Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis[*N*,*N*′-bis(trimethylsilyl)benzamidinato]-diethylhafnium(IV)

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Received 7 February 2006
Accepted 16 February 2006
Online 22 February 2006

Key indicators

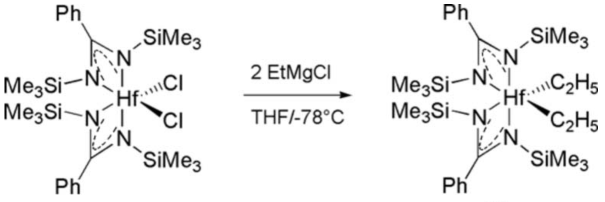
Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.013 Å
R factor = 0.041
wR factor = 0.110
Data-to-parameter ratio = 19.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $[\mathrm{Hf(C_2H_5)_2(C_{13}H_{23}N_2Si_2)_2}]$, the Hf atom is coordinated by two ethyl groups and two bis(trimethylsilyl)benzamidinate (siam) ligands binding in a bidentate coordination mode *via* their N-donor atoms. The coordination around hafnium is best described as slightly distorted tetrahedral if the siam ligands are represented by their centroids.

Comment

The zirconium-catalyzed carbomagnesation of olefins by EtMgCl has become a well established method for the synthesis of special Grignard reagents such as chiral compounds or cyclic di-Grignard compounds from α,ω-dienes (Dzhemilev *et al.*, 1983; Morken *et al.*, 1993; Knight *et al.*, 1994). If bis(cyclopentadienyl)–zirconium compounds are used as the catalytically active species, the reaction is believed to proceed *via* the initial formation of $\mathrm{Cp_2ZrEt_2}$, which, owing to the elimination of ethane, produces a complex $\mathrm{Cp_2Zr(\eta^2\text{-}C_2H_4)}$. The side-on coordinated ethylene ligand is then coupled with another alkene to produce a zirconacyclopentane derivative, which is attacked by EtMgX to yield the catalyst $\mathrm{Cp_2Zr(\eta^2\text{-}C_2H_4)}$, as well as the new Grignard reagent with an ethyl group and the MgX group attached to the former double bond (Negishi & Kondakov, 1996).



(I)

Benzamidinate ligands have frequently been used as substitutes for cyclopentadienyl ligands in order to achieve variations of reactions catalyzed by $\mathrm{Cp_2Zr}$-based compounds (for recent examples *cf.* Ray *et al.*, 2003; Volkis *et al.*, 2003; Averbuj & Eisen, 1999; Herskovics-Korine & Eisen, 1995; Flores *et al.*, 1995). In the course of these investigations a number of the above-mentioned intermediates of the catalytic cycle have been isolated and characterized (Hagadorn & Arnold, 1997; Walther *et al.*, 1996). Nevertheless, to the best of our knowledge, the title compound is still the only structurally characterized $(\mathrm{siam})_2MR_2$ [siam is bis(trimethylsilyl)benzamidinate, and M = Ti, Zr and Hf] derivative that exhibits β-H atoms in two distinct metal-bound alkyl substituents. The only other complex that comes close to this binding mode is a

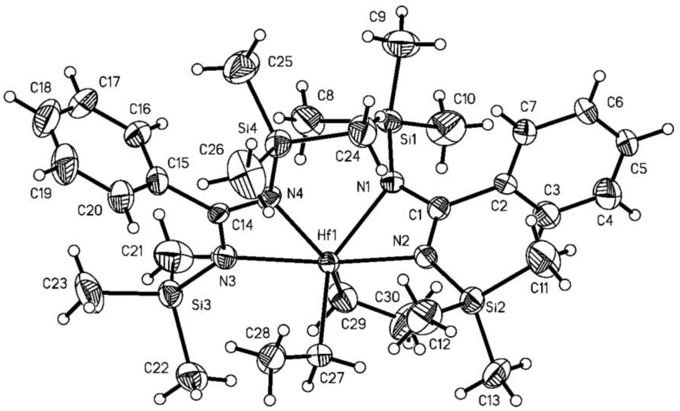


Figure 1
Molecular structure of the title compound, with displacement parameters drawn at the 40% probability level.

zirconacyclopentane compound that possesses β-H atoms, although β-hydride elimination is hampered by the cyclic nature of the ligand (Hagadorn & Arnold, 1997). All the other structurally characterized derivatives show benzyl (Bazinet *et al.*, 2003; Munslow *et al.*, 2004; Hagadorn, 2001; Duncan *et al.*, 2001; Walther *et al.*, 1996; Coles & Hitchcock, 2003; Ong *et al.*, 2003; Westmoreland *et al.*, 2004) or methyl (Hagadorn & Arnold, 1997; Littke *et al.*, 1998) groups attached to the group 4 metal.

The synthesis of the title compound is realized by the treatment of $(\text{siam})_2\text{HfCl}_2$ with two equivalents of EtMgCl in tetrahydrofuran at low temperatures (see scheme). Recrystallization of the title compound from *n*-hexane at 243 K yielded single crystals suitable for X-ray crystallography, which had to be handled at temperatures below 253 K throughout the preparation of the crystal and the collection of intensity data in order to prevent the loss of solvent from the crystalline material. If the two components are reacted in a 1:1 ratio only one of the chloride ligands is substituted and $(\text{siam})_2\text{HfCl}(\text{C}_2\text{H}_5)$ is obtained as the sole reaction product. Both the mono- and the diethyl compound are stable in solution at room temperature, demonstrating that β-hydride elimination is not a suitable reaction pathway for these hafnium species, in contrast to the comparable Zr compounds (Negishi & Kondakov, 1996).

Fig. 1 shows the molecular structure of $(\text{siam})_2\text{Hf}(\text{C}_2\text{H}_5)_2$. The Hf atom is tetrahedrally surrounded by the two siam ligands and the two ethyl groups (Table 1). The Hf—N bond lengths all lie in the range 2.255 (6)–2.279 (6) Å. The C—N bond lengths in the delocalized amidinate units (N1, C1, N2 and N3, C14, N4) have values of between 1.316 (9) and 1.334 (9) Å and are therefore virtually identical. The C1—C2 and C14—C15 bonds of the central C atoms of the benzamidinate ligands with the *ipso* C atom of the phenyl substituents are 1.531 (10) and 1.505 (10) Å, respectively. Although these values are quite high for a bond between two sp^2-hybridized C atoms, bond lengths of more than 1.5 Å are normal for benzamidinate ligands owing to the binding of the central C atom to the negatively charged N atoms (Hagadorn & Arnold, 1997; Walther *et al.*, 1996). The Hf—C bond lengths of the ethyl substituents show values of 2.244 (7) (C27—Hf) and 2.261 (8) Å (C29—Hf). Despite the bulky trimethylsilyl substituents of the siam ligands the ethyl groups adopt a conformation leading to a C28—C27—C29—C30 torsion angle of 179.6 (7)°. The crystal structure of the title compound still exhibits large solvent-accessible voids and quite high electron density peaks situated in those voids. The heights of these peaks correspond to C atoms with site occupation factors far below 1. Since there are no bond lengths and angles that make any chemical sense it was unfortunately not possible to assign atom types to the electron density peaks. Corresponding to the experimentally observed fact that the crystalline material suffers loss of hexane if the temperature rises to 253 K, the electron density in the voids might be interpreted as very diffuse and extremely weakly bound solvent molecules, which are not included in the structural model.

Experimental

To a stirred suspension of $(\text{siam})_2\text{HfCl}_2$ (3.8 g, 4.90 mmol) in diethyl ether (50 ml) a 2 *M* solution of EtMgCl (5.0 ml) in diethyl ether (10.0 mmol) was added dropwise at 223 K. After the addition of the Grignard reagent was complete, the solution was allowed to reach room temperature, leading to the precipitation of MgCl_2, which was completed by adding dioxane (1.3 ml). After filtration and washing of the filtration residue with diethyl ether (100 ml) the combined solutions were dried *in vacuo*. The solid residue was recrystallized from *n*-hexane at 243 K yielding colorless crystalline material (yield 1.77 g, 47.3%). ^{1}H NMR (298 K, C_6D_6, p.p.m.): 0.12 (*s*, 36H, SiMe$_3$), 1.07 (*q*, $^3J_{\text{HH}}$ = 8.0 Hz, 4H, CH$_2$), 2.12 (*t*, $^3J_{\text{HH}}$ = 8.0 Hz, 6H, CH$_3$), 6.94–7.29 (*m*, 10H, Ph); ^{13}C NMR (298 K, C_6D_6, p.p.m.): 2.2 (SiMe$_3$), 15.2 (CH$_3$), 66.1 (CH$_2$), 126.3, 128.3, 128.9, 141.7 (Ph), 184.8 (CN$_2$). Elemental analysis calculated for $\text{C}_{30}\text{H}_{56}\text{HfN}_4\text{Si}_4$: C 47.18, H 7.39, N 7.34%; found: C 46.97, H 7.32, N 7.22%.

Crystal data

$[\text{Hf}(\text{C}_2\text{H}_5)_2(\text{C}_{13}\text{H}_{23}\text{N}_2\text{Si}_2)_2]$
M_r = 763.64
Monoclinic, $P2_1/n$
a = 12.205 (2) Å
b = 20.790 (4) Å
c = 17.234 (3) Å
β = 101.00 (3)°
V = 4292.6 (13) Å^3
Z = 4

D_x = 1.182 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 18.5–20.1°
μ = 2.54 mm^{-1}
T = 183 (2) K
Cuboid, colorless
0.12 × 0.08 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.747, $T_{\max}$ = 0.813
7584 measured reflections
7229 independent reflections
5285 reflections with $I > 2\sigma(I)$

R_{int} = 0.039
$\theta_{\max}$ = 24.6°
$h = -14 \rightarrow 0$
$k = 0 \rightarrow 24$
$l = -19 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity decay: 2.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.110
S = 1.21
7229 reflections
366 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 17.7042P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.95 e Å^{-3}
$\Delta\rho_{\min}$ = −0.78 e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Hf1—C27	2.244 (7)	N1—C1	1.320 (9)
Hf1—C29	2.261 (8)	C1—N2	1.331 (9)
Hf1—N1	2.255 (6)	C1—C2	1.531 (10)
Hf1—N4	2.256 (5)	N3—C14	1.316 (9)
Hf1—N3	2.258 (6)	C14—N4	1.334 (9)
Hf1—N2	2.279 (6)	C14—C15	1.505 (10)
Hf1—C1	2.634 (7)	C27—C28	1.544 (11)
Hf1—C14	2.646 (7)	C29—C30	1.509 (12)
C27—Hf1—C29	98.1 (3)	C29—Hf1—C14	116.2 (3)
C27—Hf1—C1	116.6 (3)	C1—Hf1—C14	127.7 (2)
C29—Hf1—C1	94.7 (3)	C28—C27—Hf1	115.7 (5)
C27—Hf1—C14	100.5 (2)	C30—C29—Hf1	113.1 (6)

All H atoms were placed in idealized positions (C—H = 0.93–0.97 Å). The isotropic displacement parameters were set at 1.2 (CH_2, CH_{ar}) or 1.5 (CH_3) times the U_{eq} value of the corresponding parent atom.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *MolEN* (Enraf–Nonius, 1990); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

The authors greatfully acknowledge financial support by the Federal Ministry of Education and Research (BMBF).

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