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*Acta Cryst.* (1996). **C52**, 1348–1350

# Tetrakis(diphenylamido-*N*)hafnium

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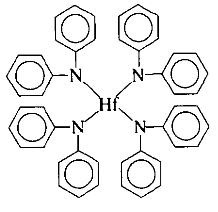
(*Received 6 November 1995; accepted 22 January 1996*)

## Abstract

The hafnium coordination in the monomeric title molecule, [Hf($C_{12}H_{10}N$)$_4$], is distorted tetrahedral, with Hf—N distances between 2.047 (4) and 2.085 (3) Å, and angles between 101.63 (14) and 121.33 (14)°. One molecule forms the asymmetric unit.

## Comment

Since the structure of tetrakis(diethylamido)uranium(IV) was reported (Jones, Karmas, Martin & Gilman, 1956), the syntheses and spectroscopic properties of numerous homoleptic dialkylamido complexes have been reported (Bradley & Gitlitz, 1969). Relatively few crystal structures of this type of compound have been reported however. The structure of the monomeric homoleptic complex tetrakis(diphenylamido)niobium(IV) has been reported recently (Bott, Hoffman & Rangarajan, 1995) and the present hafnium complex seems to have a similar structure. Corresponding dialkylamido complexes having less bulky alkyl groups have a tendency to dimerize, as can be seen in the compound tetrakis(dimethylamido)zirconium (Chisholm, Hammond & Huffman, 1988). So far, no crystal structures of hafnium dialkylamides have been reported. The only hafnium complexes related to the title compound, (I), are bis(trimethylsilylamido) complexes, which have a similar N—Hf bonding pattern (Airoldi *et al.*, 1980).



(I)

The tetrahedral coordination of the title complex is distorted (Fig. 1). The N—Hf1—N angles vary between 101.63 (14) and 121.33 (14)°, whereas the Hf—N bond distances show only slight variations, from 2.047 (4) to 2.085 (3) Å (Table 2). This is in agreement with the geometry of chlorotris[bis(trimethylsilyl)amido]hafnium, for which Hf—N bond lengths of 2.040 (10) Å have been reported (Airoldi *et al.*, 1980). The positions of the amido N atoms deviate only slightly from their respective Hf–$C_\alpha$–$C_\alpha$ planes, the largest deviation being 0.124 (4) Å for N3 from the Hf1–C25–C31 plane.

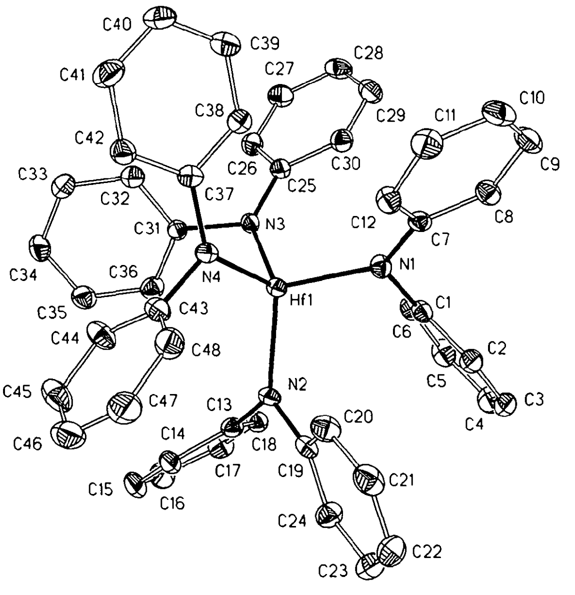


Fig. 1. View of the title molecule with 30% probability displacement ellipsoids. The H atoms have been omitted for clarity.

## Experimental

The title complex was prepared by refluxing the lithium salt of the ligand precursor and hafnium(IV) chloride in toluene for 3 h. The lithium salt of the ligand precursor was prepared in tetrahydrofuran with butyl lithium as described in the literature (Jones, Karmas, Martin & Gilman, 1956).

The reaction mixture was filtered to remove precipitated LiCl. A few drops of *n*-pentane were added to the filtrate, which was cooled to 273 K. Colorless prismatic crystals suitable for single-crystal measurements were obtained after 24 h. All reaction steps were carried out under an argon atmosphere using standard Schlenk techniques. The crystal used for the X-ray measurements was mounted on a glass fiber using the oil-drop method (Kottke & Stalke, 1993) and data were collected at 193 K.

### *Crystal data*

$[Hf(C_{12}H_{10}N)_4]$
$M_r = 851.33$
Triclinic
$P\bar{1}$
$a = 9.781\,(2)$ Å
$b = 10.597\,(2)$ Å
$c = 20.216\,(4)$ Å
$\alpha = 101.49\,(3)^\circ$
$\beta = 93.85\,(3)^\circ$
$\gamma = 109.53\,(3)^\circ$
$V = 1914.8\,(7)$ Å$^3$
$Z = 2$
$D_x = 1.477$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 5\text{–}20^\circ$
$\mu = 2.763$ mm$^{-1}$
$T = 193\,(2)$ K
Prismatic
0.45 × 0.40 × 0.40 mm
Colorless

### *Data collection*

Rigaku AFC-7*S* diffractometer
$\omega\text{–}2\theta$ scans
Absorption correction: $\psi$ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.644$, $T_{\max} = 1.000$
6606 measured reflections
6606 independent reflections

6362 observed reflections $[I > 2\sigma(I)]$
$\theta_{\max} = 24.99^\circ$
$h = -11 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = -24 \rightarrow 23$
3 standard reflections monitored every 200 reflections
intensity decay: 2.2%

### *Refinement*

Refinement on $F^2$
$R(F) = 0.0305$
$wR(F^2) = 0.0757$
$S = 1.038$
6606 reflections
639 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + 3.7344P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.092$
$\Delta\rho_{\max} = 1.517$ e Å$^{-3}$
$\Delta\rho_{\min} = -1.286$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Hf1 | 0.83215 (2) | 0.23068 (2) | 0.239672 (8) | 0.02485 (8) |
| N1 | 0.8747 (4) | 0.3222 (4) | 0.1594 (2) | 0.0294 (8) |
| N2 | 0.9800 (4) | 0.3652 (4) | 0.3239 (2) | 0.0279 (7) |
| N3 | 0.8176 (4) | 0.0281 (3) | 0.2089 (2) | 0.0264 (7) |
| N4 | 0.6211 (4) | 0.2076 (4) | 0.2581 (2) | 0.0297 (8) |
| C1 | 1.0319 (5) | 0.3794 (4) | 0.1641 (2) | 0.0291 (9) |
| C2 | 1.1034 (5) | 0.5202 (5) | 0.1702 (2) | 0.0361 (10) |
| C3 | 1.2541 (5) | 0.5747 (6) | 0.1787 (3) | 0.0421 (12) |
| C4 | 1.3371 (5) | 0.4926 (6) | 0.1835 (3) | 0.0468 (13) |
| C5 | 1.2669 (5) | 0.3533 (6) | 0.1773 (3) | 0.0432 (12) |
| C6 | 1.1142 (5) | 0.2960 (5) | 0.1671 (2) | 0.0334 (10) |
| C7 | 0.7913 (5) | 0.3472 (4) | 0.1066 (2) | 0.0283 (9) |
| C8 | 0.8397 (5) | 0.3542 (5) | 0.0441 (2) | 0.0352 (10) |
| C9 | 0.7538 (6) | 0.3682 (5) | −0.0095 (2) | 0.0441 (12) |
| C10 | 0.6166 (6) | 0.3742 (5) | −0.0011 (3) | 0.0455 (12) |
| C11 | 0.5681 (6) | 0.3694 (5) | 0.0610 (3) | 0.0436 (12) |
| C12 | 0.6554 (5) | 0.3583 (5) | 0.1151 (2) | 0.0357 (10) |
| C13 | 1.0542 (5) | 0.3232 (4) | 0.3741 (2) | 0.0299 (9) |
| C14 | 1.0129 (5) | 0.3295 (5) | 0.4393 (2) | 0.0365 (10) |
| C15 | 1.0773 (6) | 0.2790 (6) | 0.4858 (3) | 0.0459 (12) |
| C16 | 1.1835 (6) | 0.2246 (6) | 0.4687 (3) | 0.0472 (13) |
| C17 | 1.2295 (6) | 0.2240 (5) | 0.4060 (3) | 0.0421 (12) |
| C18 | 1.1654 (5) | 0.2729 (5) | 0.3581 (2) | 0.0327 (10) |
| C19 | 1.0197 (5) | 0.5095 (5) | 0.3332 (2) | 0.0309 (9) |
| C20 | 0.9220 (6) | 0.5633 (5) | 0.3057 (3) | 0.0399 (11) |
| C21 | 0.9595 (7) | 0.7031 (6) | 0.3122 (3) | 0.0468 (13) |
| C22 | 1.0941 (7) | 0.7934 (6) | 0.3463 (3) | 0.0554 (15) |
| C23 | 1.1913 (7) | 0.7440 (6) | 0.3741 (3) | 0.0519 (14) |
| C24 | 1.1549 (5) | 0.6033 (5) | 0.3680 (3) | 0.0412 (11) |
| C25 | 0.8195 (4) | −0.0619 (4) | 0.1464 (2) | 0.0290 (9) |
| C26 | 0.8225 (5) | −0.1928 (5) | 0.1445 (3) | 0.0365 (10) |
| C27 | 0.8253 (5) | −0.2785 (5) | 0.0838 (3) | 0.0398 (11) |
| C28 | 0.8287 (5) | −0.2358 (5) | 0.0238 (3) | 0.0421 (12) |
| C29 | 0.8281 (5) | −0.1041 (6) | 0.0252 (3) | 0.0414 (11) |
| C30 | 0.8223 (5) | −0.0196 (5) | 0.0853 (2) | 0.0347 (10) |
| C31 | 0.7576 (5) | −0.0385 (4) | 0.2624 (2) | 0.0285 (9) |
| C32 | 0.6123 (5) | −0.1280 (5) | 0.2524 (3) | 0.0401 (11) |
| C33 | 0.5534 (6) | −0.1826 (6) | 0.3053 (3) | 0.0460 (12) |
| C34 | 0.6386 (6) | −0.1450 (5) | 0.3690 (3) | 0.0444 (12) |
| C35 | 0.7817 (6) | −0.0591 (5) | 0.3786 (3) | 0.0422 (11) |
| C36 | 0.8420 (5) | −0.0066 (5) | 0.3248 (2) | 0.0358 (10) |
| C37 | 0.4890 (5) | 0.1145 (4) | 0.2154 (2) | 0.0309 (9) |
| C38 | 0.4932 (5) | 0.0605 (5) | 0.1477 (2) | 0.0369 (10) |
| C39 | 0.3676 (6) | −0.0304 (5) | 0.1052 (3) | 0.0464 (12) |
| C40 | 0.2342 (6) | −0.0680 (6) | 0.1296 (3) | 0.0502 (13) |
| C41 | 0.2307 (6) | −0.0162 (6) | 0.1965 (3) | 0.0503 (13) |
| C42 | 0.3547 (5) | 0.0728 (5) | 0.2394 (3) | 0.0382 (11) |
| C43 | 0.6073 (5) | 0.2737 (5) | 0.3254 (2) | 0.0350 (10) |
| C44 | 0.6290 (5) | 0.2192 (6) | 0.3800 (2) | 0.0429 (12) |
| C45 | 0.6292 (6) | 0.2893 (8) | 0.4459 (3) | 0.057 (2) |
| C46 | 0.6108 (6) | 0.4140 (7) | 0.4571 (3) | 0.059 (2) |
| C47 | 0.5836 (7) | 0.4651 (6) | 0.4028 (3) | 0.060 (2) |
| C48 | 0.5799 (6) | 0.3952 (5) | 0.3370 (3) | 0.0471 (12) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Hf1—N1 | 2.047 (4) | N2—C19 | 1.415 (6) |
| Hf1—N3 | 2.066 (3) | N2—C13 | 1.432 (5) |
| Hf1—N4 | 2.065 (4) | N3—C25 | 1.428 (5) |
| Hf1—N2 | 2.085 (3) | N3—C31 | 1.459 (5) |
| N1—C7 | 1.421 (5) | N4—C37 | 1.430 (5) |
| N1—C1 | 1.441 (5) | N4—C43 | 1.438 (6) |
| N1—Hf1—N3 | 108.73 (14) | C19—N2—C13 | 114.8 (3) |
| N1—Hf1—N4 | 109.07 (14) | C19—N2—Hf1 | 120.6 (3) |
| N3—Hf1—N4 | 101.63 (14) | C13—N2—Hf1 | 124.5 (3) |
| N1—Hf1—N2 | 106.36 (14) | C25—N3—C31 | 115.9 (3) |
| N3—Hf1—N2 | 121.33 (14) | C25—N3—Hf1 | 136.2 (3) |
| N4—Hf1—N2 | 109.30 (14) | C31—N3—Hf1 | 106.0 (2) |
| C7—N1—C1 | 116.9 (3) | C37—N4—C43 | 117.0 (3) |
| C7—N1—Hf1 | 136.6 (3) | C37—N4—Hf1 | 126.2 (3) |
| C1—N1—Hf1 | 106.4 (3) | C43—N4—Hf1 | 115.8 (3) |

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1336). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1996). C**52**, 1350–1352

# $[Li_2(\mu_3\text{-}^t Bu_2P)(\mu_2\text{-}^t Bu_2P)(thf)]_2$: a Redetermination

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(*Received 20 September 1995; accepted 19 December 1995*)

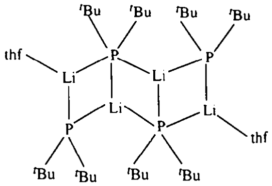
## Abstract

The crystal structure of the title compound as its *n*-hexane solvate, bis($\mu_3$-di-*tert*-butylphosphino)-1:2:3$\kappa^3P$;2:3:4$\kappa^3P$-bis($\mu_2$-di-*tert*-butylphosphino)-1:2$\kappa^2P$;3:4$\kappa^2P$-bis(tetrahydrofuran)-1$\kappa O$;4$\kappa O$-tetralithium, $[Li_4(C_8H_{18}P)_4(C_4H_8O)_2].C_6H_{14}$, has been redetermined to improved precision using diffractometer data collected at 213 K, resulting in more accurate bond distances and angles with reduced standard deviations. Furthermore, the relatively high *R* values ($R = 0.10$, $wR = 0.13$) of the previous structure determination at room temperature [Jones, Stuart & Wright (1983). *J. Am. Chem. Soc.* **105**, 7459–7460] were caused by the omission of the molecule of solvent *n*-hexane, which was not localized; the inclusion of this solvent molecule reduced the *R* value to 0.0552.

## Comment

Lithium diorganophosphides are useful transfer agents for $-PR_2$ groups. In contrast to the corresponding amido derivatives of the alkaline metals, relatively little information has been published on the related diorganophosphides (Hey, Hitchcock, Lappert & Rai, 1987). These synthetically important reagents are also of interest with respect to their solid-state structures (Bartlett, Olmstead & Power, 1986).

We have recently reported the synthesis and X-ray crystal structure determination of two formally four-coordinate lanthanide phosphido species, trivalent $(^tBu_2P)_2La[(\mu\text{-}P^tBu_2)_2Li(thf)]$ and divalent $Yb[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$ (Rabe, Riede & Schier, 1996). In our attempted synthesis of the lanthanum complex, we isolated the title compound, (I), as its *n*-hexane solvate.



(I)

The single-crystal X-ray structure determination of the title compound at room temperature has been published previously (Jones, Stuart & Wright, 1983). However, the presence of an *n*-hexane molecule in the unit cell was not reported although *n*-hexane was used for crystallization. Relatively high *R* and *wR* values of 0.0982 and 0.1312 were found. These, according to the authors, were the result of substantial thermal motion, especially of the coordinated thf molecules. Furthermore, a strikingly low calculated density of 0.842 g cm$^{-3}$ was determined for the title complex. These two points lead us to believe that both samples are identical. The authors were planning to collect a low-temperature data set in order to resolve this. However, to the best of our knowledge, this low-temperature determination has not yet been reported.

Whereas the relatively high $U_{eq}$ values of the thf C atoms in our data set are the result of slight disorder of this ligand, the values for the hexane C atoms (C5–C7) in the same range (Table 1) might be indicative of site-occupancy factors of less than 1 for the solvent molecule. This would be in accordance with our findings and the observation of Jones, Stuart & Wright (1983) that the crystals were found to rapidly crumble to a white powder in the absence of either hexane or tetrahydrofuran vapour at room temperature. Thus, it is very likely that the solvent molecule, which shows substantial