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DIALKYLBIS[BIS(TRIMETHYLSILYL)AMIDO]HAFNIUM(IV); UNSYMMETRICAL DIALKYL AND ALKYLOXIDE DERIVATIVES

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Summary

The unsymmetrical dialkylbis[bis(trimethylsilyl)amido]hafnium compounds of the type $RR'Hf[N(SiMe_3)_2]_2$ where R is Me_3CCH_2 or Me_3SiCH_2 and R′ is Me or Et have been prepared. The alkyl-alkoxo compounds where R is Me_3SiO and R′ is Me or Et are also described.

Symmetrical dialkylbis[bis(trimethylsilyl)]hafnium compounds, $R_2Hf[N(SiMe_3)_2]_2$, where R is Me, Et, or Me_3SiCH_2, have recently been described [1]. The methyl-hafnium and zirconiumtris[bis(trimethylsilyl)amides, have also been prepared [2]. In this paper we describe the synthesis of related unsymmetrical dialkyls of the type $RR'Hf[N(SiMe_3)_2]_2$.

Dichlorobis[bis(trimethylsilyl)amido]hafnium reacts with either one-half or one molar equivalent of dimethyl- or diethyl-magnesium in pentane or diethyl ether to give the previously described $Me_2Hf[N(SiMe_3)_2]_2$ or $Et_2Hf[N(SiMe_3)_2]_2$ as the only isolable products. In contrast, one-half molar equivalent of the sterically larger dialkylmagnesium reagents, $(Me_3CCH_2)_2Mg$ or $(Me_3SiCH_2)_2Mg$, react with $Cl_2Hf[N(SiMe_3)_2]_2$ yielding the monoalkyl-monochloro derivatives $(Me_3CCH_2)(Cl)Hf[N(SiMe_3)_2]_2$ or $(Me_3SiCH_2)(Cl)Hf[N(SiMe_3)_2]_2$, respectively. Analytical and physical properties of the new compounds are shown in Tables 1 and 2. The observation that both chloride ligands can be replaced by the smaller alkyl groups whereas only one chloride ligand can be replaced by the larger alkyl groups is most reasonably ascribed to steric effects upon the rate of substitution. The rate of substitution of both chloride ligands by the methyl or ethyl groups is similar. However, with the trimethylsilyl or neopentyl groups the rates are sufficiently different to allow isolation of the monoalkyl-monochloro derivatives.

We have been unable to prepare $(Me_3CCH_2)_2Hf[N(SiMe_3)_2]_2$, the monochloro derivative, $(Me_3CCH_2)(Cl)Hf[N(SiMe_3)_2]_2$, being the only isolable product. In contrast, the $(Me_3SiCH_2)_2Hf[N(SiMe_3)_2]_2$ is readily prepared [1]. This

TABLE 1

ANALYTICAL AND SPECTROSCOPIC PROPERTIES OF $RR^1Hf[N(SiMe_3)_2]_2$

Compound		M.p. (°C)	Analysis [a] Found (calc.) (%)				Infrared [b] (cm^{-1})(Nujol mulls)		
R	R^1		C	H	N	Cl	Hf—N	Hf—Cl	HfOSi
Me_3CCH_2	Cl	52—54	32.9 (33.7)	7.69 (7.77)	4.58 (4.63)	5.73 (5.87)	403,390	347	
Me_3SiCH_2	Cl	liquid	31.1 (30.9)	7.61 (7.57)	4.41 (4.51)	5.60 (5.72)	410,385	355	
Me_3SiO	Cl	82—86	28.4 (28.9)	7.17 (7.22)	4.33 (4.49)	5.51 (5.70)	415,383	350	967
Me_3CCH_2	Me	59—61	36.8 (37.0)	8.60 (8.55)	4.93 (4.79)		405,385		
Me_3SiCH_2	Me	liquid	33.3 (33.0)	8.26 (8.26)	4.59 (4.59)		380,365		
Me_3SiO	Me	98—102	31.1 (31.9)	7.90 (7.97)	4.57 (4.65)				972
Me_3CCH_2	Et	66—67	37.7 (38.1)	8.59 (8.68)	4.76 (4.68)		398,380		
Me_3SiO	Et	116—118	32.7 (33.1)	8.05 (8.11)	4.47 (4.54)		405,380		968

observation is most easily rationalized on the basis of steric effects, a trimethylsilyl group being smaller than a neopentyl group. This is shown, by way of example, by the observation that $(Me_3SiCH_2)_2Mg$ and $(Me_3SiCH_2)_2Mn$ are infinite, linear polymers whereas the neopentyl analogues are trimeric and tetrameric, respectively [3,4].

The monomeric (by mass spectrometry), pentane-soluble chloro-alkyls $(R)(Cl)Hf[N(SiMe_3)_2]_2$, where R is Me_3CCH_2 or Me_3SiCH_2, react with one-half molar equivalent of dimethyl- or diethyl-magnesium in pentane to give the unsymmetrical dialkyls $RR'Hf[N(SiMe_3)_2]_2$ where R is Me_3SiCCH_2 or Me_3SiCH_2 and R′ is Me or Et, respectively. The trimethylsiloxo compound, $(Me_3SiO)(Cl)Hf[N(SiMe_3)_2]_2$, can also be prepared from $Cl_2Hf[N(SiMe_3)_2]_2$ and one molar equivalent of sodium trimethylsiloxide. The pentane-soluble alkoxide is monomeric in gas phase (by mass spectrometry). The chloride ligand in the latter can also be replaced by a methyl or ethyl group giving $(R)(Me_3SiO)Hf[N(SiMe_3)_2]_2$, where R is Me or Et.

Experimental

All operations were performed under a nitrogen atmosphere. Microanalyses were performed by the microanalytical laboratory of this department. The magnesium dialkyls were prepared as previously described [5].

Chloro-2,2-dimethylpropylbis[bis(trimethylsilyl)amido]hafnium(IV). Bis(2,2-dimethylpropyl)magnesium (1.7 ml of a 0.77 *M* diethyl ether solution, 0.00095 mol) was added to dichlorobis[bis(trimethylsilyl)amido]hafnium [1] (1.1 g, 0.0019 mol) in pentane (40 ml) at 0°C. After stirring for 12 h at 0°C the volatile material was removed in vacuum. The residue was extracted with pentane (40 ml), filtered, and the filtrate was concentrated to ca. 3 ml. Cooling

TABLE 2

NUCLEAR MAGNETIC RESONANCE SPECTRA OF $RR^1Hf[N(SiMe_3)_2]_2$

R	R^1	^1H NMR [a]				$^{13}C\{^1H\}$NMR [b]				
		$(Me_3Si)_2N$	Me_3	CH_2	Me	$(Me_3Si)_2N$	Me_3	CH_2	Me	Other
Me_3CCH_2	Cl [c]	0.51	1.40	1.99		5.46	35.5	100		31.6 [d]
Me_3SiCH_2	Cl	0.50	0.43	1.08		5.35	3.07	73.5		
Me_3SiO	Cl	0.50	0.37			5.10	2.60			
Me_3CCH_2	Me	0.45	1.30	1.12	0.70	5.43	35.7	104	62.5	31.6 [d]
Me_3SiCH_2	Me [e]	0.42	0.34	0.70 [f]	0.70 [f]	5.42	3.34	75.2	62.2	
Me_3SiO	Me	0.49	0.38		0.62	5.20	2.52		47.2	
Me_3CCH_2	Et	0.40	1.30	1.15 s [g] 1.03 q [h] $J = 7$ Hz	1.90 t $J = 7$ Hz	4.85	31.6	94.7 [g] 77.4 [h]	35.7	28.3 [d]
Me_3SiO	Et	0.43	0.36	1.14 q $J = 7$ Hz	1.82 t $J = 7$ Hz	5.16	4.75	61.3	14.2	

[a] ^1H NMR, 60 MHz, in benzene, expressed in δ units relative to Me_4Si, positive values to high frequency. [b] ^{13}C NMR, 25.1 MHz, in benzene-d_6, expressed in δ units relative to Me_4Si, positive values to high frequency. [c] Proton coupled-^{13}C spectrum shows a quartet ($J = 118$ Hz), a quartet ($J = 110$ Hz), triplet ($J = 95$ Hz), and a singlet, respectively. [d] The quaternary carbon atom of Me_3CCH_2. [e] Proton coupled-^{13}C spectrum shows a quartet ($J = 118$ Hz), a quartet ($J = 113$ Hz), a triplet ($J = 101$ Hz), and a quartet ($J = 114$ Hz), respectively. [f] The methylene and methyl resonances are accidentally degenerate, yielding a slightly broadened resonance of relative area five. [g] Methylene resonance of the neopentyl group. [h] Methylene resonance of the ethyl group.

(—70° C) yielded colorless needles in 70% (0.80 g) yield. The mass spectrum gave a *M* —15 peak (591).

Bis[bis(trimethylsilylmethyl)(chloro)hafnium(IV). Bis(trimethylsilylmethyl)-magnesium (2.2 ml of a 0.82 *M* diethyl ether solution, 0.0018 mol) was added to dichlorobis[bis(trimethylsilyl)amido]hafnium (2.0 g, 0.0036 mol) in pentane (45 ml) at 0° C. The suspension was stirred for 9 h at 0° C, then evaporated to dryness. Pentane (35 ml) was added, the suspension was stirred for 15 min, allowed to settle, and then was filtered. The filtrate was evaporated to yield a pale yellow liquid in 94% (2.1 g) yield.

Bis[bis(trimethylsilyl)amido](trimethylsiloxo)(chloro)hafnium(IV). Sodium trimethylsiloxide (0.34 g, 0.0029 mol) dissolved in diethyl ether (25 ml) was added to dichlorobis[bis(trimethylsilyl)amido]hafnium (1.7 g, 0.0029 mol) in pentane (30 ml) at 0° C. The suspension was stirred for 12 h (0° C). The volatile material was removed in vacuum and pentane (30 ml) was added to the residue. The supernatant liquid was filtered and the filtrate was evaporated to dryness yielding a semi-solid material which sublimed as a colorless solid at 70—90° C/ 10^{-2} Torr. Yield was 1.1 g (61%). The mass spectrum afforded a molecular ion (*M* —15) at 609.

Bis[bis(trimethylsilyl)amido](2,2-dimethylpropyl)methylhafnium (IV). Dimethylmagnesium (1.4 ml of a 0.88 *M* diethyl ether solution, 0.0012 mol) was added to bis[bis(trimethylsilyl)amido]neopentylchlorohafnium (1.5 g, 0.0024 mol) in pentane (40 ml) at 0° C. The suspension was stirred (0° C) for 12 h. The volatile material was removed in vacuum at 0° C and pentane (30 ml) was added to the residue. The suspension was stirred for 15 min, allowed to settle and filtered. The filtrate was evaporated to ca. 3 ml and cooled (—70° C). The colorless prisms were collected and dried in vacuum. The yield was 1.1 g (78%).

Bis[bis(trimethylsilyl)amido](trimethylsilylmethyl)methylhafnium(IV). Dimethylmagnesium (1.4 ml of a 0.88 *M* diethyl ether solution, 0.0012 mol) was added to chlorotrimethylsilylmethylbis[bis(trimethylsilyl)amido]hafnium (1.5 g, 0.0024 mol) in pentane (40 ml) at 0° C. The suspension was stirred for 12 h at 0° C. The volatile material was removed in vacuum and pentane (30 ml) was added. The suspension was stirred (15 min), filtered, and the filtrate was evaporated yielding a pale yellow, viscous liquid in 76% (1.1 g) yield.

Bis[bis(trimethylsilyl)amido](trimethylsiloxo)methylhafnium(IV). Dimethylmagnesium (0.71 ml of a 0.88 *M* diethyl ether solution, 0.0062 mol) was added to chlorotrimethylsiloxobis[bis(trimethylsilyl)amido]hafnium (0.77 g, 0.0012 mol) in pentane (40 ml) at 0° C. The suspension was stirred for 8 h at 0° C and a further 4 h at room temperature. The volatile material was removed in vacuum and the residue was extracted with pentane (25 ml). The extract was evaporated to ca. 2 ml and cooled (—70° C). The colorless prisms were collected and dried in vacuum. The yield was 0.60 g (83%).

Bis[bis(trimethylsilyl)amido](2,2-dimethylpropyl)ethylhafnium(IV). Diethylmagnesium (0.70 ml of a 1.0 *M* diethyl ether solution, 0.00070 mol) was added to chloroneopentylbis[bis(trimethylsilyl)amido]hafnium (0.85 g, 0.0014 mol) in pentane (40 ml) at 0° C. The suspension was stirred at 0° C for 11 h. The volatile material was removed in vacuum and pentane (25 ml) was added to the residue. The suspension was stirred for 15 min, allowed to settle and filtered. The filtrate was evaporated to ca. 2 ml and cooled (—70° C). The colorless prisms were collected and dried in vacuum. The yield was 0.51 g (61%).

Bis[bis(trimethylsilyl)amido](trimethylsiloxo)ethylhafnium(IV). Diethylmagnesium (0.56 ml of a 1.0 *M* diethyl ether solution, 0.00056 mol) was added to chlorotrimethylsiloxobis[bis(trimethylsilyl)amido]hafnium (0.70 g, 0.0011 mol) in pentane (40 ml) at 0° C. The suspension was stirred at 0° C for 6 h, then at room temperature for 3 h. The volatile material was evaporated to dryness and the residue was extracted with pentane (30 ml). The extract was filtered and the filtrate was evaporated to ca. 2 ml. Cooling to —70° C yielded colorless prisms in 81% (0.55 g) yield.

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