

Bis(2-butyl-*N,N'*-diisopropyl- amidinato)dichlorohafnium(IV)

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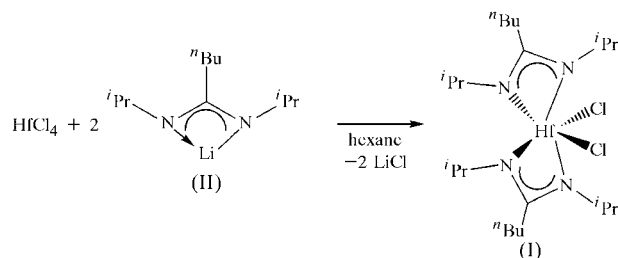
The title compound, [Hf(C₁₁H₂₃N₂)₂Cl₂], is a monomeric hafnium(IV) complex containing two bidentate amidinate ligands and two *cis* Cl atoms. The crystals are triclinic (space group *P* $\bar{1}$) and there is one independent six-coordinate monomer with a highly distorted octahedral geometry in the asymmetric unit. The reported structure is the first hafnium–amidinate complex to be characterized successfully by single-crystal X-ray diffraction.

Comment

Amidinate ligands are well established as versatile ligands for a variety of transition metal complexes and particularly for compounds of early transition metals. The possibility of modifying amidinate ligands at the C and N atoms by having various substituent groups provides a means of tuning the chemical reactivity and thermal properties of the resulting complex (Wedler *et al.*, 1990; Zhou & Richeson, 1996*a,b*; Walther, Fischer, Friedrich *et al.*, 1996; Coles *et al.*, 1997). The importance of these ligands lies mainly in the generation of element–nitrogen bonds, which could be useful for chemical vapor deposition (CVD) and for the synthesis of new catalysts.

Bidentate amidinate ligands offer the possibility of tuning the coordination sphere of a metal. By varying the organic substituents on the N atom as well as on the bridging C atom, it is possible to adjust the coordination of the ligand on the metal center, as has been shown in the case of germanium and silicon (Karsch *et al.*, 1998). However, the amidinate chemistry of group 4 elements has mostly been investigated for titanium and zirconium (Littke *et al.*, 1998; Wood *et al.*, 1999; Boyd *et al.*, 2002; Li *et al.*, 2003). A search of the May 2005 release of the Cambridge Structural Database (Allen, 2002) for structures containing the [RC(NR)₂]₂Hf fragment revealed no similar complex containing two amidinate ligands attached to a hafnium center. The objective of our work was to investigate the reactions leading to hafnium–amidinate derivatives,

because of their possible applications as CVD precursors or for catalysis. Our study concentrates on the structural stability and the coordination geometry around the Hf atom, which is very relevant for CVD precursor characteristics such as volatility and reactivity.



The reaction of two equivalents of the anionic amidinate compound [n-BuC(N^{*i*}Pr)₂]₂Li, (II), synthesized according to a modification of the procedure described by Hao *et al.* (1993), with one equivalent of HfCl₄ resulted in the formation of the six-coordinate title complex [n-BuC(N^{*i*}Pr)₂]₂HfCl₂, (I), which was obtained as a colorless crystalline solid. The crystallographic data for (I) are presented in Table 1. The molecular geometry of (I) revealed from the structural analysis is shown in Fig. 1, and selected bond distances and angles are summarized in Table 1. The metal center is in a pseudo-octahedral environment, surrounded by the four N atoms of the two amidinate ligands positioned *cis* to each other and two *cis* chloride ligands. A similar pseudo-octahedral orientation around a hafnium center has been reported (Wood *et al.*, 1999) for a guanidinate–Hf^{IV} complex of formula [(SiMe₃)₂NC(NCy)₂]₂HfCl₂. Although the structures show similar ligand orientation, some structural differences concerning the substituents attached to the chelating ligand are evident. Furthermore, the perpendicular orientation of the N(SiMe₃)₂ function relative to the MNCN plane in the guanidinate complex eliminates the π conjugation, which explains the observed similarity to the amidinate complex reported in our

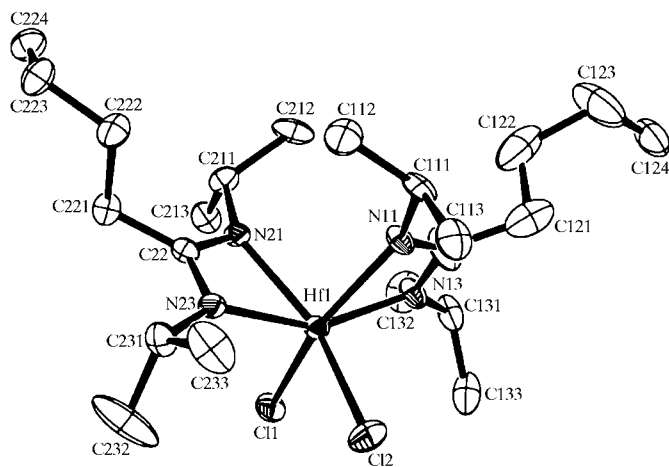


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted.

study. The geometry of the monomeric octahedral complex (I) could be described according to the two planes Cl1/N11/N23/Hf1 and Cl2/N13/N21/Hf1, each containing ML_3 atoms. The average deviation of the atoms from the corresponding planes is in the region of 0.06 Å. In the case of an ideal octahedral geometry, the bond angles within each of the two planes should be 90, 90 and 180°. The bond angles for (I) (Cl1—Hf1—N23, N23—Hf1—N11 and N11—Hf1—Cl1 for plane 1, and Cl2—Hf1—N21, N21—Hf1—N13 and N13—Hf1—Cl2 for plane 2; Table 1) deviate significantly from ideal octahedral values. The deviation is especially remarkable for the Cl1—Hf1—N11 [152.84 (10)°] and Cl2—Hf1—N21 [154.01 (10)°] angles, as the differences are about 26–28°, comparable to those reported for the hafnium–guanidinate complex (29–31°; Wood *et al.*, 1999). Because of the presence of the four bulky isopropyl groups in the girdle, an ideal symmetric arrangement around the metal is impossible and large distortions from ideal geometry are required to minimize the repulsions between the isopropyl groups.

Both amidinate ligands show a bidentate coordination. Their bonding parameters are the same, with bite angles of 60.61 (14) and 60.68 (13)°, and are in a good agreement with those reported for similar zirconium (59.2 and 60.3°), hafnium (59.9 and 60.1°) and tantalum (59.3 and 61.9°) complexes (Littke *et al.*, 1998; Wood *et al.*, 1999; Drew & Wilkins, 1975). Considering the bonding properties of the amidinate ligands in the zirconium complex dichlorobis(2-methyl-*N,N'*-dicyclohexylamidinato)zirconium(IV), one can see that the two *cis* Zr—N bond lengths [2.186 (8) and 2.192 (7) Å] are slightly shorter than the *trans* Zr—N values [2.228 (7) and 2.234 (8) Å]. A possible reason for such behavior could be the *trans* effect of the two chlorine ligands, which have π -donating properties. In contrast, the Hf—N bond lengths in (I) and those reported by Wood *et al.* (1999) for the hafnium–guanidinate complex cannot be divided into two groups, because of their similarity at the 2σ level. Additionally there are no significant differences between the N^iPr groups *cis* to the Cl co-ligands (atoms N11 and N21) and the N^iPr groups *trans* to the Cl co-ligands (atoms N13 and N23), for example, in terms of N—C bond lengths. These observations are consistent with the configuration of the hafnium–guanidinate complex but in disagreement with the results published for several analogous zirconium complexes (Littke *et al.*, 1998; Wood *et al.*, 1999; Herskovics-Korine & Eisen, 1995; Walther, Fischer, Friedrich *et al.*, 1996; Walther, Fischer, Görls *et al.*, 1996), in which there are marked differences in N—C and Zr—N bond lengths.

To summarize, the present structure demonstrates the versatility of the amidinate ligand, in that varying the substituents on the N atom as well as on the bridging C atoms can be used effectively to tune the electronic properties of the ligand around the metal center.

Experimental

A stirred suspension of $HfCl_4$ (2.56 g, 8 mmol) in hexane (50 ml) was cooled to 195 K. To this suspension, a solution of [$^nBuC(N^iPr)_2$] Li (16 mmol) was added dropwise over a period of approximately 1 h

and the reaction mixture was allowed to warm to room temperature. After refluxing for an additional 2 h, the resulting clear pale-yellow solution was concentrated and stored at 253 K overnight to afford clear colorless crystals [yield 4.26 g, 87% based on $HfCl_4$; m.p. 366 K (uncorrected)].

Crystal data

[$Hf(C_{11}H_{23}N_2)_2Cl_2$]
 $M_r = 616.02$
 Triclinic, $P\bar{1}$
 $a = 8.4969$ (7) Å
 $b = 12.6309$ (9) Å
 $c = 13.5716$ (9) Å
 $\alpha = 76.537$ (6)°
 $\beta = 76.106$ (7)°
 $\gamma = 82.191$ (6)°
 $V = 1370.14$ (17) Å³

$Z = 2$
 $D_x = 1.493$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 9828 reflections
 $\theta = 2.8$ – 27.5 °
 $\mu = 4.02$ mm⁻¹
 $T = 105$ (2) K
 Prism, colorless
 $0.38 \times 0.23 \times 0.13$ mm

Data collection

Oxford Diffraction Sapphire2 CCD diffractometer
 ω scans
 Absorption correction: multi-scan (Blessing, 1995)
 $T_{min} = 0.335$, $T_{max} = 0.588$
 25779 measured reflections

6267 independent reflections
 5602 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.063$
 $\theta_{max} = 27.6$ °
 $h = -11 \rightarrow 11$
 $k = -16 \rightarrow 16$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.090$
 $S = 1.02$
 6267 reflections
 272 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 5.2988P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.002$
 $\Delta\rho_{max} = 3.44$ e Å⁻³
 $\Delta\rho_{min} = -2.15$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Hf1—N13	2.175 (4)	Hf1—Cl2	2.4121 (12)
Hf1—N11	2.186 (4)	N11—C111	1.460 (5)
Hf1—N23	2.187 (4)	N13—C131	1.465 (6)
Hf1—N21	2.191 (3)	N21—C211	1.456 (5)
Hf1—Cl1	2.4116 (11)	N23—C231	1.462 (6)
N13—Hf1—N11	60.61 (14)	N11—Hf1—Cl1	152.84 (10)
N13—Hf1—N23	154.36 (14)	N23—Hf1—Cl1	104.43 (10)
N11—Hf1—N23	100.53 (14)	N13—Hf1—Cl2	104.40 (12)
N13—Hf1—N21	99.74 (14)	N21—Hf1—Cl2	154.01 (10)
N11—Hf1—N21	89.77 (14)	Cl1—Hf1—Cl2	95.31 (4)
N23—Hf1—N21	60.68 (13)		

H atoms were treated using a riding model (C—H = 0.98–1.00 Å), with isotropic displacement parameters fixed at 120% (150% for methyl groups) of the U_{eq} values of the parent C atoms. Owing to the higher degree of freedom for the vibrational modes of the CH_3 moieties belonging to the isopropyl groups, the displacement ellipsoids are larger and more anisotropic than those of the other C atoms. The maximum residual electron density is located within about 1 Å of the Hf center.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2000); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2000); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Bruker, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1201). Services for accessing these data are described at the back of the journal.

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