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Remarkably Robust Group 4 Metal Half-Sandwich Complexes Containing Two Higher Alkyl Ligands: X-ray Structure and Reactivity of the Di-*n*-butyl Complex $[\mathrm{Hf}(\eta^5{:}\eta^1{:}\eta^1\text{-}\mathrm{C_5Me_4SiMe_2NCH_2CH_2OMe})^n\mathrm{Bu_2}]$

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Summary: The reaction of LiR with $M(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$ *(**1**, M = Zr (**a**), Hf (**b**)) gives the isolable, thermally stable complexes* $M(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)R_2$ *(R = Et (**2**),* ^{n}*Pr (**3**),* ^{n}*Bu-(**4**)), which contain two alkyl ligands with β-hydrogen atoms.*

Alkyl ligands with β-hydrogen atoms at d^0 metal centers are of pivotal importance as models for the growing alkyl chain during oligo- and polymerization of ethylene at electrophilic metal centers.[1,2] Depending subtly on the nature of the metal center and on the ancillary ligand set, stabilization by steric constraint, agostic bonding, or decomposition through β-hydrogen elimination may occur. For instance, zirconocene di-*n*-butyl $[Zr(\eta^5\text{-}C_5H_5)_2{}^nBu_2]$, formed in situ by reacting $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$ with Li^nBu at low temperatures, is known to decompose to the 1-butene complex $[Zr(\eta^5\text{-}C_5H_5)_2(H_2C{=}CHEt)]$, which serves as a versatile source for the $Zr(\eta^5\text{-}C_5H_5)_2$ fragment.[3] More recently, the half-sandwich complex $[Zr(\eta^5\text{-}C_5H_5)^nBu_3(THF)_n]$ has been mentioned,[4] but like some hafnocene complexes with two higher alkyl ligands,[5−7] no full structural characterization has been undertaken. We report here the unexpectedly facile synthesis of thermally robust zirconium and hafnium complexes that contain two alkyl ligands with β-hydrogen atoms. The tridentate functionalized cyclopentadienyl ligand $C_5Me_4SiMe_2NCH_2CH_2OMe$[8] is used as a supporting ligand that acts as a substitute for the familiar bridged bis(cyclopentadienyl) ligand.

Reaction of the dichloro complexes $M(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$ (**1**, M = Zr (**a**), Hf (**b**)) with LiR gives dialkyl complexes of the type $M(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)R_2$ (R = Et (**2**), ^{n}Pr (**3**), ^{n}Bu(**4**)) as pentane-soluble, colorless crystals in good, reproducible yields (Scheme 1).[9] Generally, the thermal stability follows the order **a** < **b** and **2** < **3** < **4**. The most stable

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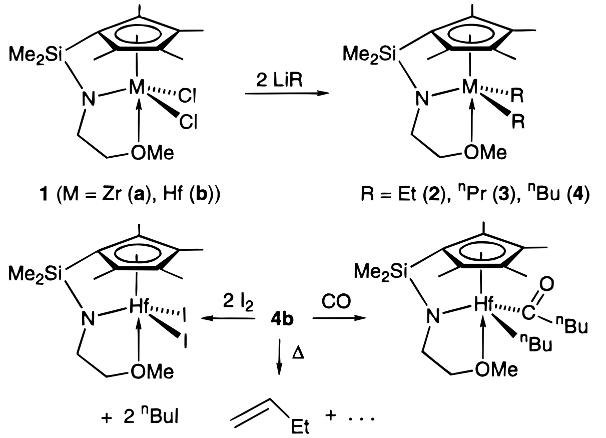
(9) $[Zr(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)^nBu_2]$ (**4a**): Li^nBu (1.0 mL of a 2.3 M solution in hexane) was added to a suspension of **1a** (0.48 g, 1.16 mmol) in hexane (30 mL) at 0 °C. After the mixture was stirred for 16 h at room temperature, all volatiles were removed *in vacuo*. The residue was extracted into pentane and filtered. Recrystallization from pentane at −78 °C afforded off-white crystals: yield 0.35 g (67%); mp 60 °C dec; ^1H NMR (400 MHz, C_6D_6, 298 K) δ −0.18 (m, 2 H, $ZrCH_2$), 0.41 (s, 6 H, $SiCH_3$), 0.54 (m, 2 H, $ZrCH_2$), 1.04 (t, 6 H, $^3J(H,H) = 7$ Hz, δ-CH_3), 1.20−1.50 (overlap. m, 8 H, β-, γ-CH_2), 2.06, 2.14 (s, 6 H, $C_5(CH_3)_4$), 3.10 ("t", 2 H, NCH_2), 3.42 (s, 3 H, OCH_3), 3.49 ("t", 2 H, CH_2O); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) δ 2.9 (q, $SiCH_3$, $^1J(C,H) = 117$ Hz), 11.3, 14.1 (q, $C_5(CH_3)_4$, $^1J(C,H) = 125$ Hz), 14.3 (q, δ-CH_3, $^1J(C,H) = 125$ Hz), 30.1 (t, β-CH_2, $^1J(C,H) = 124$ Hz), 30.7 (t, γ-CH_2, $^1J(C,H) = 124$ Hz), 45.9 (t, NCH_2, $^1J(C,H) = 133$ Hz), 51.0 (t, $ZrCH_2$, $^1J(C,H) = 112$ Hz), 60.8 (q, OCH_3, $^1J(C,H) = 143$ Hz), 79.4 (t, CH_2O, $^1J(C,H) = 142$ Hz), 96.8 (s, ipso $C_5(CH_3)_4$), 123.6, 125.4 (s, $C_5(CH_3)_4$); EI MS *m/z* 398 (10%, $[M - C_4H_9]^+$), 342 (100%, $[M - C_4H_8, - C_4H_9]^+$), 340 (48%, $[M - C_4H_9, - C_4H_{10}]^+$). Anal. Calcd for $C_{22}H_{43}NOSiZr$: C, 57.86; H, 9.42; N, 3.06. Found: C, 57.60; H, 9.25; N, 3.16. The compounds **2**, **3**, and **4b** were synthesized and isolated following a procedure analogous to that described for **4a**. **2a**: brown oil at room temperature; ^1H NMR (400 MHz, C_6D_6, 298 K) δ −0.14 (m, 2 H, $ZrCH_2$), 0.22 (s, 6H, $SiCH_3$), 0.50 (m, 2 H, $ZrCH_2$), 1.01 (m, 6H, β-CH_3), 2.10 (s, 12 H, $C_5(CH_3)_4$), 3.10 ("t", $^3J(H,H) = 6$ Hz, 2H, NCH_2), 3.30 (s, 3H, OCH_3), 3.40 ("t", $^3J(H,H) = 6$ Hz, 2H, CH_2O). **2b**: colorless crystals, 66% yield; ^1H NMR (400 MHz, C_6D_6, 298 K) δ −0.27 (m, 2H, $HfCH_2$), 0.42 (s, 6H, $SiCH_3$), 0.48 (m, 2 H, $HfCH_2$), 1.21 (t, $^3J(H,H) = 8$ Hz, 6 H, β-CH_3), 2.04, 2.16 (s, 6H, $C_5(CH_3)_4$), 3.11 ("t", $^3J(H,H) = 6$ Hz, 2 H, NCH_2), 3.34 (s, 3 H, OCH_3), 3.42 ("t", $^3J(H,H) = 6$ Hz, 2 H, CH_2O); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) δ 2.8 ($SiCH_3$), 11.3 ($C_5(CH_3)_4$), 11.6 ($HfCH_2$), 13.9 ($C_5(CH_3)_4$), 45.5 (NCH_2), 49.5 (β-CH_3), 60.6 (OCH_3), 79.5 (CH_2O), 97.5 (ipso $C_5(CH_3)_4$), 123.1, 124.1 ($C_5(CH_3)_4$); EI MS: *m/z* 460 (10%, $[M - C_2H_6]^+$), 431 (80%, $[M - 2C_2H_6]^+$). Anal. Calcd for $C_{18}H_{35}NOSiHf$: C, 44.31; H, 7.17; N, 2.87. Found: C, 44.19; H, 7.07; N, 2.76. **3a:** brown oil at room temperature, 77%. ^1H NMR (400 MHz, C_6D_6, 298 K) δ −0.14 (td, $^3J(H,H) = 12$ Hz, $^2J(H,H) = 5$ Hz, 2 H, $ZrCH_2$), 0.40 (s, 6H, $SiCH_3$), 0.60 (td, $^3J(H,H) = 12$ Hz, $^2J(H,H) = 5$ Hz, 2H, $ZrCH_2$), 1.14 (t, $^3J(H,H) = 7$ Hz, 6 H, γ-CH_3), 1.3−1.5 (m, 4 H, β-CH_2), 2.0, 2.09 (s, 6 H, $C_5(CH_3)_4$), 3.08 ("t", $^3J(H,H) = 6$ Hz, 2 H, NCH_2), 3.36 (s, 3 H, OCH_3), 3.47 ("t", $^3J(H,H) = 6$ Hz, 2H, CH_2O); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 2.9 ($SiCH_3$), 11.3, 14.1 ($C_5(CH_3)_4$), 21.9 ($ZrCH_2$), 46.0 (NCH_2), 54.8 (β-CH_2, γ-CH_3), 60.9 (OCH_3), 79.4 (CH_2O), 96.8 (C-ipso $C_5(CH_3)_4$), 123.7, 125.4 ($C_5(CH_3)_4$). **3b:** pale yellow needles, melting at room temperature, 63%; ^1H NMR (400 MHz, C_6D_6, 298 K) δ −0.37 (td, $^2J(H,H) = 12$ Hz, $^3J(H,H) = 5$ Hz, 2H, $HfCH_2$), 0.40 (s, 6 H, $SiCH_3$), 0.49 (td, $^2J(H,H) = 12$ Hz, $^3J(H,H) = 5$ Hz, 2H, $HfCH_2$), 1.16 (t, $^3J(H,H) = 6$Hz, 6H, γ-CH_3), 1.2−1.5 (m, 4H, β-CH_2), 2.04, 2.13 (s, 6H, $C_5(CH_3)_4$), 3.1 ("t", $^3J(H,H) = 6$ Hz, 2H, NCH_2), 3.33 (s, 3H, OCH_3), 3.42 ("t", $^3J(H,H) = 6$ Hz, 2H, CH_2O); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) δ 2.8 ($SiCH_3$), 11.2, 14.0 ($C_5(CH_3)_4$), 22.5 (γ-CH_3), 23.0 (β-CH_2), 45.5 (NCH_2), 60.7 (OCH_3), 64.7 ($HfCH_2$), 79.5 (CH_2O), 98.0 (ipso $C_5(CH_3)_4$), 123.3, 124.2 ($C_5(CH_3)_4$); EI MS *m/z* 474 (18%, $[M - C_3H_7]^+$), 432 (28%, $[M - C_3H_7 - C_3H_6]^+$), 431 (16%, $[M - 2C_3H_7]^+$), 430 (29%, $[M - C_3H_7 - C_3H_8]^+$). **4b:** colorless crystals, 55% yield; mp 90 °C dec; ^1H NMR (400 MHz, C_6D_6, 298 K) δ −0.47 (m, 2 H, $HfCH_2$), 0.42 (s, 6 H, $SiCH_3$), 0.49 (m, 2 H, $HfCH_2$), 1.06 (t, 6 H, $^3J(H,H) = 7$ Hz, δ-CH_3), 1.20 (m, 2 H, β-CH_2), 1.50 (overlapping m, 6 H, β-, γ-CH_2), 2.06, 2.14 (s, 6 H, $C_5(CH_3)_4$), 3.13 ("t", 2 H, NCH_2), 3.39 (s, 3 H, OCH_3), 3.45 ("t", 2 H, CH_2O); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) δ 2.8 (q, $SiCH_3$, $^1J(C,H)$ 117 Hz), 11.3, 13.9 (q, $C_5(CH_3)_4$, $^1J(C,H) = 125$ Hz), 14.3 (q, δ-CH_3, $^1J(C,H) = 123$ Hz), 31.1 (t, β-CH_2, $^1J(C,H) = 124$ Hz), 31.2 (t, γ-CH_2, $^1J(C,H) = 124$ Hz), 45.9 (t, NCH_2, $^1J(C,H) = 133$ Hz), 60.4 (t, $HfCH_2$, $^1J(C,H) = 110$ Hz), 60.8 (q, OCH_3, $^1J(C,H) = 144$ Hz), 79.6 (t, CH_2O, $^1J(C,H) = 141$ Hz), 97.4 (s, ipso $C_5(CH_3)_4$), 123.4, 124.2 (s, $C_5(CH_3)_4$); EI MS *m/z* 488 (26%, $[M - C_4H_9]^+$), 432 (83%, $[M - C_4H_8, - C_4H_9]^+$), 430 (100%, $[M - C_4H_9, - C_4H_{10}]^+$). Anal. Calcd for $C_{22}H_{43}NOSiHf$: C, 48.57; H, 7.91; N, 2.57. Found: C, 48.30; H, 7.75; N, 2.43.

S0276-7333(97)00446-9 CCC: $14.00

Scheme 1



member of the series, $[Hf(\eta^5:\eta^1:\eta^1-C_5Me_4SiMe_2NCH_2CH_2OMe)^nBu_2]$ (**4b**), decomposes in the solid state only above 90 °C, giving 1-butene as the sole volatile product detectable by GC−MS. Solutions of **2**−**4**, however, appear more thermally sensitive, although no transparent decomposition pathway has been identified so far by NMR spectroscopy. Iodinolysis of **4b** affords quantitative yields of 1-iodobutane along with the dark yellow diiodo homologue of **1b**.

A crystal structure determination of **4b** was performed.[10] The molecular structure of **4b** is depicted in Figure 1. The compound adopts a distorted-pseudo-trigonal-bipyramidal structure with the tetramethylcyclopentadienyl and methoxy groups occupying the apical positions. The two *n*-butyl groups are slightly turned away from the bulky ring ligand, one (C11−C14) exhibiting an antiperiplanar and the other (C15−C18) a synperiplanar conformation. The two *n*-butyl groups in the only other crystallographically authenticated di-*n*-butyl transition-metal complex, $[Mo(\eta^5-C_5H_5)_2{}^nBu_2]$, both show the energetically favored antiperiplanar conformation.[11] The two alkyl groups form an angle at the hafnium atom of 110.0(2)°. The hafnium−α-carbon bond lengths are 2.256(5) and 2.261(4) Å and are in the expected region for Hf−C(sp^3) bond distances.[12] The angles at the chemically equivalent α-carbons are 113.4(3) and 117.1(3)°. The average carbon−carbon distance found for the *n*-butyl groups is 1.51 Å. The tetramethylcyclopentadienyl ligand is bonded in a η^5 fashion, as judged by the sum of the angles at the ring (540°), and the hafnium−ring-carbon distances range from 2.445(4) to 2.606(4) Å. The hafnium−nitrogen bond length of 2.090(3) Å is in the typical range for an amido ligand bound at a d^0 hafnium center such as $[Hf\{N(SiMe_3)_2\}_3Cl]$ (2.04(1) Å) and $[Hf(\eta^5-C_5Me_5)_2(H)NHMe]$ (2.027(8) Å).[13] The sum of the angles at the nitrogen atom amounts to 359°, implying that the nitrogen atom adopts a trigonal-planar configuration and that the amido ligand functions as a three-electron donor. The hafnium−oxygen bond length of 2.380(3) Å is slightly larger than those found in hafnium complexes with THF, such as in $[Hf(\eta^5-C_5Me_5)_2CH_2CHMe_2(THF)]^+$ (2.221(6) Å).[5]

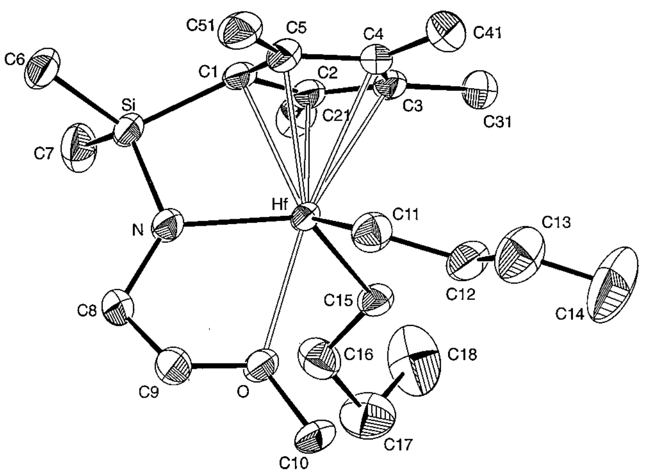


Figure 1. ORTEP diagram of the molecular structure of $[Hf(\eta^5:\eta^1:\eta^1-C_5Me_4SiMe_2NCH_2CH_2OMe)^nBu_2]$ (**4b**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Hf−C11, 2.256(5); Hf−C15, 2.261(4); Hf−N, 2.090(3); Hf−O, 2.380(3); Hf−Cp, 2.222(4) (Cp denotes the centroid of the ring C1−C5); C11−Hf−C15, 110.0(2); N−Hf−O, 70.11(12); Hf−C11−C12; 113.4(3); C16−C15−Hf, 117.1(3); C11−C12−C13, 114.5(5); C15−C16−C17, 116.2(5).

In the ^{13}C NMR spectrum of **4b**, the carbon attached to Hf is detected at δ 60.4 with $^1J(C,H) = 110$ Hz, whereas the resonance due to the β-carbon is found at δ 31.1 with $^1J(C,H) = 124$ Hz, indicating the absence of any agostic bonding.[1,2] The diastereotopic protons on the the α-carbon appear as a pair of multiplets at δ −0.47 and +0.49, whereas those on the β-carbon appear at δ +1.20 and +1.50 in the ^1H NMR spectrum. Initial experiments show that **4a** and **4b** do not react with hydrogen or ethylene under ambient conditions. Carbon monoxide, however, reacts with **4b** over a period of 20 h to give the monoacyl complex, characterized by the loss of the symmetry plane in the molecule and a ^{13}C NMR signal at δ 343.2, assigned to the η^2-acyl carbon.[14]

In the complexes described above, the tridentate ligand $C_5Me_4SiMe_2NCH_2CH_2OMe$ acts as a 10-electron ligand, involving a 3-electron amido and a 2-electron methoxy group. This electronic situation obviously

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(10) Crystal data for **4b**: $C_{22}H_{43}NOSiHf$, $M_r = 544.15$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.165(6)$ Å, $b = 10.984(4)$ Å, $c = 12.826(5)$ Å, $\alpha = 71.05(3)°$, $\beta = 73.61(4)°$, $\gamma = 65.80(4)°$, $V = 1217(1)$ Å^3, $Z = 2$, $D_c = 1.485$ g cm^{-3}, $F(000) = 552$, Mo Kα radiation ($\lambda = 0.710\ 71$ Å), μ(Mo Kα) = 4.346 mm^{-1}, empirical absorption correction. The structure was solved by heavy-atom methods and refined on F^2 using all data by a full-matrix least-squares procedure (SHELXL-93). H atoms at the α-carbon atom were refined in their position; all other H atoms were included in calculated positions with fixed isotropic parameters. Refinement details: crystal dimensions 0.5 × 0.5 × 0.4 mm, $T = 193(2)$ K, 5897 independent reflections for $3.0 \leq \theta \leq 28.0°$, $R = 0.0319$, $R_w = 0.0756$ for 5340 reflections with $I > 2\sigma(I)$, largest difference peak and hole 1.786 and −1.980 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center.

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(14) $[Hf(\eta^5:\eta^1:\eta^1-C_5Me_4SiMe_2NCH_2CH_2OMe)(CO^nBu)^nBu]$: ^1H NMR (C_6D_6) δ 0.35 (m, 2 H, HfCH_2), 0.53, 0.55 (s, 3 H, SiCH_3), 0.55−1.2 (overlapping m, 12 H, HfCH_2, β-, γ-CH$_2$), 0.89, 1.23 (t, $^3J(H,H) = 7$ Hz, 3 H, δ-CH$_3$), 1.32, 1.99, 2.26, 2.48 (s, 3 H, C$_5$(CH_3)$_4$), 2.5 (m, 2H, NCH_2), 2.69 (s, 3H, OCH_3), 2.7 (m, 2 H, CH_2O); ^{13}C NMR (C_6D_6) δ 2.8, 3.3 (SiCH$_3$), 10.6, 11.1, 14.2, 14.4 (C$_5$(CH$_3$)$_4$), 14.5, 14.6 (CH$_3$), 23.3, 26.2, 32.1, 33.4 (β- and γ-CH$_2$), 43.2 (COCH$_2$), 45.1 (NCH$_2$), 49.1 (HfCH$_2$), 58.8 (OCH$_3$), 79.1 (CH$_2$O), 98.6 (ipso C_5(CH$_3$)$_4$), 121.1, 121.2, 123.7, 125.3 (C_5(CH$_3$)$_4$), 343.2 (CO).

leads to the unusually effective blocking of β-hydrogen-elimination pathways within the sterically fairly open mono(cyclopentadienyl) coordination sphere.[15] In view of the technological importance of group 4 metal complexes with the linked amido−cyclopentadienyl ligand as a novel family of copolymerization catalysts of ethylene with α-olefins,[16] we are currently studying polymerization and activation mechanisms involving the afore mentioned derivatives.

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Supporting Information Available: Listings of all crystal data and refinement parameters, atomic parameters, including those of the hydrogen atoms, thermal parameters, and bond lengths and angles for **4b** (6 pages). Ordering information is given on any current masthead page.

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(15) If the additional chelation is absent as in the prototypal [Zr(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)Cl_2], the reaction with Li^{n}Bu does not result in the formation of thermally stable dialkyl derivatives. Amor, F.; Okuda, J., unpublished results.

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