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Divalent Diene and Triene Compounds of Zirconium and Hafnium; *X*-Ray Crystal Structures of [Hf(η^4-CH_2=CMe–CMe=CH_2)(PMe_3)$_2$$Cl_2$], [Zr($\eta^5$-$C_5H_5$)$_2$($PMe_3$)($\eta^2$-$C_7H_8$)], and {[Hf($\eta^7$-$C_7H_7$)($\eta^5$-$C_9H_7$)]$_2$($\mu$-$Me_2PCH_2CH_2PMe_2$)}

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The synthesis and reactions of divalent compounds [Hf(η^4-CH_2=CMe–CMe=CH_2)(PMe_3)$_2$$Cl_2$] and [M($\eta^6$-$C_7H_8$)($PMe_3$)$_2$$Cl_2$] (M = Zr, Hf) are described.

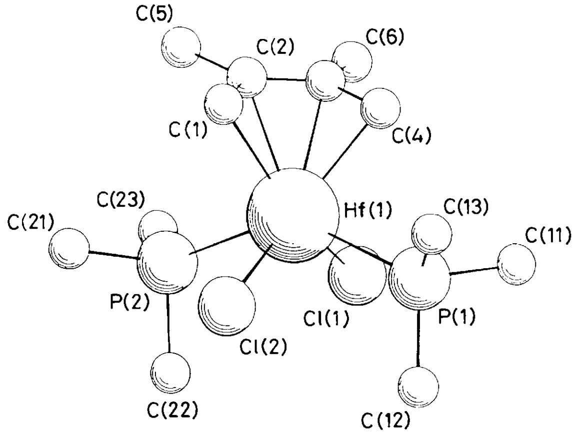

Figure 1. Molecular structure of (**2**). Selected bond lengths (Å) and angles (°): Hf–Cl(1) 2.444(1), Hf–Cl(2) 2.460(2), Hf–P(1) 2.712(2), Hf–P(2) 2.761(2), Hf–C(1) 2.307(5), Hf–C(2) 2.479(5), Hf–C(3) 2.4797(7), Hf–C(4) 2.307(8), C(1)–C(2) 1.463(9), C(2)–C(3) 1.38(1), C(3)–C(4) 1.448(9), C(2)–C(5) 1.54(1), C(3)–C(6) 1.48(1); Cl(2)–Hf–Cl(1) 118.49(5), P(1)–Hf–Cl(1) 83.52(6), P(2)–Hf–P(1) 140.92(5), Hf–C(1)–C(2) 78.8(3), C(1)–C(2)–C(3) 119.0(6).

Recently we have described the synthesis of the η-cycloheptatrienezirconium compounds [Zr(η^6-C_7H_8)$_2$] and the divalent [Zr(η^6-C_7H_8)(PMe_3)$_2$$Cl_2$] (**1**).[1,2] Here we describe the convenient laboratory scale syntheses of divalent η-triene and η-diene derivatives of zirconium and hafnium. When pure [$HfCl_4$] is reduced with sodium amalgam in the presence of PMe_3 and 2,3-dimethylbutadiene, air- and water-sensitive, orange crystals of [Hf(η^4-CH_2=CMe–CMe=CH_2)(PMe_3)$_2$$Cl_2$] (**2**) may be isolated in 50% yield. In a typical experiment, [$HfCl_4$] (4 g) with PMe_3 (2 g) and then 2,3-dimethylbutadiene (5 g) were stirred with sodium (0.6 g in 30 g of mercury) at room temperature for 14 h giving (**2**) (3.1 g). The crystal structure of (**2**) has been determined† and the molecular structure is shown in Figure 1, together with selected data. The short C(2)–C(3) bond distance of 1.38 Å indicates there is a strong contribution in the diene–metal bonding of the σ^2,π-metallocyclopentene resonance form rather than the η^4-diene form. The molecular structure determination and the solid state ^{13}C NMR (CP/MAS) spectrum show that the diene ligand is not symmetrically located with respect to the Hf(PMe_3)$_2$$Cl_2$ moiety. In contrast, the ^1H, ^{13}C, and ^{31}P NMR

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† *Crystal data* for (**2**): $HfC_{12}H_{28}P_2Cl_2$, M = 473.628, monoclinic, space group $P2_1/c$, a = 14.221(2), b = 10.065(1), c = 13.721(2) Å, β = 98.58(1)°, U = 1942.0 Å^3, D_c = 1.62 g cm^{-3}, Z = 4, μ = 57.5 cm^{-1}, $F(000)$ = 904, R = 0.022, R_w = 0.025 for 1968 observed reflections, $I > 3\sigma(I)$, λ(Mo-K_α) = 0.71069 Å.

For (**7**): $ZrC_{20}H_{27}P$, M = 389.6, orthorhombic, space group $Pbca$, a = 14.946(2), b = 15.385(2), c = 16.024(3) Å, U = 3684.7 Å^3, D_c = 1.405 g cm^{-3}, Z = 8, μ = 6.7 cm^{-1}, $F(000)$ = 1616, R = 0.032, R_w = 0.036 for 1820 observed reflections, $I > 3\sigma(I)$, λ(Mo-K_α) = 0.71069 Å.

For (**15**): $Hf_2C_{34}H_{48}P_2$, M = 875.7, triclinic, space group $P\bar{1}$, a = 8.100(2), b = 8.433(2), c = 12.672(3) Å, α = 101.26(2), β = 90.21(2), γ = 106.65(2), U = 811.7 Å^3, D_c = 1.79 g cm^{-3}, Z = 1, μ = 64.5 cm^{-1}, $F(000)$ = 426, R = 0.019, R_w = 0.021 for 3357 observed reflections, $I > 3\sigma(I)$, λ(Mo-K_α) = 0.71069 Å.

Data was collected using an Enraf-Nonius CAD4 diffractometer ($3 \leqslant \theta \leqslant 50$). The structures were solved from Patterson and Fourier synthesis and refined by full-matrix least-squares procedures, with anisotropic thermal parameters for all the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions. Crystallographic calculations were carried out using the Oxford CRYSTALS package.[10] Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

solution spectra‡ correspond to a symmetrical diene which presumably reflects a rotational fluxional motion about the metal–diene axis. It appears that (**2**) is a unique example of a divalent 14-electron hafnium compound. However, the presence of agostic C–H–Hf bonding cannot be wholly excluded and further structural studies are in progress.

Reduction of [MCl_4] (M = Zr or Hf) in the presence of PMe_3 and cyclohexa-1,3-diene gives purple crystals of [Zr(η^4-C_6H_8)(PMe_3)$_2$$Cl_2$] (**3**) in 18% yield or red crystals of [Hf(η^4-C_6H_8)(PMe_3)$_2$$Cl_2$] (**4**) in 34% yield, respectively. The NMR data are consistent with the structures proposed in Scheme 1, which are analogous to that of (**2**). The ^{31}P NMR of (**3**) shows an AB quartet at −90 °C corresponding to the lower symmetry found for (**2**).

The reduction using sodium amalgam of [$HfCl_4$] in the presence of trimethylphosphine and cycloheptatriene yields highly sensitive, orange crystals of [Hf(η^6-C_7H_8)(PMe_3)$_2$$Cl_2$] (**5**) in 46% yield. In a typical experiment, [$HfCl_4$] (8 g), PMe_3 (2 equiv.), and sodium amalgam (2 equiv.) at −78 °C were treated with C_7H_8 (20 cm^3) and stirred at room temperature for 16 h giving (**5**) (5.7 g). This is the first triene derivative of hafnium and is analogous to the previously reported compound (**1**).[2] In a series of preliminary experiments we have shown that the compounds (**1**), (**2**), (**3**), and (**5**) are likely to be precursors towards an extensive chemistry of low-valent compounds of zirconium and hafnium. For example, treatment of (**2**) with lithium indenide yields [Hf(η^5-C_9H_7)$_2$(η^4-CH_2=CMe–CMe=CH_2)] (**6**), which is similar to the previously described [Hf(η^5-C_5H_5)$_2$(η^4-CH_2=CMe–CMe=CH_2)].[3]

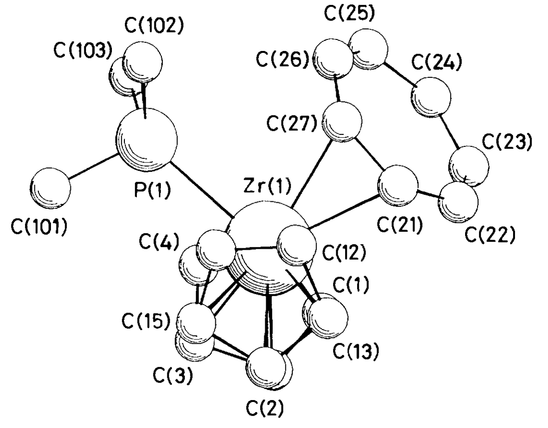

Figure 2. Molecular structure of (**7**). Selected bond lengths (Å) and angles (°): Zr–P(1) 2.726(2), Zr–C(1—5 mean) 2.500(3), Zr–C(11—15 mean) 2.51(3), Zr–C(21) 2.408(6), Zr–C(27) 2.418(6), C(21)–C(22) 1.47(1), C(22)–C(23) 1.33(1), C(23)–C(24) 1.46(1), C(24)–C(25) 1.48(1), C(26)–C(27) 1.47(1), C(27)–C(21) 1.406(9); Cp–Zr–Cp 129.3, Zr–C(21)–C(22) 123.3(4), Zr–C(21)–C(27) 103.9(5), P(1)–Zr–C(27) 80.4(2), P(1)–Zr–C(21) 114.3(2).

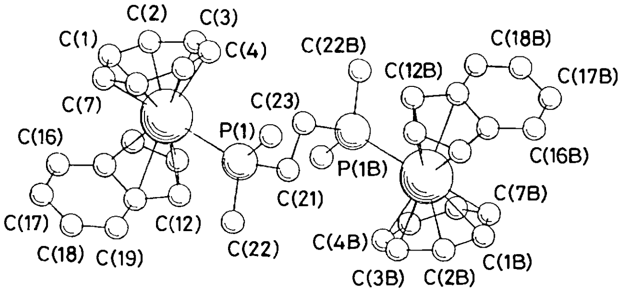

Figure 3. Molecular structure of (**15**). Selected bond lengths (Å) and angles (°): Hf–C(7 centroid) 1.730, Hf–C(indene centroid) 2.241, Hf–C(1—7 mean) 2.37(4), Hf–P(1) 2.7888(7), Hf–C(11) 2.573(3), Hf–C(12) 2.519(3), Hf–C(13) 2.521(3), Hf–C(14) 2.525(3), Hf–C(15) 2.589(3), P(1)–C(21) 1.850(3), C(21)–C(21B) 1.515(7); C(1—7)–Hf–C(11—15) 145.65, C(11—15)–C(15—19) 4.43, C(1)–Hf–P(1) 156.1(1), C(11)–Hf–P(1) 87.58(8), Hf–P(1)–C(21) 112.2(1), P(1)–C(21)–C(21B) 113.2(3).

Treatment of (**1**) or (**5**) with sodium cyclopentadienide at 22 °C produces compounds [Zr(η^5-C_5H_5)$_2$(PMe_3)(η^2-C_7H_8)] (**7**) (major) and (**8**), and [Hf(η^5-C_5H_5)$_2$(PMe_3)(η^2-C_7H_8)] (**9**) (major) and (**10**), respectively, each as an inseparable mixture of isomers (*ca*. 80 : 20). Only the NMR spectra of the major isomers could be fully assigned, and the structures proposed for the minor isomers (**8**) and (**10**) are inferred from the structures given for (**7**) and (**8**). A crystal was chosen from the mixture of (**7**) and (**8**), and the crystal structure was determined. This confirms the molecular structure to be that assigned to (**7**) from the NMR data. The molecular structure of (**7**) and selected data are given in Figure 2.† The η^2-C_7H_8 ligand in (**7**) is rare[4] but otherwise compound (**7**) is closely related to the recently reported [Zr(η^5-C_5H_5)$_2$(PMe_3)L], where L = η^2-C_2H_4 and η^2-*cis*-PhHC=CHPh.[5,6]

Treatment of (**1**) and (**5**) with lithium indenide gives [Zr(η^7-C_7H_7)(η^5-C_9H_7)] (**11**) and [Hf(η^7-C_7H_7)(η^5-C_9H_7)] (**12**), respectively. Compounds (**11**) and (**12**) react reversibly with trimethylphosphine giving the 18-electron compounds

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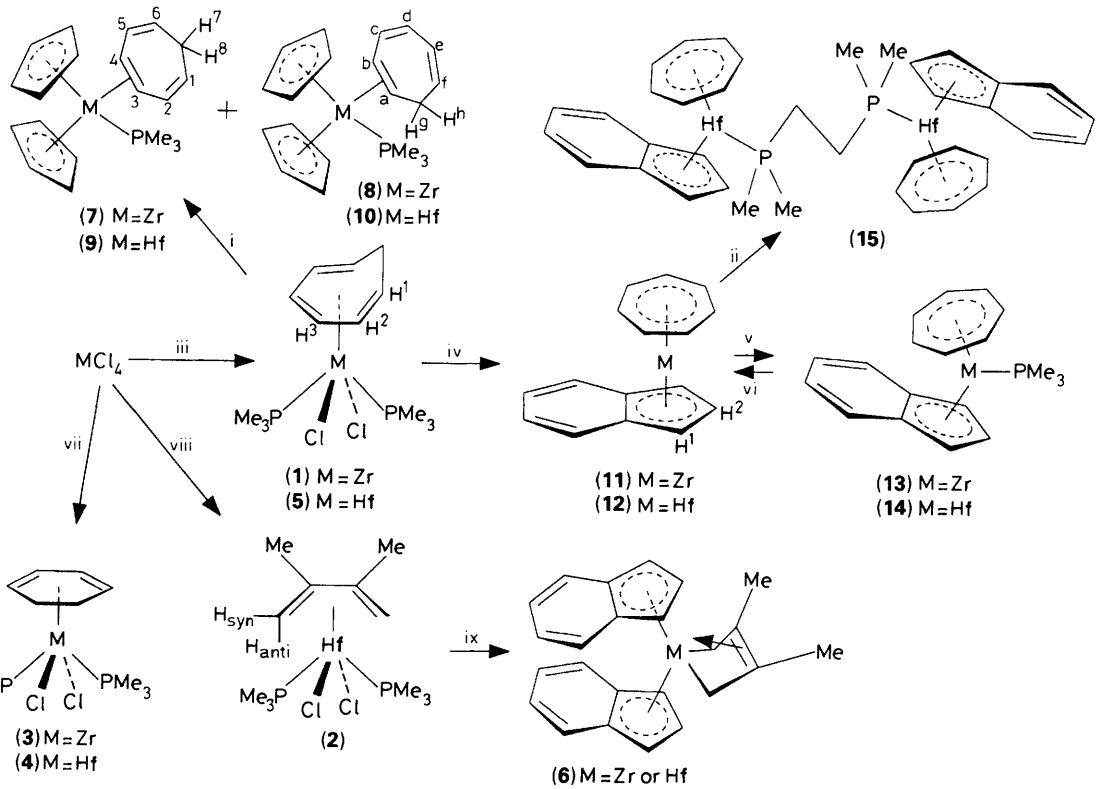
‡ *Selected n.m.r. data* (*J*/Hz, δ_P/p.p.m., Cp = η-C_5H_5). (**2**): δ_H(C_6D_6) 2.3 (6 H, s, 2 Me), 2.0 [2 H, d, *J*($H_{anti}H_{syn}$) 6, H_{syn}], 1.1 [18 H, d, *J*(PH) 6, 3 P–Me], 0.9 [2 H, d, *J*(PH) 6, H_{anti}]; δ_P(C_6D_6) −15.9 (1P, s). (**3**): δ_H ($C_6D_5CD_3$) 5.75 (2 H, m, C*H*), 3.25 (2 H, m, C*H*), 2.29 (2 H, m, CH*H*), 1.70 (2 H, m, CH*H*), 1.06 [18 H, t, *J*(PH) 6.2, 6 P–Me]; δ_P ($C_6D_5CD_3$) −24.55 (s). (**4**): δ_H (C_6D_6) 6.15 (2 H, m, C*H*), 2.97 (2 H, m, C*H*), 2.80 (2 H, m, CH*H*), 2.18 (2 H, m, CH*H*), 1.06 (18 H, t, *J*(PH) 3.4, 6 P–Me); δ_P (C_6D_6) −16.1 (s). (**5**): δ_H (C_6D_6) 5.90 (2 H, m, H^2), 5.15 (2 H, m, H^3), 4.03 (2 H, m, H^1), 1.52 [1 H, dt, *J*($H_{exo}H_{endo}$) 10, *J*(H^1H_{endo}) 7, H_{endo}], 1.34 [9 H, d, *J*(PH) 6, 3 P–Me], 1.04 [9 H, d, *J*(PH) 6, 3 P–Me], −0.48 (1 H, m, H_{exo}); δ_P (C_6D_6) −23.1 [1 P, d, *J*(PP) 71], −32.05 [1 P, d, *J*(PP) 71]. (**6**): δ_H ($C_6D_5CD_3$) 7.2 (4 H, m, H_{aryl}), 6.9 (4H, m, H_{aryl}), 5.34 [4 H, d, *J*(H^1H^2) 3.3, H^1], 4.39 [2 H, d, *J*(H^1H^2) 3.3, H^2], 1.77 (6 H, s), −0.1 (4 H, s). (**7**): δ_H (C_6D_6) 6.65 (1 H, m, $H^{1 \text{ or } 6}$), 6.15 (1 H, m, $H^{1 \text{ or } 6}$), 5.2 (1 H, m, $H^{5 \text{ or } 2}$), 5.05 [5 H, d, *J*(PH) 1.8, Cp], 4.90 [5 H, d, *J*(PH) 1.9, Cp], 4.75 (1 H, m, $H^{5 \text{ or } 2}$), 3.3 (2 H, m, H^3 and H^4), 2.25 (1 H, m, $H^{7 \text{ or } 8}$), 1.85 (1 H, m, $H^{7 \text{ or } 8}$); δ_P (C_6D_6) −1.3 (s). (**8**): δ_H (C_6D_6) 6.4 (1 H, m, H^f), 6.15 (obscured, m, H^d), 5.75 (1 H, m, H^c), 5.0 [6 H, d, *J*(PH) 1.6, Cp and H^e], 4.95 [5 H, d, *J*(PH) 1.4, Cp], 4.35 (1 H, m, H^a), 3.3 (partly obscured, m, H^b), 2.5 (1 H, m, $H^{g \text{ or } h}$), 2.0 (1 H, m, $H^{g \text{ or } h}$), 0.8 [partly obscured, *J*(PH) 5.6]; δ_P (C_6D_6) −2.8 (s). (**9**): δ_H (C_6D_6) 6.80 (1 H, m, $H^{1 \text{ or } 6}$), 6.20 (1 H, m, $H^{1 \text{ or } 6}$), 5.2 (1 H, m, $H^{5 \text{ or } 2}$), 5.01 [5 H, d, *J*(PH) 1.7, Cp], 4.90 [5 H, d, *J*(PH) 1.7, Cp], 4.75 (1 H, m, $H^{5 \text{ or } 2}$), 3.5 and 3.8 (2 H, m, H^3 and H^4), 1.9 (1 H, m, $H^{7 \text{ or } 8}$), 1.7 (1 H, m, $H^{7 \text{ or } 8}$); δ_P (C_6D_6) −13.0 (s). (**10**): δ_H (C_6D_6) 6.5 (1 H, m, H^f), 6.2 (obscured, m, H^d), 5.75 (1 H, m, H^c), 4.93 [5 H, d, *J*(PH) 2, Cp], 4.91 [5 H, d, *J*(PH) 2, Cp], 5.05 (partly obscured, m, H^a), 2.35 (1 H, m, $H^{g \text{ or } i}$), 1.7 (1 H, m, $H^{g \text{ or } i}$), 0.9 (obscured, 3 P–Me); δ_P (C_6D_6) −13.4 (s). (**11**): δ_H (C_6D_6) 7.2 (2 H, m, H_{aryl}), 6.7 (2 H, m, H_{aryl}), 5.6 [2 H, d, *J*(H^1H^2) 3.6, H^1], 5.4 [1 H, d, *J*(H^1H^2) 3.6, H^2] 5.0 (7 H, s, C_7H_7). (**12**): δ_H (C_6D_6) 7.15 (2 H, m, H_{aryl}), 6.7 (2 H, m, H_{aryl}), 5.58 [2 H, d, *J*(H^1H^2) 3.6, H^1], 5.32 [1 H, d, *J*(H^1H^2) 3.6, H^2], 4.89 (7 H, s, C_7H_7). (**13**): δ_H ($C_6D_5CD_3$) 7.17 (2 H, m, H_{aryl}), 6.84 (2 H, m, H_{aryl}), 5.62 [2 H, d, *J*(H^1H^2) 3.4, H^1], 5.26 [1 H, d, *J*(H^1H^2) 3.4, H^2], 4.32 (7 H, s, C_7H_7), 0.69 [9 H, d, *J*(PH) 4, 3 P–Me]; δ_P (C_7D_8) −51.6 (s). (**14**): δ_H ($C_6D_5CD_3$) 7.17 (2 H, m, H_{aryl}), 6.84 (2 H, m, H_{aryl}), 5.62 [2 H, d, *J*(H^1H^2) 3.2, H^1], 5.18 [1 H, d, *J*(H^1H^2) 3.2, H^2], 4.32 (7 H, s, C_7H_7), 0.69 [9 H, d, *J*(PH) 4.3, 3 P–Me]; δ_P (C_6D_6) −51.4 (s). (**15**): δ_H ($C_6D_5CD_3$) 7.16 (2 H, m, H_{aryl}), 6.74 (2 H, m, H_{aryl}), 5.60 [2 H, d, *J*(H^1H^2) 3.5, H^1], 5.31 [1 H, d, *J*(H^1H^2) 3.5, H^2], 4.32 (7 H, s, C_7H_7), 1.3 (4 H, m, 2 P–CH_2), 0.80 (12 H, s, 4 P–Me); δ_P (C_6D_6) −47.3 (s). Satisfactory microanalysis has been obtained for all new compounds except (**13**), which is thermally sensitive.



Scheme 1. *Reagents and conditions:* i, Na(C_5H_5) in tetrahydrofuran (THF) at room temp. for 12 h (Zr 64%, Hf 84%); ii, dmpe in toluene for 10 min at room temp. (92%); iii, 2 Na/Hg at −80 °C, gradual warm up then stirred at room temp. for 20 h (Hf 46%); iv, lithium indenide in THF for 20 h at room temp. (Zr 46%, Hf 67%); v, PMe_3 in toluene for 10 min at room temp. (>90%); vi, at 80 °C at 10^{-5} mmHg for 10 min then sublimation (Zr 40%, Hf 83%); vii, 2 Na/Hg at −80 °C, gradual warm up then stirred at room temp. for 20 h (Zr 18%, Hf 34%); viii, 2 Na/Hg at −80 °C, gradual warm up then stirred at room temp. for 20 h (52%); ix, lithium indenide in THF for 2 h at room temp. (75%).

[Zr(η^7-C_7H_7)(η^5-C_9H_7)(PMe_3)] (**13**) and [Hf(η^7-C_7H_7)(η^5-C_9H_7)(PMe_3)] (**14**).

Compound (**11**) also reacts with dmpe (bis-1,2-dimethylphosphinoethane) to form the bridged dimer {[Hf(η^7-C_7H_7)(η^5-C_9H_7)]$_2$(dmpe)} (**15**).

The crystal structure of (**15**) has been determined and the molecular structure is shown in Figure 3. The molecule has a bridging dmpe ligand and an η^5-C_9H_7 ligand, in preference to a 16-electron η^3-C_9H_7 arrangement.

In conclusion, the reactions and the structures proposed for the new compounds are shown in Scheme 1. It is clear that the divalent alkene-zirconium and -hafnium compounds are likely to be precursors to an extensive new chemistry of low-valent compounds of these metals. Most previous examples of divalent Zr and Hf compounds are stabilised by η-cyclopentadienyl[7] and η-pentamethylcyclopentadienyl[8] ligands: an exception being the divalent compound [Zr(η^4-C_6H_8)(dmpe)Cl_2]$_2$ which has been reported by Wreford.[9]

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