

Christian Adler, Marc Schmidtman and Rüdiger Beckhaus*

Crystal structure of *n*-butyl-tris(dicyclohexylamido)hafnium(IV), C₄₀H₇₅HfN₃

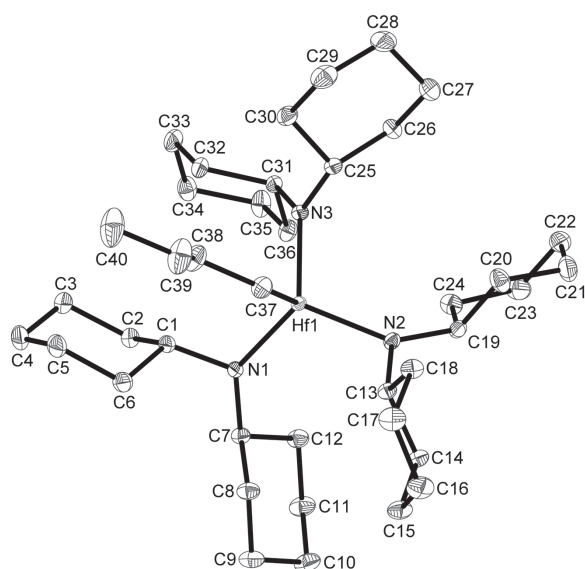


Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.36 × 0.36 × 0.32 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	27.1 cm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{\max}$, completeness:	76°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	225553, 20900, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 19301
$N(\text{param})_{\text{refined}}$:	398
Programs:	SHELX [1], Bruker programs [2]

Source of material

All reactions were carried out under a dry nitrogen atmosphere using Schlenk-technique. Tris(dicyclohexylamido) hafnium(IV) chloride is easily available by a literature known synthesis [3]. The reaction with *n*-butyllithium was carried out according to the procedure known for the analogous zirconium complex [4]. To a solution of (Cy₂N)₃HfCl (500 mg, 0.662 mmol) in 20 mL *n*-hexane was added a *n*-butyllithium solution in *n*-hexane (0.27 mL, 0.662 mmol, 2.5 mol/l). The resulting mixture was stirred at ambient temperature. The mixture was filtered over a pad of celite and concentrated to 10 mL. Colourless crystals were obtained from this solution at –30 °C after three days, identified as the title compound *n*-butyl-tris(dicyclohexylamido)hafnium(IV).

Experimental details

All hydrogen atoms were located in the difference Fourier syntheses, and subsequently fixed to geometric positions using appropriate riding models.

Comment

The title compound is a rare example of a structural characterized hafnium complex with a terminal *n*-butyl group. The complex *n*-BuHf(NCy₂)₃ is the first structural characterized hafnium-*n*-butyl complex employing three amido ligands at the electron deficient metal center. It is isostructural to the analogous zirconium compound [4]. There are only three other examples for related hafnium complexes listed in the Cambridge Crystallographic Database [5–7].

DOI 10.1515/ncrs-2016-0380

Received November 29, 2016; accepted April 5, 2017; available online May 4, 2017

Abstract

C₄₀H₇₅HfN₃, monoclinic, $P2_1/n$ (no. 14), $a = 10.7446(3)$ Å, $b = 13.6547(4)$ Å, $c = 26.5464(9)$ Å, $\beta = 92.2375(15)^\circ$, $V = 3891.8(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0195$, $wR_{\text{ref}}(F^2) = 0.0461$, $T = 100(2)$ K.

CCDC no.: 1542041

The asymmetric unit of the title crystal structure is shown in the figure (hydrogen atoms are omitted for clarity). Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Rüdiger Beckhaus**, Institut für Chemie, Fakultät für Mathematik und Naturwissenschaften, Carl von Ossietzky Universität Oldenburg, Carl-von-Ossietzky-Strasse 9-11, 26129 Oldenburg, Germany, e-mail: ruediger.beckhaus@uni-oldenburg.de
Christian Adler and Marc Schmidtman: Institut für Chemie, Fakultät für Mathematik und Naturwissenschaften, Carl von Ossietzky Universität Oldenburg, Carl-von-Ossietzky-Strasse 9-11, 26129 Oldenburg, Germany

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Hf1	0.41335(2)	0.76960(2)	0.11955(2)	0.00992(1)
N1	0.47000(7)	0.62661(6)	0.12569(3)	0.01208(13)
N2	0.22680(8)	0.78168(6)	0.10233(3)	0.01219(13)
N3	0.46600(8)	0.85440(6)	0.18020(3)	0.01237(13)
C1	0.60777(9)	0.62364(7)	0.12819(4)	0.01329(15)
H1	0.6361	0.6932	0.1312	0.016*
C2	0.66360(9)	0.57003(8)	0.17489(4)	0.01623(16)
H2A	0.6271	0.5971	0.2056	0.019*
H2B	0.6416	0.4997	0.1728	0.019*
C3	0.80570(10)	0.58074(9)	0.17898(5)	0.0212(2)
H3A	0.8274	0.6503	0.1849	0.025*
H3B	0.8387	0.5423	0.2082	0.025*
C4	0.86654(11)	0.54538(10)	0.13121(5)	0.0247(2)
H4A	0.9570	0.5594	0.1338	0.030*
H4B	0.8556	0.4736	0.1279	0.030*
C5	0.80913(11)	0.59594(9)	0.08458(5)	0.0221(2)
H5A	0.8461	0.5686	0.0540	0.027*
H5B	0.8288	0.6667	0.0860	0.027*
C6	0.66744(10)	0.58236(9)	0.08089(4)	0.01835(18)
H6A	0.6474	0.5118	0.0775	0.022*
H6B	0.6328	0.6166	0.0506	0.022*
C7	0.40903(9)	0.53027(7)	0.12424(4)	0.01355(15)
H7	0.4710	0.4811	0.1375	0.016*
C8	0.36691(10)	0.49809(8)	0.07081(4)	0.01663(17)
H8A	0.3059	0.5459	0.0565	0.020*
H8B	0.4396	0.4974	0.0490	0.020*
C9	0.30760(12)	0.39625(9)	0.07093(4)	0.02057(19)
H9A	0.2774	0.3794	0.0363	0.025*
H9B	0.3712	0.3473	0.0817	0.025*
C10	0.19903(12)	0.39196(9)	0.10627(5)	0.0227(2)
H10A	0.1682	0.3238	0.1080	0.027*
H10B	0.1302	0.4334	0.0925	0.027*
C11	0.23708(12)	0.42695(9)	0.15927(4)	0.0212(2)
H11A	0.2962	0.3794	0.1751	0.025*
H11B	0.1625	0.4295	0.1800	0.025*
C12	0.29799(10)	0.52817(8)	0.15863(4)	0.01693(17)
H12A	0.3264	0.5462	0.1933	0.020*
H12B	0.2357	0.5772	0.1468	0.020*
C13	0.21032(9)	0.75034(7)	0.04917(4)	0.01308(15)
H13	0.2895	0.7163	0.0411	0.016*
C14	0.10656(10)	0.67473(8)	0.03891(4)	0.01632(16)
H14A	0.1155	0.6206	0.0636	0.020*
H14B	0.0245	0.7060	0.0432	0.020*
C15	0.11261(12)	0.63366(9)	−0.01464(4)	0.0212(2)
H15A	0.1913	0.5969	−0.0177	0.025*
H15B	0.0427	0.5875	−0.0209	0.025*
C16	0.10565(13)	0.71478(10)	−0.05421(5)	0.0248(2)
H16A	0.0220	0.7452	−0.0546	0.030*
H16B	0.1179	0.6862	−0.0879	0.030*
C17	0.20469(13)	0.79331(10)	−0.04327(4)	0.0231(2)
H17A	0.2885	0.7649	−0.0472	0.028*
H17B	0.1936	0.8475	−0.0678	0.028*
C18	0.19518(11)	0.83334(8)	0.01023(4)	0.01709(17)
H18A	0.1132	0.8653	0.0136	0.021*
H18B	0.2607	0.8832	0.0167	0.021*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C19	0.11512(9)	0.81571(8)	0.12730(4)	0.01483(15)
H19	0.0432	0.7752	0.1145	0.018*
C20	0.08316(11)	0.92372(9)	0.11686(4)	0.02080(19)
H20A	0.1549	0.9651	0.1278	0.025*
H20B	0.0683	0.9332	0.0801	0.025*
C21	−0.03235(12)	0.95645(11)	0.14440(5)	0.0276(3)
H21A	−0.0492	1.0264	0.1371	0.033*
H21B	−0.1054	0.9180	0.1320	0.033*
C22	−0.01346(11)	0.94214(10)	0.20110(5)	0.0238(2)
H22A	−0.0906	0.9605	0.2180	0.029*
H22B	0.0545	0.9853	0.2141	0.029*
C23	0.01906(12)	0.83571(10)	0.21313(5)	0.0249(2)
H23A	−0.0542	0.7940	0.2046	0.030*
H23B	0.0382	0.8293	0.2498	0.030*
C24	0.13045(11)	0.79887(8)	0.18427(4)	0.01809(17)
H24A	0.1416	0.7279	0.1907	0.022*
H24B	0.2067	0.8328	0.1971	0.022*
C25	0.44877(9)	0.95792(7)	0.16540(4)	0.01409(15)
H25	0.4039	0.9567	0.1317	0.017*
C26	0.36608(10)	1.01802(8)	0.19989(5)	0.01922(18)
H26A	0.2868	0.9827	0.2044	0.023*
H26B	0.4086	1.0253	0.2334	0.023*
C27	0.33837(12)	1.11967(9)	0.17762(6)	0.0267(2)
H27A	0.2891	1.1126	0.1455	0.032*
H27B	0.2882	1.1577	0.2012	0.032*
C28	0.45894(13)	1.17459(9)	0.16809(6)	0.0289(3)
H28A	0.4389	1.2380	0.1516	0.035*
H28B	0.5033	1.1884	0.2007	0.035*
C29	0.54318(13)	1.11567(10)	0.13491(5)	0.0259(2)
H29A	0.6225	1.1513	0.1311	0.031*
H29B	0.5027	1.1078	0.1010	0.031*
C30	0.57017(10)	1.01465(8)	0.15781(4)	0.01818(17)
H30A	0.6159	1.0224	0.1907	0.022*
H30B	0.6236	0.9770	0.1352	0.022*
C31	0.51963(9)	0.83741(7)	0.23106(4)	0.01325(15)
H31	0.5051	0.8976	0.2514	0.016*
C32	0.66064(9)	0.81862(8)	0.23196(4)	0.01644(16)
H32A	0.6780	0.7625	0.2097	0.020*
H32B	0.7031	0.8769	0.2186	0.020*
C33	0.71334(10)	0.79679(10)	0.28522(5)	0.02072(19)
H33A	0.8031	0.7813	0.2838	0.025*
H33B	0.7048	0.8556	0.3066	0.025*
C34	0.64561(11)	0.71081(9)	0.30888(4)	0.02002(19)
H34A	0.6614	0.6503	0.2896	0.024*
H34B	0.6781	0.7009	0.3439	0.024*
C35	0.50579(11)	0.73036(10)	0.30892(4)	0.0213(2)
H35A	0.4898	0.7867	0.3312	0.026*
H35B	0.4631	0.6724	0.3225	0.026*
C36	0.45243(10)	0.75231(8)	0.25595(4)	0.01631(16)
H36A	0.3629	0.7685	0.2578	0.020*
H36B	0.4595	0.6930	0.2348	0.020*
C37	0.50835(10)	0.83298(8)	0.05218(4)	0.01800(17)
H37A	0.4786	0.7940	0.0227	0.022*
H37B	0.4737	0.8996	0.0472	0.022*
C38	0.64836(11)	0.84276(11)	0.04786(5)	0.0240(2)
H38A	0.6869	0.7777	0.0537	0.029*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H38B	0.6806	0.8870	0.0749	0.029*
C39	0.68963(13)	0.88184(13)	−0.00260(6)	0.0342(3)
H39A	0.6572	0.8383	−0.0299	0.041*
H39B	0.6530	0.9476	−0.0084	0.041*
C40	0.83016(14)	0.88879(14)	−0.00522(8)	0.0417(4)
H40A	0.8517	0.9132	−0.0385	0.063*
H40B	0.8670	0.8238	0.0003	0.063*
H40C	0.8625	0.9339	0.0209	0.063*

One of them is the recently published crystal structure of Di-*n*-butylbis(η^5 -pentamethyl-cyclopentadienyl)hafnium(IV) [5]. Di-*n*-butylbis(η^5 -cyclopentadienyl)hafnium(IV) ($Cp_2Hf(n-Bu)_2$) is known and used as a Hf(II) source at elevated temperatures (100 °C), analogues to the Negishi System $Cp_2ZrCl_2/n-BuLi$ which eliminates butane and 1-butene to give the free metallocene [8, 9]. Analogous to $Cp_2Hf(n-Bu)_2$ the complex *n*-BuHf(NCy_2)₃ is remarkably robust. There are no hints for a β -agostic interaction in the molecular structure. The angle Hf(1)-C(37)-C(38) is 124.84(8)° and thereby within the range for non-agostic compounds [10, 11]. The metal-carbon σ -bond Hf(1)-C(37) (2.2653(11) Å) is within the expected range for such a bond. The hafnium-nitrogen bonds are very similar (Hf(1)-N(1) 2.0497(8) Å, Hf(1)-N(2) 2.0450(8) Å, Hf(1)-N(3) 2.0451(8) Å). These bond lengths are shortened in comparison to a typical single bond due to attractive interactions between the nitrogen lone pair and the electron deficient metal center [12]. All nitrogen atoms are coordinated trigonal planar (sum of all angles: N1 359.8°, N2 359.9°, N3 359.9°).

References

- Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
- Bruker. SADABS, SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA 2007.
- Adler, C.; Frerichs, N.; Schmidtman, M.; Beckhaus, R.: Zwitterionic d^0 metal complexes $[(Cy_2N)_3M]^+[(\mu-Me)B(C_6F_5)_3]^-$ ($M = Ti, Zr, Hf$) derived from tris(dicyclohexylamido)methyl metal precursors. *Organometallics* **35** (2016) 3728–3733.
- Adler, C.; Tomaschun, G.; Schmidtman, M.; Beckhaus, R.: Remarkably robust mono-*n*-butyl group IV dicyclohexylamido complexes $\{(Cy)_2N\}_3M(n-butyl)$ (Cy : cyclohexyl [C_6H_{11}], M : Ti, Zr). *Organometallics* **33** (2014) 7011–7014.
- Arndt, P.; Schubert, K.; Burlakov, V. V.; Spannenberg, A.; Rosenthal, U.: Crystal structure of di-*n*-butylbis(η^5 -pentamethylcyclopentadienyl)-hafnium(IV). *Acta Crystallogr. E* **71** (2015) m19–m20.
- Amor, F.; Spaniol, T. P.; Okuda, J.: Remarkably robust group 4 metal half-sandwich complexes containing two higher alkyl ligands: X-ray structure and reactivity of the di-*n*-butyl complex $[Hf(\eta^5-\eta^1-C_5Me_4SiMe_2NCH_2CH_2OMe)nBu_2]$. *Organometallics* **16** (1997) 4765–4767.
- Miyazaki, T.; Tanabe, Y.; Yuki, M.; Miyake, Y.; Nishibayashi, Y.: Synthesis, structure, and reactivity of group VI metal complexes bearing group IV metallocenyldiphosphine moieties and a pentamethylcyclopentadienyl ligand. *Organometallics* **32** (2013) 2007–2013.
- Burlakov, V. V.; Beweries, T.; Bogdanov, V. S.; Arndt, P.; Baumann, W.; Petrovskii, P. V.; Spannenberg, A.; Lyssenko, K. A.; Shur, V. B.; Rosenthal, U.: Synthesis and isolation of di-*n*-butylhafnocene and its application as a versatile starting material for the synthesis of new hafnacycles. *Organometallics* **28** (2009) 2864–2870.
- Negishi, E.-I.; Takahashi, T.: Alkene and alkyne complexes of zirconocene. Their preparation, structure, and novel transformations. *Bull. Chem. Soc. Jpn.* **71** (1998) 755–769.
- Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K.; Schultz, A. J.; Williams, J. M.; Koetzle, T. F.: Evidence for carbon-hydrogen-titanium interactions: synthesis and crystal structures of the agostic alkyls $[TiCl_3(Me_2PCH_2CH_2PMe_2)R](R = Et \text{ or } Me)$. *Dalton Trans.* (1986) 1629–1637.
- Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E.: β -Agostic interactions in $(C_5H_4Me)_2Zr(CH_2CH_2R)(PMe_3)^+$ complexes. *J. Am. Chem. Soc.* **112** (1990) 1289–1291.
- Yu, X.; Bi, S.; Guzei, I. A.; Lin, Z.; Xue, Z.-L.: Zirconium, hafnium, and tantalum amide silyl complexes: their preparation and conversion to metallaheterocyclic complexes via γ -hydrogen abstraction by silyl ligands. *Inorg. Chem.* **43** (2004) 7111–7119.