(44C)	4*e*	0.50	0.7814	0.3417	0.0493	0.081

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*	0.4774(5)	0.5453(5)	0.1241(3)	0.034(3)	0.037(3)	0.028(3)	0.004(3)	0.004(2)	0.003(2)
C(2)	4*e*	0.4519(5)	0.4538(5)	0.1142(3)	0.037(4)	0.036(3)	0.030(3)	0.001(3)	0.003(2)	–0.004(2)
C(3)	4*e*	0.4565(4)	0.3880(4)	0.1682(3)	0.026(3)	0.029(3)	0.032(3)	0.000(2)	0.009(2)	–0.002(2)
C(4)	4*e*	0.4967(4)	0.4238(4)	0.2255(3)	0.028(3)	0.024(3)	0.033(3)	0.002(2)	0.008(2)	0.001(2)
C(5)	4*e*	0.5348(4)	0.5198(4)	0.2333(2)	0.023(3)	0.029(3)	0.029(3)	0.006(2)	0.008(2)	0.000(2)
C(6)	4*e*	0.5908(4)	0.5541(4)	0.2886(3)	0.028(3)	0.021(3)	0.032(3)	0.003(2)	0.008(2)	0.001(2)
C(7)	4*e*	0.6142(5)	0.5003(4)	0.3467(3)	0.034(3)	0.023(3)	0.033(3)	0.002(2)	0.008(2)	–0.002(2)
C(8)	4*e*	0.6812(5)	0.5320(4)	0.3959(3)	0.033(3)	0.028(3)	0.031(3)	0.005(3)	0.007(2)	–0.002(2)
C(9)	4*e*	0.7284(5)	0.6224(5)	0.3876(3)	0.032(3)	0.036(3)	0.036(3)	–0.004(3)	0.002(2)	–0.006(2)
C(10)	4*e*	0.6975(5)	0.6764(5)	0.3363(3)	0.035(3)	0.030(3)	0.038(3)	–0.008(3)	0.008(2)	–0.003(2)
C(11)	4*e*	0.4172(5)	0.2874(4)	0.1562(3)	0.034(3)	0.025(3)	0.039(3)	–0.001(2)	0.007(2)	–0.005(2)
C(12)	4*e*	0.4834(7)	0.2354(5)	0.1133(4)	0.072(5)	0.030(3)	0.052(4)	0.000(4)	0.022(4)	–0.011(3)
C(13)	4*e*	0.4190(6)	0.2299(5)	0.2179(3)	0.053(4)	0.031(3)	0.049(4)	–0.012(3)	0.009(3)	–0.002(3)
C(14)	4*e*	0.3077(6)	0.2900(5)	0.1228(4)	0.042(4)	0.043(5)	0.077(5)	–0.012(3)	–0.010(4)	–0.002(3)
C(15)	4*e*	0.7039(5)	0.4791(5)	0.4595(3)	0.048(4)	0.039(4)	0.026(3)	0.003(3)	0.002(3)	–0.002(2)
C(16)	4*e*	0.6704(7)	0.5430(6)	0.5117(3)	0.078(6)	0.061(5)	0.034(3)	0.005(4)	0.020(4)	–0.004(3)
C(17)	4*e*	0.8180(6)	0.4601(6)	0.4744(3)	0.055(5)	0.053(5)	0.048(4)	0.012(4)	–0.004(3)	0.010(3)
C(18)	4*e*	0.6500(7)	0.3849(5)	0.4601(3)	0.075(6)	0.045(4)	0.039(3)	–0.010(4)	–0.001(3)	0.012(3)
C(19)	4*e*	0.4300(5)	0.7437(5)	0.3176(3)	0.040(4)	0.043(4)	0.037(3)	0.000(3)	0.010(3)	–0.006(3)
C(20)	4*e*	0.3836(5)	0.6633(4)	0.2841(3)	0.036(4)	0.026(3)	0.050(3)	–0.002(3)	0.021(3)	–0.004(3)
C(21)	4*e*	0.3363(5)	0.6946(5)	0.2241(3)	0.025(3)	0.046(4)	0.051(4)	0.000(3)	0.012(3)	–0.015(3)
C(22)	4*e*	0.3462(5)	0.7945(5)	0.2200(3)	0.033(3)	0.044(4)	0.042(3)	0.012(3)	0.016(3)	0.004(3)
C(23)	4*e*	0.4051(5)	0.8265(5)	0.2780(3)	0.035(3)	0.033(4)	0.051(3)	–0.003(3)	0.022(3)	–0.007(3)
C(24)	4*e*	0.4810(7)	0.7475(7)	0.3846(3)	0.062(6)	0.097(7)	0.037(4)	0.014(5)	0.015(4)	–0.006(4)
C(25)	4*e*	0.3659(7)	0.5688(5)	0.3147(4)	0.065(5)	0.039(4)	0.100(6)	0.008(4)	0.057(5)	0.018(4)
C(26)	4*e*	0.2712(6)	0.6328(7)	0.1767(4)	0.034(4)	0.088(7)	0.092(6)	–0.010(4)	0.015(4)	–0.042(5)
C(27)	4*e*	0.2854(6)	0.8546(7)	0.1702(4)	0.050(5)	0.095(7)	0.073(5)	0.032(5)	0.022(4)	0.032(5)
C(28)	4*e*	0.4204(7)	0.9272(5)	0.3015(4)	0.076(6)	0.032(4)	0.094(6)	–0.011(4)	0.049(5)	–0.024(4)
C(29)	4*e*	0.6263(5)	0.7442(4)	0.1305(3)	0.039(4)	0.023(3)	0.044(3)	–0.003(2)	0.020(3)	0.000(2)
C(30)	4*e*	0.6888(5)	0.7748(5)	0.1857(3)	0.037(3)	0.033(3)	0.042(3)	0.000(3)	0.015(3)	0.005(3)
C(31)	4*e*	0.6447(5)	0.8567(5)	0.2091(3)	0.049(4)	0.031(3)	0.040(3)	–0.007(3)	0.018(3)	0.003(3)
C(32)	4*e*	0.5555(5)	0.8776(4)	0.1667(3)	0.042(4)	0.028(3)	0.045(3)	0.009(3)	0.018(3)	0.003(3)
C(33)	4*e*	0.5436(5)	0.8061(5)	0.1187(3)	0.040(4)	0.035(3)	0.037(3)	0.000(3)	0.017(3)	0.007(2)
C(34)	4*e*	0.6550(6)	0.6671(5)	0.0870(4)	0.065(5)	0.045(4)	0.059(4)	–0.012(4)	0.039(4)	–0.016(3)
C(35)	4*e*	0.7896(6)	0.7329(6)	0.2094(4)	0.036(4)	0.066(5)	0.062(4)	0.004(4)	0.017(3)	0.017(4)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(36)	4*e*	0.6922(6)	0.9231(5)	0.2609(3)	0.064(5)	0.045(4)	0.056(4)	–0.030(4)	0.018(4)	–0.011(3)
C(37)	4*e*	0.5077(7)	0.9760(5)	0.1601(4)	0.085(6)	0.024(3)	0.084(6)	0.011(4)	0.041(5)	0.017(3)
C(38)	4*e*	0.4667(6)	0.8071(6)	0.0594(3)	0.057(5)	0.063(5)	0.039(3)	–0.002(4)	0.006(3)	0.014(3)
Hf(1)	4*e*	0.52011(2)	0.72528(2)	0.22075(1)	0.0275(1)	0.0212(1)	0.0289(1)	0.0008(1)	0.00834(8)	0.0011(1)
N(1)	4*e*	0.5147(4)	0.5848(4)	0.1815(2)	0.024(3)	0.032(3)	0.029(2)	–0.005(2)	0.006(2)	–0.001(2)
N(2)	4*e*	0.6247(4)	0.6497(3)	0.2873(2)	0.031(3)	0.025(2)	0.028(2)	–0.001(2)	0.008(2)	0.000(2)

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