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Derivatives of Group 4 metal amide chlorides and fluorides: synthesis, structure and characterization of novel dimethyl and fluoro–chloro complexes

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Reaction of MgMeBr with $[MCl_2L_2]$ and $[MCl_2(\eta\text{-}C_5Me_5)L]$ $[L = (2,6\text{-}Pr^i{}_2C_6H_3)N(SiMe_3)$, M = Zr or Hf] gave the corresponding dimethyl complexes $[MMe_2L_2]$ (M = Zr **1a** or Hf **1b**) and $[MMe_2(\eta\text{-}C_5Me_5)L]$ (M = Zr **2a** or Hf **2b**). Reaction of $[ZrF_2L_2]$ with $AlMe_3$ also yielded **1a**. The structures of **1a** and **2a** have been determined by single-crystal X-ray crystallography. Upon reaction of 1 molar equivalent of $SnMe_3F$ with $[MCl_2L_2]$ and $[MCl_2(\eta\text{-}C_5Me_5)L]$ mixed fluoro–chloro complexes, $[MCl(F)L_2]$ (M = Zr **3a** or Hf **3b**) and $[MCl(F)(\eta\text{-}C_5Me_5)L]$ (M = Zr **4a** or Hf **4b**) were formed, *via* elimination of $SnMe_3Cl$. The structure of **4a** has been determined by single-crystal X-ray analysis.

Recently, there has been considerable interest in bifunctional cyclopentadienyl ligands containing an intramolecular donor, due to their ability to influence the Lewis acidity and reduce the steric congestion at an electrophilic d^0 metal centre.[1] This type of ligand system has been utilized to develop a range of 'constrained geometry' catalysts for ethylene–alk-1-ene copolymerizations.[2] There are also many examples of unbridged amido cyclopentadienyl Group 4 complexes,[3] but little is known about their catalytic activities. However, unbridged bis(amido) complexes of zirconium are known,[4] with several zirconium benzamidinate complexes found to be catalytically active.[5]

In a recent communication we introduced a series of zirconium and hafnium bis(amido) and amido cyclopentadienyl fluorides and chlorides.[6] These compounds were investigated as potential catalysts for the polymerization of ethylene and for the first time the catalytic activities of chlorides and the corresponding fluorides were compared under identical conditions. Herein, we report an extension of our previous studies with the synthesis of new dimethyl derivatives of Group 4 metal amide halides, as well as mixed fluoro–chloro complexes.

Results and Discussion

Reaction of $[MCl_2L_2]$ or $[MCl_2(\eta\text{-}C_5Me_5)L]$ $[L = (2,6\text{-}Pr^i{}_2C_6H_3)N(SiMe_3)$, M = Zr or Hf] with 2 molar equivalents of MgMeBr in diethyl ether proceeds smoothly to afford the dimethyl complexes **1** and **2** (Scheme 1). It was found that reaction of the bis(amido)zirconium difluoride, $[ZrF_2L_2]$, with 1 molar equivalent of trimethylaluminium in toluene also leads to the dimethyl complex **1a**. Interestingly, a similar reaction of the bis(amido)zirconium dichloride, $[ZrCl_2L_2]$, with $AlMe_3$ does not yield any tractable products. This can be explained by the high affinity of aluminium for fluorine and thus the formation of a strong Al–F bond, compared to an Al–Cl bond, is highly favoured.[7] Fluorine atoms at the zirconium centre are therefore exchanged with methyl groups from trimethylaluminium to give **1a**.

The analytical data as well as the resonance patterns observed in the NMR spectra of complexes **1** and **2** are consistent with the formulae in Scheme 1. Single-crystal structure analyses of **1a** and **2a** were also carried out and these confirm the formulation. The crystal structures are shown in Figs. 1 and 2, while relevant bond distances and angles are reported in Table 1. A Flack parameter[8] of −0.06(5) is associated with the chosen absolute configuration of the chiral compound **1a**. The CH_3–Zr–CH_3 angles in **1a** and **2a** are 100.4(1)° and 100.7(1)°, with the average Zr–CH_3 bond lengths being 2.276(3) and 2.265(3) Å, respectively. This is comparable with the average Zr–CH_3 bond length in $[ZrMe_2(\eta\text{-}C_5H_5)_2]$[9] [2.28(5) Å]. The Zr–N distance in **1a** is in the same range as that for the dichloro complex, $[ZrCl_2L_2]$,[6] *i.e.* 2.056(3) Å for **1a**

$$[MCl_2L_2] + 2\ MgMeBr \xrightarrow{(i)} [MMe_2L_2] + 2\ MgBrCl$$

1a M = Zr
1b M = Hf

$$[MCl_2(\eta\text{-}C_5Me_5)L] + 2\ MgMeBr \xrightarrow{(i)} [MMe_2(\eta\text{-}C_5Me_5)L] + 2\ MgBrCl$$

2a M = Zr
2b M = Hf

Scheme 1 $L = (2,6\text{-}Pr^i{}_2C_6H_3)N(SiMe_3)$. (*i*) Et_2O, room temperature (r.t.)

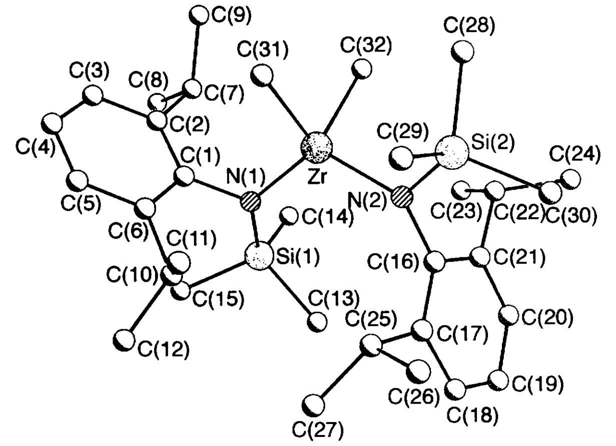

Fig. 1 Crystal structure of complex **1a** giving the numbering scheme used in Table 1. Hydrogen atoms have been omitted for clarity

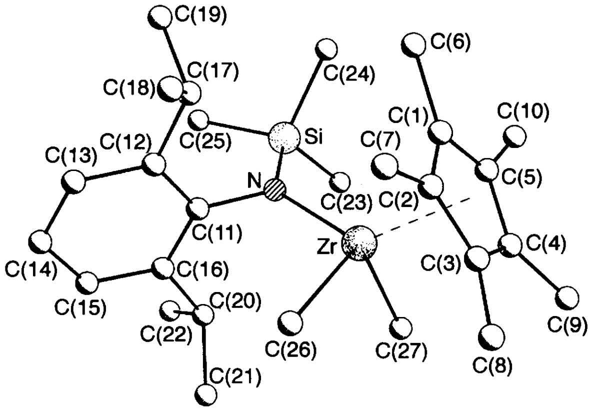

Fig. 2 Crystal structure of complex **2a** giving the numbering scheme used in Table 1. Hydrogen atoms have been omitted for clarity

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1a** and **2a**

1a		**2a**	
Zr–C(31)	2.224(4)	Zr–C(26)	2.243(3)
Zr–C(32)	2.327(3)	Zr–C(27)	2.272(3)
Zr–N(1)	2.056(3)	Zr–N	2.104(2)
Zr–N(2)	2.066(3)	Zr–X(1A)	2.258(2)
Si(1)–N(1)	1.757(3)	Si–N	1.759(2)
Si(2)–N(2)	1.773(3)		
N(1)–C(1)	1.456(5)	N–C(11)	1.454(3)
N(2)–C(16)	1.456(5)		
C(31)–Zr–C(32)	100.4(1)	C(26)–Zr–C(27)	100.7(1)
N(1)–Zr–N(2)	120.7(1)	N–Zr–X(1A)	133.3(1)

compared with 2.030(2) Å for the dichloro complex. The sterically demanding C_5Me_5 ligand in **2a** causes a slight lengthening of the Zr–N distance [2.104(2) Å] compared with the bis(amido) complexes, as well as a distortion in the tetrahedral geometry of the Zr atom. The N–Zr–X(1A) angle in **2a** [where X(1A) is the centroid of the C_5Me_5 ligand] is 133.3(1)°, whereas the N(1)–Zr–N(2) angle in **1a** is 120.7(1)°. The structures of the 1,2-diisopropylphenylamide ligand in both **1a** and **2a** do not show any significant variations in terms of internal geometrical parameters.

Following our work on Group 4 metal amide fluorides,[6] we decided to explore the possibility of partial fluorination of the dichlorides, using trimethyltin fluoride, for the preparation of mixed fluoro–chloro complexes. The use of trimethyltin fluoride as a fluorinating agent in the synthesis of a wide range of Group 4 organometallic fluorides is now well established.[10] Recently, mixed fluoro–chloro metallocenes were isolated from the reaction of 1 molar equivalent of $SnMe_3F$ and the appropriate metallocene dichloride.[11] Similarly, treatment of $[MCl_2L_2]$ or $[MCl_2(\eta\text{-}C_5Me_5)L]$ with $SnMe_3F$ in a 1:1 molar ratio leads to the corresponding mixed fluoro–chloro complexes (Scheme 2). Compounds **3** and **4** were obtained as crystalline materials after recrystallization from hexane. The parent molecular ion was always observed in the electron impact (EI) mass spectra.

The crystal structure of complex **4a** is shown in Fig. 3, with selected bond distances and angles collated in Table 2. The Zr–Cl bond length is 2.395(1) Å, slightly shorter than that in the fluoro–chloro metallocene complex $[ZrCl(F)(C_5Me_4Et)_2]$[11] [2.443(2) Å]. Conversely, the Zr–F bond length [2.182(2) Å] is longer than that in $[ZrCl(F)(C_5Me_4Et)_2]$ [2.001(3) Å], but in agreement with the Zr–F distance in $[ZrF_2\{C_5H_3(SiMe_3)_2\}_2]$[12] [2.212(6) Å]. The Zr–N bond distance of **4a** is comparable to that determined for **2a** [2.075(3) *vs.* 2.104(2) Å].

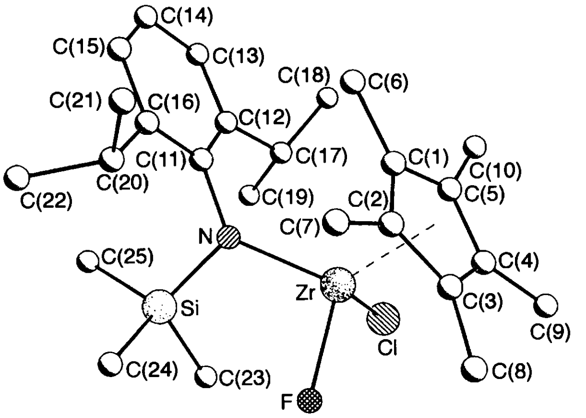

Fig. 3 Crystal structure of complex **4a** giving the numbering scheme used in Table 2. Hydrogen atoms have been omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) for complex **4a**

Zr–Cl	2.395(1)	Zr–N	2.075(3)
Zr–F	2.182(2)	Zr–X(1A)	2.202(3)
Si–N	1.792(3)	N–C(11)	1.450(4)
Cl–Zr–F	103.3(1)	N–Zr–X(1A)	122.3(1)

$$[MCl_2L_2] + SnMe_3F \xrightarrow{(i)} [MCl(F)L_2] + SnMe_3Cl$$

3a M = Zr
3b M = Hf

$$[MCl_2(\eta\text{-}C_5Me_5)L] + SnMe_3F \xrightarrow{(i)} [MCl(F)(\eta\text{-}C_5Me_5)L] + SnMe_3Cl$$

4a M = Zr
4b M = Hf

Scheme 2 L = $(2,6\text{-}Pr^i{}_2C_6H_3)N(SiMe_3)$. (*i*) CH_2Cl_2, r.t.

$$2\,[MCl(F)L_2] \rightleftharpoons [MCl_2L_2] + [MF_2L_2]$$

$$2\,[MCl(F)(\eta\text{-}C_5Me_5)L] \rightleftharpoons [MCl_2(\eta\text{-}C_5Me_5)L] + [MF_2(\eta\text{-}C_5Me_5)L]$$

Scheme 3 L = $(2,6\text{-}Pr^i{}_2C_6H_3)N(SiMe_3)$

The ^1H NMR spectra, at room temperature, of complexes **3** and **4** gave the expected signals, but these are all multiplets. This suggested an equilibrium process in solution. Furthermore, the ^{19}F NMR spectra gave two singlets. The main peak can be attributed to the fluorine atom of the fluoro–chloro complex, while the second signal, shifted upfield, corresponds to the difluoride species.[6] At higher temperatures (353 K) both the ^1H and ^{19}F NMR spectra remain unchanged. From this evidence we propose that, in solution, an equilibrium exists between the fluoro–chloro complexes and the dichloride and difluoride species, even at elevated temperatures (Scheme 3).

Conclusion

The study presented represents an extension of our previous work on Group 4 metal amide halides.[6] It was possible to isolate the dimethyl derivatives, as well as the mixed fluoro–chloro complexes. In view of the documented catalytic activity of bridged cyclopentadienyl amido complexes towards olefin polymerization and the reactivity of metal fluorides with aluminium alkyls, compounds **1**–**4** may be of interest with regard to their own catalytic potential. Further work in this respect is currently being undertaken.

Experimental

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and purified by known procedures and distilled from benzophenone ketyl under nitrogen prior to use. The compounds $[\mathrm{MCl_2\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}_2}]$ (M = Zr or Hf),[6] $[\mathrm{ZrF_2\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}_2}]$,[6] $[\mathrm{MCl_2(\eta\text{-}C_5Me_5)\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}}]$ (M = Zr or Hf)[6] and $\mathrm{SnMe_3F}$[13] were prepared according to literature methods; MgMeBr and $\mathrm{AlMe_3}$ were obtained from Aldrich and used without further purification.

The NMR spectra were recorded on a Bruker AM 250 spectrometer. The solvent $\mathrm{C_6D_6}$ was trap-to-trap distilled from $\mathrm{CaH_2}$. Proton and ^{19}F NMR data are listed in ppm downfield from $\mathrm{SiMe_4}$ and $\mathrm{CFCl_3}$, respectively. Infrared spectra were recorded on a Perkin-Elmer Bio-Rad Digilab FTS-7 spectrometer (Nujol mulls between CsI plates), mass spectra on a Finnigan MAT system 8230 and a Varian MAT CH 5 mass spectrometer. Melting points (uncorrected) were obtained using a Büchi 510 and an HWS-SG 3000 apparatus. Elemental analyses were performed by the Beller Laboratory (Göttingen) or in our institute.

Preparations

$[\mathrm{ZrMe_2\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}_2}]$ 1a. (*i*) *From the reaction of* $[\mathrm{ZrCl_2\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}_2}]$ *and* MgMeBr (1:2). To a solution of $[\mathrm{ZrCl_2\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}_2}]$ (1.30 g, 1.97 mmol) in diethyl ether (30 cm^3) was added dropwise a 3.0 mol dm^{-3} solution of MgMeBr in diethyl ether (1.32 cm^3, 3.96 mmol) at 0 °C. After stirring for 36 h, and removal of the solvent under reduced pressure, hexane (25 cm^3) was added and the mixture filtered. The filtrate was concentrated to $\approx$15 cm^3 and stored at -25 °C overnight. Colourless crystals of compound **1a** were deposited (1.13 g, 93%), m.p. 141–143 °C (Found: C, 62.1; H, 9.5; N, 4.5. $\mathrm{C_{32}H_{58}N_2Si_2Zr}$ requires C, 62.15; H, 9.45; N, 4.55%); ν_{max}(Nujol) 1250s, 1234m, 1167s, 1103s, 1051m, 1040m, 895vs, 835vs, 795s, 783s, 750m, 677m, 532m, 474m, 431m and 350m cm^{-1}; $\delta_H(\mathrm{C_6D_6})$ 7.12 (6 H, s, $\mathrm{C_6H_3}$), 3.73 [4 H, spt, ^3J(HH) 6.78, $\mathrm{CH_3}$C*H*$\mathrm{CH_3}$], 1.33 [12 H, d, ^3J(HH) 6.82, C*H*$_3$CHC*H*$_3$], 1.19 [12 H, d, ^3J(HH) 6.71 Hz, C*H*$_3$CHC*H*$_3$], 0.57 (6 H, s, $\mathrm{CH_3}$) and 0.17 (18 H, s, $\mathrm{SiMe_3}$); *m*/*z* 603 (*M* − Me), 588 (*M* − 2Me) and 73 ($\mathrm{Me_3Si}$).

(*ii*) *From the reaction of* $[\mathrm{ZrF_2\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}_2}]$ *and* $\mathrm{AlMe_3}$ (1:1). To a solution of $[\mathrm{ZrF_2\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}_2}]$ (0.72 g, 1.15 mmol) in toluene (20 cm^3) was added 2.0 mol dm^{-3} $\mathrm{AlMe_3}$ in hexane (0.57 cm^3, 1.14 mmol) at 0 °C. After stirring for 18 h and removal of the solvents under reduced pressure, hexane (30 cm^3) was added and the mixture filtered. The filtrate was partially concentrated and cooled at 0 °C for 48 h to yield compound **1a** as colourless crystals (0.64 g, 91%).

$[\mathrm{HfMe_2\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}_2}]$ 1b. The reaction was performed in the same manner as described for preparation (*i*) of compound **1a**. The complex $[\mathrm{HfCl_2\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}_2}]$ (1.06 g, 1.42 mmol) in diethyl ether (25 cm^3) was treated with a 3.0 mol dm^{-3} solution of MgMeBr in diethyl ether (0.95 cm^3, 2.85 mmol), at 0 °C. After filtration, the filtrate was partially concentrated and stored at -25 °C overnight to yield colourless crystals of **1b** (0.91 g, 91%), m.p. 110–112 °C (Found: C, 54.5; H, 8.3; N, 3.9. $\mathrm{C_{32}H_{58}HfN_2Si_2}$ requires C, 54.5; H, 8.3; N, 3.95%); ν_{max}(Nujol) 1251s, 1234m, 1167s, 1153m, 1102s, 1051m, 1040m, 894vs, 848s, 836vs, 797s, 785vs, 750m, 677m, 534m, 479m, 431m and 342m cm^{-1}; $\delta_H(\mathrm{C_6D_6})$ 7.11 (6 H, s, $\mathrm{C_6H_3}$), 3.80 [4 H, spt, ^3J(HH) 6.78, $\mathrm{CH_3}$C*H*$\mathrm{CH_3}$], 1.35 [12 H, d, ^3J(HH) 6.83, C*H*$_3$CHC*H*$_3$], 1.21 [12 H, d, ^3J(HH) 6.73 Hz, C*H*$_3$CHC*H*$_3$], 0.41 (6 H, s, $\mathrm{CH_3}$) and 0.17 (18 H, s, $\mathrm{SiMe_3}$); *m*/*z* 691 (*M* − Me), 633 (*M* − $\mathrm{SiMe_3}$) and 73 ($\mathrm{Me_3Si}$).

$[\mathrm{ZrMe_2(\eta\text{-}C_5Me_5)\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}}]$ 2a. To a solution of $[\mathrm{ZrCl_2(\eta\text{-}C_5Me_5)\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}}]$ (0.92 g, 1.69 mmol) in diethyl ether (30 cm^3) was slowly added a 3.0 mol dm^{-3} solution of MgMeBr in diethyl ether (1.13 cm^3, 3.38 mmol) at 0 °C. After stirring for 36 h and removal of the solvent under reduced pressure, hexane (25 cm^3) was added and the mixture filtered. The filtrate was partially concentrated and stored at -25 °C overnight to give complex **2a** as colourless crystals (0.73 g, 85%), m.p. 147 °C (Found: C, 63.4; H, 9.1; N, 2.8. $\mathrm{C_{27}H_{47}NSiZr}$ requires C, 64.2; H, 9.4; N, 2.75%); ν_{max}(Nujol) 1249s, 1161s, 1098m, 885m, 863vs, 847vs, 786s, 735m, 681m, 473m and 350m cm^{-1}; $\delta_H(\mathrm{C_6D_6})$ 7.12 (3 H, s, $\mathrm{C_6H_3}$), 3.80 [2 H, spt, ^3J(HH) 6.79, $\mathrm{CH_3}$C*H*$\mathrm{CH_3}$], 1.87 (15 H, s, $\mathrm{C_5Me_5}$), 1.36 (6 H, d, ^3J(HH) 6.83, C*H*$_3$CHC*H*$_3$], 1.26 [6 H, d, ^3J(HH) 6.74 Hz, C*H*$_3$CHC*H*$_3$], 0.18 (9 H, s, $\mathrm{SiMe_3}$) and 0.08 (6 H, s, $\mathrm{CH_3}$); *m*/*z* 490 (*M* − Me) and 73 ($\mathrm{Me_3Si}$).

$[\mathrm{HfMe_2(\eta\text{-}C_5Me_5)\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}}]$ 2b. The reaction was performed by the same procedure as described for the preparation of complex **2a**. The complex $[\mathrm{HfCl_2(\eta\text{-}C_5Me_5)\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}}]$ (0.84 g, 1.33 mmol) in diethyl ether (30 cm^3) was treated with a 3.0 mol dm^{-3} solution of MgMeBr in diethyl ether (0.88 cm^3, 2.64 mmol) at 0 °C. After filtration, the filtrate was partially concentrated and stored at -25 °C overnight to yield colourless crystals of **2b** (0.72 g, 91%), m.p. 183–185 °C (Found: C, 54.7; H, 8.0; N, 2.4. $\mathrm{C_{27}H_{47}HfNSi}$ requires C, 54.75; H, 8.0; N, 2.35%); ν_{max}(Nujol) 1249m, 1160s, 1098m, 1040m, 869vs, 851vs, 788s, 683m, 476s and 334m cm^{-1}; $\delta_H(\mathrm{C_6D_6})$ 7.13 (3 H, s, $\mathrm{C_6H_3}$), 3.80 [2 H, spt, ^3J(HH) 6.79, $\mathrm{CH_3}$C*H*$\mathrm{CH_3}$], 1.90 (15 H, s, $\mathrm{C_5Me_5}$), 1.37 [6 H, d, ^3J(HH) 6.81, C*H*$_3$CHC*H*$_3$], 1.27 [6 H, d, ^3J(HH) 6.74 Hz, C*H*$_3$CHC*H*$_3$], 0.18 (9 H, s, $\mathrm{SiMe_3}$) and -0.08 (6 H, s, $\mathrm{CH_3}$); *m*/*z* 578 (*M* − Me), 520 (*M* − $\mathrm{SiMe_3}$) and 73 ($\mathrm{Me_3Si}$).

$[\mathrm{ZrCl(F)\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}_2}]$ 3a. A suspension of $[\mathrm{ZrCl_2\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}_2}]$ (1.00 g, 1.52 mmol) and $\mathrm{SnMe_3F}$ (0.28 g, 1.53 mmol) in dichloromethane (30 cm^3) was stirred, at room temperature, for 3 h. All the volatiles were removed under reduced pressure to yield complex **3a** as colourless crystals, after recrystallization from hexane (0.92 g, 94%), m.p. 136–138 °C (Found: C, 55.9; H, 8.0; F, 3.1; N, 4.3. $\mathrm{C_{30}H_{52}ClFN_2Si_2Zr}$ requires C, 56.05; H, 8.15; F, 2.95; N, 4.35%); ν_{max}(Nujol) 1252s, 1159s, 1102s, 1052m, 1038m, 892s, 844vs, 799s, 784vs, 752m, 708s, 615s, 601s, 524m and 370m cm^{-1}; $\delta_H(\mathrm{C_6D_6})$ 7.08 (6 H, m, $\mathrm{C_6H_3}$), 3.64 (4 H, m, $\mathrm{CH_3}$C*H*$\mathrm{CH_3}$), 1.42 (12 H, m, C*H*$_3$CHC*H*$_3$), 1.16 (12 H, m, C*H*$_3$CHC*H*$_3$) and 0.12 (18 H, m, $\mathrm{SiMe_3}$); $\delta_F(\mathrm{C_6D_6})$ 152.2 (s) and 113.6 (s); *m*/*z* 640 (M^+) and 248 $[\mathrm{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)}]$.

$[\mathrm{HfCl(F)\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}_2}]$ 3b. A mixture of $[\mathrm{HfCl_2\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}_2}]$ (1.00 g, 1.34 mmol) and $\mathrm{SnMe_3F}$ (0.24 g, 1.31 mmol) was treated in dichloromethane (30 cm^3) as described for complex **3a** to yield colourless crystals of **3b** (0.86 g, 88%), m.p. 127–129 °C (Found: C, 49.1; H, 7.1; F, 2.6; N, 3.9. $\mathrm{C_{30}H_{52}ClFHfN_2Si_2}$ requires C, 49.35; H, 7.2; F, 2.6; N, 3.85%); ν_{max}(Nujol) 1252s, 1169s, 1158s, 1103s, 1038m, 894s, 843vs, 799s, 785vs, 751m, 713s, 616s, 602s, 531m and 360m cm^{-1}; $\delta_H(\mathrm{C_6D_6})$ 7.08 (6 H, m, $\mathrm{C_6H_3}$), 3.69 (4 H, m, $\mathrm{CH_3}$C*H*$\mathrm{CH_3}$), 1.40 (12 H, m, C*H*$_3$CHC*H*$_3$), 1.18 (12 H, m, C*H*$_3$CHC*H*$_3$) and 0.12 (18 H, m, $\mathrm{SiMe_3}$); $\delta_F(\mathrm{C_6D_6})$ 118.6 (s) and 75.4 (s); *m*/*z* 730 (M^+) and 248 $[\mathrm{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)}]$.

$[\mathrm{ZrCl(F)(\eta\text{-}C_5Me_5)\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}}]$ 4a. A mixture of $[\mathrm{ZrCl_2(\eta\text{-}C_5Me_5)\{(2,6\text{-}Pr^i_2C_6H_3)N(SiMe_3)\}}]$ (1.10 g, 2.02 mmol) and $\mathrm{SnMe_3F}$ (0.37 g, 2.02 mmol) was treated in dichloromethane (30 cm^3) as described for complex **3a** to yield colourless crystals of **4a** (0.92 g, 86%), m.p. 122 °C (Found: C, 55.8; H, 7.8; F, 3.9; N, 2.6. $\mathrm{C_{25}H_{41}ClFNSiZr}$ requires C, 56.7; H, 7.8; F, 3.6; N, 2.65%); ν_{max}(Nujol) 1423m, 1251vs, 1171s, 871m, 843vs, 779s, 585s, 526m, 383m and 341m cm^{-1}; $\delta_H(\mathrm{C_6D_6})$ 7.06 (3 H, m, $\mathrm{C_6H_3}$), 3.48 (2 H, m, $\mathrm{CH_3}$C*H*$\mathrm{CH_3}$), 1.87

(15 H, m, C_5Me_5), 1.39 (6 H, m, CH_3CHCH_3), 1.19 (6 H, m, CH_3CHCH_3) and 0.32 (9 H, m, $SiMe_3$); $\delta_F(C_6D_6)$ 108.0 (s) and 78.1 (s); *m/z* 527 (M^+) and 248 [$(2,6\text{-}Pr^i{}_2C_6H_3)N(SiMe_3)$].

[$HfCl(F)(\eta\text{-}C_5Me_5)\{(2,6\text{-}Pr^i{}_2C_6H_3)N(SiMe_3)\}$] 4b. A mixture of [$HfCl_2(\eta\text{-}C_5Me_5)\{(2,6\text{-}Pr^i{}_2C_6H_3)N(SiMe_3)\}$] (1.25 g, 1.97 mmol) and $SnMe_3F$ (0.36 g, 1.97 mmol) was treated in dichloromethane (30 cm^3) as described for complex **3a** to give colourless crystals of **4b** (1.12 g, 92%), m.p. 113–115 °C (Found: C, 48.4; H, 6.4; F, 2.9; N, 2.3. $C_{25}H_{41}ClFHfNSi$ requires C, 48.7; H, 6.7; F, 3.1; N, 2.25%); ν_{max}(Nujol) 1250s, 1172s, 1113m, 1101m, 873vs, 781s, 755m, 711s, 586s, 571m, 526m, 367m and 331m cm^{-1}; $\delta_H(C_6D_6)$ 7.06 (3 H, m, C_6H_3), 3.52 (2 H, m, CH_3CHCH_3), 1.87 (15 H, m, C_5Me_5), 1.37 (6 H, m, CH_3CHCH_3), 1.21 (6 H, m, CH_3CHCH_3) and 0.31 (9 H, m, $SiMe_3$); $\delta_F(C_6D_6)$ 69.9 (s) and 36.3 (s); *m/z* 617 (M^+) and 248 [$(2,6\text{-}Pr^i{}_2C_6H_3)N(SiMe_3)$].

Crystallography

Crystal Data. *For complex* **1a**. $C_{32}H_{58}N_2Si_2Zr$, $M = 618.20$, orthorhombic, $a = 9.697(2)$, $b = 15.039(3)$, $c = 24.295(5)$ Å, $U = 3543(1)$ Å^3, space group $P2_12_12_1$, $Z = 4$, $D_c = 1.159$ g cm^{-3}, $F(000) = 1328$. Colourless crystals. Crystal dimensions 0.60 × 0.50 × 0.40 mm, μ(Mo-Kα) = 0.399 mm^{-1}.

For complex **2a**. $C_{27}H_{47}NSiZr$, $M = 504.97$, monoclinic, $a = 16.857(6)$, $b = 10.340(4)$, $c = 17.746(6)$ Å, $\beta = 115.27(2)°$, $U = 2797(2)$ Å^3, space group $P2_1/c$, $Z = 4$, $D_c = 1.199$ g cm^{-3}, $F(000) = 1080$. Colourless crystals. Crystal dimensions 0.50 × 0.50 × 0.40 mm, μ(Mo-Kα) = 0.449 mm^{-1}.

For complex **4a**. $C_{25}H_{41}ClFNSiZr$, $M = 529.35$, monoclinic, $a = 16.992(3)$, $b = 9.425(2)$, $c = 16.925(3)$ Å, $\beta = 91.11(3)°$, $U = 2710(1)$ Å^3, space group $P2_1/c$, $Z = 4$, $D_c = 1.297$ g cm^{-3}, $F(000) = 1112$. Colourless crystals. Crystal dimensions 0.70 × 0.30 × 0.20 mm, μ(Mo-Kα) = 0.567 mm^{-1}.

Data collection and processing. Intensity data for all the structures were collected by the ω–2θ scan method at 153(2) K on a Siemens AED2 four-circle diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) and according to the learnt-profile method.[14] For complex **1a**, of the 3677 reflections measured in the range $3.5 \leqslant 2\theta \leqslant 25°$, 3518 were unique and all used in the refinement; for **2a**, of the 6740 reflections measured in the range $3.5 \leqslant 2\theta \leqslant 22.5°$, 3626 were unique and all used in the refinement; for **4a**, of the 3610 reflections measured in the range $3.5 \leqslant 2\theta \leqslant 22.5°$, 3539 were unique and all used in the refinement.

Structure analysis and refinement. All the structures were solved by direct methods (SHELXS 90)[15] and refined *versus* F^2 by the least-squares method with all data (SHELXL 93).[16] For complex **1a**, the weighting scheme $w^{-1} = \sigma^2(F_o{}^2) + (0.0383P)^2 + (3.640P)$ with $P = (F_o{}^2 + 2F_c{}^2)^2/3$ was applied in the final cycles of the refinement. The converged residuals were $R1 = 0.032$ [for $I > 2\sigma(I)$] and $wR2 = 0.083$ (for all data). A final Fourier-difference map showed no electron density > 0.614 or < -0.300 e Å^{-3}. For **2a**, the weighting scheme $w^{-1} = \sigma^2(F_o{}^2) + (0.0297P)^2 + (2.203P)$ with $P = (F_o{}^2 + 2F_c{}^2)^2/3$ was applied. The converged residuals were $R1 = 0.026$ [for $I > 2\sigma(I)$] and $wR2 = 0.067$ (for all data). A final Fourier-difference map showed no electron density > 0.293 or < -0.317 e Å^{-3}. For **4a**, the weighting scheme $w^{-1} = \sigma^2(F_o{}^2) + (0.0440P)^2 + (5.749P)$ with $P = (F_o{}^2 + 2F_c{}^2)^2/3$ was applied. The converged residuals were $R1 = 0.035$ [for $I > 2\sigma(I)$] and $wR2 = 0.093$ (for all data). A final Fourier-difference map showed no electron density > 0.910 or < -0.409 e Å^{-3}. No absorption corrections were applied to **1a**, **2a** and **4a** as those based on ψ scans did not significantly improve the quality of the data. All non-hydrogen atoms in the three structures were refined anisotropically. The hydrogen atoms were included in ideal positions.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/220.

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