Alkyl for hydride exchange between alane-trimethylamine and Group IVB metal alkyls

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Abstract

Reaction of equimolar amounts of $AlH_3 \cdot NMe_3$ and $M(CH_2SiMe_3)_4$ in benzene (for M = Zr, Hf) led to exchange of all three Al–H bonds for $Al–CH_2SiMe_3$ bonds and isolation of $Al(CH_2SiMe_3)_3 \cdot NMe_3$. The latter compound crystallized in the $P\bar{1}$ space group, $a = 9.535(2)$, $b = 10.913(2)$, $c = 12.273(2)$ Å, $\alpha = 88.03(1)$, $\beta = 86.03(1)$, $\gamma = 86.93(1)°$, $U = 1271.6(4)$ Å^3, $D_c = 1.002$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 0.217 mm^{-1}, $F(000) = 424$. Similar reactions between $AlH_3 \cdot NMe_3$ and Cp_2ZrR_2 ($R = CH_3$, CH_2SiMe_3) yielded Cp_2ZrH_2 and $AlR_3 \cdot NMe_3$. Reaction of $AlH_3 \cdot NMe_3$ with $Zr(CH_2Ph)_4$ produced $Al(CH_2Ph)_3 \cdot NMe_3$.

Key words: Crystal structures; Zirconium complexes; Hafnium complexes; Alkyl complexes; Aluminum complexes; Hydride complexes

Introduction

We wish to report the serendipitous observation of the exchange of aluminum–hydrogen bonds for aluminum–carbon bonds in reactions of $AlH_3 \cdot NMe_3$ with zirconium and hafnium alkyls (reaction (1)). While this reaction is not a useful procedure for preparation of aluminum alkyls, it is, to our knowledge, only the second example of such an exchange reaction involving aluminum–hydrogen bonds and transition metal–carbon bonds. Exchange of alkyl for hydride ligands in aluminum chemistry is well known [1], while the reaction of alane trimethylamine with mercury alkyls yielded the corresponding aluminum alkyl, elemental mercury and hydrogen as the only example of this reaction involving transition metal alkyls [2].

$$MR_4 + AlH_3 \cdot NMe_3 \longrightarrow AlR_3 \cdot NMe_3 + \text{'}MRH_3\text{'} \qquad (1a)$$

M = Hf, $R = CH_2SiMe_3$; M = Zr, $R = CH_2SiMe_3$, CH_2Ph

$$Cp_2ZrR'_2 + \tfrac{2}{3}AlH_3 \cdot NMe_3 \longrightarrow \tfrac{2}{3}AlR_3 \cdot NMe_3 + Cp_2ZrH_2 \qquad (1b)$$

R′ = Me, CH_2SiMe_3

Experimental

All compounds described in this work were handled using Schlenk techniques, in an M.I. Braun glovebox under a purified argon atmosphere or on a vacuum line [3]. $ZrCl_4$, $HfCl_4$ and Cp_2ZrCl_2 were purchased from Strem Chemical Co. and used as received. 1.0 M $LiCH_2SiMe_3$ in hexanes, 1.0 M $LiCH_3$ in diethyl ether and benzylmagnesium bromide in THF were purchased from Aldrich Chemical Co. Solvents were purified by refluxing over Na/benzophenone (benzene, toluene, tetrahydrofuran, dioxane, diethyl ether, hexane) and distilled prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried as described above. $AlH_3 \cdot NMe_3$ [4], Cp_2ZrMe_2 [5], $Cp_2Zr(CH_2SiMe_3)_2$ [6], $Zr(CH_2Ph)_4$ [3b], $Zr(CH_2SiMe_3)_4$ [7] and $Hf(CH_2SiMe_3)_4$ [7] were prepared by literature methods.

^1H and $^{27}Al\{^1H\}$ spectra were recorded on a Varian 300XL spectrometer in 5 mm tubes equipped with a Teflon valve (J. Youngs). Proton chemical shifts are listed relative to residual protons in the solvent ($C_6D_5\mathit{H}$ at δ 7.15 ppm). Aluminum chemical shifts are referenced to $\mathit{Al}Me_3$ at 156 ppm in C_6D_6. IR spectra were recorded as KBr discs on a Perkin-Elmer 1310 infrared spec-

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trophotometer. Elemental analyses (C, H) were performed by Galbraith Laboratories and Desert Analytics.

Reaction of $Hf(CH_2SiMe_3)_4$ *with* $AlH_3 \cdot NMe_3$

A solution of 33 mg (0.38 mmol) $AlH_3 \cdot NMe_3$ in 1 ml of benzene was added to a solution of 198 mg (0.38 mmol) of $Hf(CH_2SiMe_3)_4$ dissolved in 1 ml of benzene at ambient temperature under dry nitrogen. After stirring for 20 min, the solvent was evaporated under vacuum and the crude product transferred to a sublimator in the glove box. Sublimation at 80–90 °C at 10^{-4} Torr yielded 104 mg (80% yield) of white, crystalline, $Al(CH_2SiMe_3)_3 \cdot NMe_3$; m.p. 68–69 °C. ^1H NMR (C_6D_6, ppm): -0.96 (s, CH_2SiMe_3, intensity 6H), 0.28 (s, $(CH_3)_3SiCH_2$, intensity 27H), 1.67 (s, NMe_3, intensity 9H). $^{27}Al(C_6D_6)$ 171 ppm. IR (KBr): 2955(s), 2890(s), 1405(m, sh), 1345(m), 1250(s), 1100(m), 970(s, br), 850(s, br), 750(s, br) cm^{-1}. We were unable to obtain an accurate elemental analysis for the compound prepared by this method, hence the product was characterized by single crystal X-ray structure determination. A spectroscopically identical sample of $Al(CH_2SiMe_3)_3 \cdot NMe_3$ was prepared by addition of NMe_3 to $Al(CH_2SiMe_3)_3$ [7] followed by sublimation. *Anal.* Calc. for $C_{15}H_{42}AlNSi_3$: C, 51.81; H, 12.17; N, 4.04. Found: C, 50.23; H, 11.86; N, 3.49%.

Reaction of 8 mg (0.09 mmol) $AlH_3 \cdot NMe_3$ and 16 mg (0.09 mmol) $Hf(CH_2SiMe_3)_4$ in benzene-d^6 in a sealed 5 mm tube produced ^1H NMR spectra identical with those obtained from dissolution of the sublimed $Al(CH_2SiMe_3)_3 \cdot NMe_3$.

In a separate experiment, 100 mg (0.19 mmol) $Hf(CH_2SiMe_3)_4$ and 16 mg (0.19 mmol) $AlH_3 \cdot NMe_3$ were stirred under nitrogen at ambient temperature in hexane for 24 h leading to precipitation of a white solid. Filtration under nitrogen yielded 26 mg of white powder after drying under vacuum (76% yield based on HfH_2). *Anal.* Calc. for HfH_2: C, 0.00; H, 1.12. Found: C, 5.21; H, 1.70%.

Crystal structure determination

A single crystal suitable for study by X-ray diffraction was selected from the sublimed $Al(CH_2SiMe_3)_3 \cdot NMe_3$ and mounted in a sealed capillary on a Siemens R3m/V diffractometer. Data were collected for 6684 reflections over a full sphere of $2\theta = 5$–$45°$, which merged to 3341 independent data with $R(\text{int}) = 1.14\%$. Convergence was reached with $R = 7.54\%$ for all 3341 reflections and $R = 4.25\%$ for those 2017 reflections with $F > 6\sigma(F)$. Triclinic $Al(CH_2SiMe_3)_3 \cdot NMe_3$, $C_{15}H_{42}AlNSi_3$, $M = 347.7$, crystallized in the $P\bar{1}$ space group, with $a = 9.535(2)$, $b = 10.913(2)$, $c = 12.273(2)$ Å, $\alpha = 88.03(1)$, $\beta = 86.03(1)$, $\gamma = 86.93(1)°$, $U = 1271.6(4)$ Å^3, $D_c = 1.002$ g cm^{-3}, $Z = 2$, $\mu(\text{Mo K}\alpha) = 0.217$ mm^{-1}, $F(000) = 424$.

Reaction of $Zr(CH_2SiMe_3)_4$ *with* $AlH_3 \cdot NMe_3$

In a procedure identical to that described for $Hf(CH_2SiMe_3)_4$ reactions, solutions of 100 mg (0.23 mmol) $Zr(CH_2SiMe_3)_4$ and 20 mg (0.23 mmol) $AlH_3 \cdot NMe_3$ in C_6D_6 were mixed in the glove box in a 5 mm tube. ^1H NMR spectra were identical to those for mixtures of $Hf(CH_2SiMe_3)_4$ and $AlH_3 \cdot NMe_3$. After 5 min, a dark precipitate had formed in the tube with no changes in the ^1H NMR spectrum of the $Al(CH_2SiMe_3)_3 \cdot NMe_3$ product.

Reaction of Cp_2ZrMe_2 *with* $AlH_3 \cdot NMe_3$

A solution of 24 mg (0.27 mmol) $AlH_3 \cdot NMe_3$ in 2 ml of benzene was added to a solution of 100 mg (0.40 mmol) of Cp_2ZrMe_2 dissolved in 3 ml of benzene at ambient temperature under dry nitrogen. Immediate precipitation of a white solid was observed. After stirring for 20 min, the mixture was filtered, yielding 60 mg (68% yield) of white powder after drying under vacuum. *Anal.* Calc. for $C_{10}H_{12}Zr$: C, 53.76; H, 5.41. Found: C, 52.23; H, 5.58%. IR (KBr): Zr–H–Zr 1520, 1300 cm^{-1} identical to the reported spectrum of Cp_2ZrH_2 [8].

The filtrate was dried under vacuum, redissolved in hexane, and cooled to -78 °C yielding 28 mg (78% yield) of $AlMe_3 \cdot NMe_3$. ^1H NMR (C_6D_6, ppm): -0.58 (s, $AlMe_3$, intensity 9H), 1.67 (s, NMe_3, intensity 9H). The NMR was identical to an authentic sample of $AlMe_3 \cdot NMe_3$ prepared from $AlMe_3$ and NMe_3.

Reaction of 12 mg (0.14 mmol) $AlH_3 \cdot NMe_3$ and 50 mg (0.20 mmol) Cp_2ZrMe_2 in benzene-d^6 in a sealed 5 mm tube produced a ^1H NMR spectrum identical to that observed for $AlMe_3 \cdot NMe_3$ above.

Reaction of $Cp^*_2ZrMe_2$ *with* $AlH_3 \cdot NMe_3$

Reaction of 11 mg (0.09 mmol) $AlH_3 \cdot NMe_3$ and 50 mg (0.13 mmol) $Cp^*_2ZrMe_2$ in benzene-d^6 in a sealed 5 mm tube at ambient temperature produced no changes in the ^1H NMR spectra after 24 h at ambient temperature. Heating the tube to 80 °C for 48 h led to decomposition of the $AlH_3 \cdot NMe_3$. The formation of $AlMe_3 \cdot NMe_3$ was not observed under these conditions.

Reaction of $Zr(CH_2Ph)_4$ *and* $AlH_3 \cdot NMe_3$

A solution of 59 mg (0.66 mmol) $AlH_3 \cdot NMe_3$ in 5 ml of hexane was added to a solution of 300 mg (0.66 mmol) of $Zr(CH_2Ph)_4$ dissolved in 15 ml of hexane at ambient temperature under dry nitrogen. Immediate precipitation of a black solid was observed. After stirring for 20 min, the mixture was filtered. The filtrate volume was reduced under vacuum and cooled to -78 °C yielding 35 mg (16% yield) of $Al(CH_2Ph)_3 \cdot NMe_3$; m.p. 89–91 °C. ^1H NMR (C_6D_6, ppm): 1.40 (s, NMe_3, intensity 9H), 1.75 (s, CH_2Ph, intensity 6H), 6.90–7.20 (m, CH_2Ph, intensity 15H). $^{27}Al(C_6D_6)$: 171 ppm.

Reaction of 10 mg (0.11 mmol) $AlH_3 \cdot NMe_3$ and 0.50 mg (0.11 mmol) $Zr(CH_2Ph)_4$ in benzene-d^6 in a sealed 5 mm tube produced ^1H NMR spectra identical to the $Al(CH_2Ph)_3 \cdot NMe_3$ observed above.

Results and discussion

Reaction of equimolar amounts of $AlH_3 \cdot NMe_3$ and $Hf(CH_2SiMe_3)_4$ in benzene at room temperature gave a transparent, colorless solution. Evaporation of the reaction mixture and sublimation of the residue at 80–90 °C/10^{-4} Torr yielded $Al(CH_2SiMe_3)_4 \cdot NMe_3$ in 80% yield as a white crystalline solid. No attempt was made to optimize the yield by changing the stoichiometry of the reaction. The structure was determined by single crystal X-ray structure determination (Fig. 1, Table 1). Atomic coordinates are collected in Table 2 with bond lengths and bond angles reported in Tables 3 and 4. The structure of $Al(CH_2SiMe_3)_3 \cdot NMe_3$ is typical for Lewis base adducts of aluminum alkyls. The structure of $Al(CH_2SiMe_3)_3 \cdot NMe_3$ can be compared with solid state structures for trimethyl(quinuclidine)aluminum, $AlMe_3 \cdot NC_7H_{13}$ [9], trichloro(trimethylamine)-aluminum, $AlCl_3 \cdot NMe_3$ [10], as well as the gas phase electron diffraction study of trimethyl(trimethylamine)aluminum, $AlMe_3 \cdot NMe_3$ [11]. Distances of note include Al(1)–C(21) = 1.984(3), Al(1)–C(31) = 1.984(4), Al(1)–C(41) = 1.989(3) Å (av. Al–C = 1.986 ± 0.003 Å) and Al(1)–N(1) = 2.058(3) Å. The latter distance is nearly identical to the 2.06 Å Al–N distance reported for $AlMe_3 \cdot NC_7H_{13}$ and in between the Al–N distances for $AlCl_3 \cdot NMe_3$ (1.96 Å) and $AlMe_3 \cdot NMe_3$ (2.10 Å). The average Al–C bond distances of 1.986 Å in $Al(CH_2SiMe_3)_3 \cdot NMe_3$ is nearly identical to the Al–C distance in $AlMe_3 \cdot NMe_3$ (1.987 Å) and shorter than that observed in $AlMe_3 \cdot NC_7H_{13}$ (2.017 Å). The C–Al–C angles in $Al(CH_2SiMe_3)_3 \cdot NMe_3$ are greater than the ideal tetrahedral angle (C(21)–Al(1)–C(31) = 115.3(2), C(21)–Al(1)–C(41) = 115.9(1), C(31)–Al(1)–C(41) = 115.2(2)°; av. 115.5°) while the C–Al–N angles are all contracted (C(21)–Al(1)–N(1) = 101.9(1), C(31)–Al(1)–N(1) = 102.5(1), C(41)–Al(1)–N(1) = 102.6(1)°; av. 102.3°). The C–Al–C and C–Al–N bond angles reflect the trends observed for the other three Lewis base adducts. The average C–Al–C angle of 115.5° in $Al(CH_2SiMe_3)_3 \cdot NMe_3$ is larger than the 114.8° angle in $AlMe_3 \cdot NMe_3$ and the 113.8° angle in $AlMe_3 \cdot NC_7H_{13}$. In the latter case, the steric bulk of the quinuclidine ligand acts to compress the C–Al–C bond angle relative to $AlMe_3 \cdot NMe_3$ while in $Al(CH_2SiMe_3)_3 \cdot NMe_3$, the size of the CH_2SiMe_3 ligand leads to larger C–Al–C bond angles and smaller C–Al–N angles (102.3° in $Al(CH_2SiMe_3)_3 \cdot NMe_3$ versus 104.5° in $AlMe_3 \cdot NC_7H_{13}$). For comparison, the C–Al–N bond angle in $AlMe_3 \cdot NMe_3$ is 102.3 °C. Other distances of interest include CH_2–Si = 1.817(4)–1.848(4) Å, Si–C(Me) = 1.828(6)–1.881(4) Å, which are typical for C–Si bonds, and N–C(Me) = 1.477(6)–1.489(5) Å. The N–C distance in $AlMe_3 \cdot NMe_3$ was observed to be slighly shorter, at 1.474 Å.

When the reaction between $Hf(CH_2SiMe_3)_4$ and $AlH_3 \cdot NMe_3$ was performed in a sealed tube in C_6D_6, three ^1H NMR signals were observed at −0.96 (s, CH_2SiMe_3, intensity 6H), 0.28 (s, $(CH_3)_3SiCH_2$, intensity 27H) and 1.67 (s, NMe_3, intensity 9H) ppm. The trimethylamine protons of $AlH_3 \cdot NMe_3$ were observed at 2.04 ppm in C_6D_6 while the ^1H NMR resonances of tetrakis(trimethylsilylmethyl)hafnium were observed at 0.18 (s, $(CH_3)_3SiCH_2$, intensity 9H) and 0.44 (s, CH_2SiMe_3, intensity 2H) ppm. A 34 ppm downfield shift in the ^{27}Al NMR chemical shift (171 ppm) was observed relative to $AlH_3 \cdot NMe_3$ (137 ppm). The ^1H NMR spectrum was identical with those obtained from

TABLE 1. Solution and refinement

System used	Siemens SHELXTL PLUS (VMS)
Solution	direct methods
Refinement method	full-matrix least-squares
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Extinction coefficient	N/A
Hydrogen atoms	riding model, refined group isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$
No. parameters refined	184
Final R indices (obs. data) (%)	$R = 7.54$, $R_w = 6.82$
R indices (6.0 σ data) (%)	$R = 4.25$, $R_w = 5.68$
Goodness-of-fit	1.22
Largest and mean Δ/σ	0.001, 0.000
Data to parameter ratio	18.2:1
Largest difference peak (e $Å^{-3}$)	0.25
Largest difference hole (e $Å^{-3}$)	−0.18

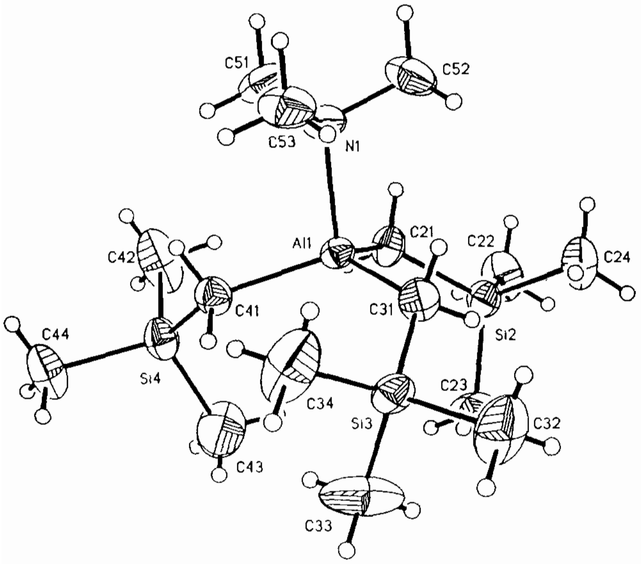

Fig. 1. Crystal structure of $Al(CH_2SiMe_3)_3 \cdot NMe_3$.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq}[a]
Al(1)	1146(1)	1888(1)	2562(1)	62(1)
C(21)	1552(4)	2216(3)	974(3)	83(1)
Si(2)	2639(1)	3471(1)	412(1)	82(1)
C(22)	2784(5)	3470(4)	−1125(3)	131(2)
C(23)	4435(4)	3305(5)	902(4)	153(3)
C(24)	1862(5)	5007(3)	799(3)	123(2)
C(31)	1541(4)	3239(3)	3519(3)	94(2)
Si(3)	2531(1)	3084(1)	4734(1)	84(1)
C(32)	2746(7)	4578(4)	5364(4)	168(3)
C(33)	4309(5)	2433(7)	4361(5)	215(4)
C(34)	1713(7)	2087(5)	5795(4)	191(4)
C(41)	1684(4)	204(3)	3112(3)	82(1)
Si(4)	2725(1)	−944(1)	2297(1)	91(1)
C(42)	1810(7)	−1326(4)	1070(4)	178(3)
C(43)	4476(6)	−345(5)	1858(6)	192(4)
C(44)	3020(6)	−2423(4)	3082(4)	139(2)
N(1)	−1018(3)	1909(3)	2684(2)	85(1)
C(51)	−1510(4)	896(5)	2066(4)	129(2)
C(52)	−1627(4)	3083(4)	2239(4)	126(2)
C(53)	−1543(4)	1748(5)	3848(3)	123(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Bond lengths (Å)

Al(1)–C(21)	1.984(3)	Al(1)–C(31)	1.984(4)
Al(1)–C(41)	1.989(3)	Al(1)–N(1)	2.058(3)
C(21)–Si(2)	1.848(4)	Si(2)–C(22)	1.881(4)
Si(2)–C(23)	1.851(4)	Si(2)–C(24)	1.860(4)
C(31)–Si(3)	1.817(4)	Si(3)–C(32)	1.856(5)
Si(3)–C(33)	1.837(6)	Si(3)–C(34)	1.828(6)
C(41)–Si(4)	1.836(3)	Si(4)–C(42)	1.862(6)
Si(4)–C(43)	1.864(5)	Si(4)–C(44)	1.870(4)
N(1)–C(51)	1.477(6)	N(1)–C(52)	1.481(5)
N(1)–C(53)	1.489(5)		

TABLE 4 Bond angles (°)

C(21)–Al(1)–C(31)	115.3(2)	C(21)–Al(1)–C(41)	115.9(1)
C(31)–Al(1)–C(41)	115.5(2)	C(21)–Al(1)–N(1)	101.9(1)
C(31)–Al(1)–N(1)	102.5(1)	C(41)–Al(1)–N(1)	102.6(1)
Al(1)–C(21)–Si(2)	123.5(2)	C(21)–Si(2)–C(22)	110.6(2)
C(21)–Si(2)–C(23)	110.9(2)	C(22)–Si(2)–C(23)	108.5(2)
C(21)–Si(2)–C(24)	112.1(2)	C(22)–Si(2)–C(24)	106.6(2)
C(23)–Si(2)–C(24)	108.1(2)	Al(1)–C(31)–Si(3)	125.8(2)
C(31)–Si(3)–C(32)	112.7(2)	C(31)–Si(3)–C(33)	109.2(2)
C(32)–Si(3)–C(33)	106.8(3)	C(31)–Si(3)–C(34)	112.7(2)
C(32)–Si(3)–C(34)	106.9(2)	C(33)–Si(3)–C(34)	108.3(3)
Al(1)–C(41)–Si(4)	124.1(2)	C(41)–Si(4)–C(42)	111.2(2)
C(41)–Si(4)–C(43)	109.6(2)	C(42)–Si(4)–C(43)	109.4(3)
C(41)–Si(4)–C(44)	112.1(2)	C(42)–Si(4)–C(44)	106.2(2)
C(43)–Si(4)–C(44)	108.2(2)	Al(1)–N(1)–C(51)	110.2(2)
Al(1)–N(1)–C(52)	110.8(2)	C(51)–N(1)–C(52)	108.5(3)
Al(1)–N(1)–C(53)	110.1(2)	C(51)–N(1)–C(53)	108.3(3)
C(52)–N(1)–C(53)	108.9(3)		

dissolution of the independently prepared, sublimed $Al(CH_2SiMe_3)_3 \cdot NMe_3$.

The fate of the hafnium was less clear; the stoichiometry for exchange of Al–H for $Al–CH_2SiMe_3$ groups implies the formation of '$H_3HfCH_2SiMe_3$'. With the exception of small amounts of Me_4Si (0.00 ppm), ^1H NMR resonances clearly assignable to a new hafnium compound were not observed in mixtures of $Hf(CH_2SiMe_3)_4$ and $AlH_3 \cdot NMe_3$ in sealed tubes. Over a period of several hours, formation of a white precipitate was observed in the NMR tube. Elemental analyses of this material were deficient in both carbon and hydrogen for '$H_3HfCH_2SiMe_3$' (calc. 17.88% C, 5.25% H) but contained excess carbon to be consistent with a composition HfH_2 (calc. 0.0% C, 1.12% H). Overlapping absorptions in the solution IR spectra of the reaction mixture did not allow for detection of Hf–H IR absorption bands. It is also possible that a redistribution reaction of '$H_3HfCH_2SiMe_3$' yielding $Hf(CH_2SiMe_3)_4$ and HfH_2 is occurring. While the apparent thermal instability of '$H_3HfCH_2SiMe_3$' has prevented isolation and characterization of this compound, reaction of Cp_2ZrMe_2 or $Cp_2Zr(CH_2SiMe_3)_2$ with $AlH_3 \cdot NMe_3$ yielded insoluble Cp_2ZrH_2 and $AlMe_3 \cdot NMe_3$ or $Al(CH_2SiMe_3)_3 \cdot NMe_3$, respectively (reaction (1b)). The products were identified by a combination of elemental analysis, IR and NMR spectroscopy and support the notion of metal hydride intermediates in the reactions of $Hf(CH_2SiMe_3)_4$ with $AlH_3 \cdot NMe_3$. The insolubility of Cp_2ZrH_2 prevented direct spectroscopic identification of the metal–hydride product.

Bis(pentamethylcyclopentadienyl)zirconium dihydride [12] was reported to be soluble in hydrocarbon solvents, however, no reaction was observed between

$Cp^*_2ZrMe_2$ and $AlH_3 \cdot NMe_3$ at ambient temperature. Prolonged heating at 80 °C led to changes in the ^1H NMR spectra, however, resonances at 7.46 ppm for $Cp^*_2ZrH_2$ were completely absent. Reaction of $Zr(CH_2SiMe_3)_4$ with $AlH_3 \cdot NMe_3$ in benzene solution also led to the formation of $Al(CH_2SiMe_3)_3 \cdot NMe_3$ as the sole spectroscopically observed product. Formation of a black solid was observed after 5 min of reaction at ambient temperature, possibly from decomposition of an '$H_3ZrCH_2SiMe_3$' intermediate. Reaction of $Zr(CH_2Ph)_4$ with $AlH_3 \cdot NMe_3$ under the same conditions produced a trimethylamine adduct of tribenzyl aluminum and precipitated a black solid.

Supplementary material

Supplementary data on the crystal structure are available from M.R.C.

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