

## Enediamide Complexes of Hafnium; X-Ray Structure of $[(\text{C}_5\text{Me}_5)\text{Hf}(\text{Pr}^i\text{NCHCHNPr}^i)(\mu\text{-H})]_2$

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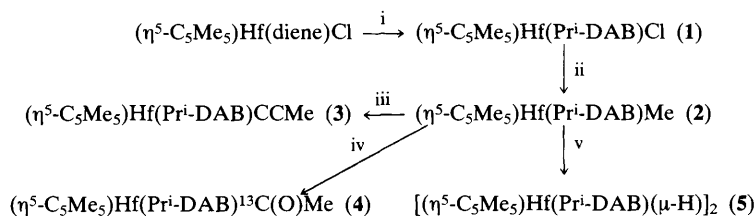
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The new hafnium complex  $(\eta^5\text{-C}_5\text{Me}_5)\text{Hf}(\text{Pr}^i\text{-DAB})\text{Cl}$  ( $\text{Pr}^i\text{-DAB} = N,N'$ -di-isopropyl-1,4-diazabuta-1,3-diene), containing an enediamide ancillary ligand, a precursor to methyl, propynyl, acyl and hydride derivatives is reported; the structure of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Hf}(\text{Pr}^i\text{-DAB})(\mu\text{-H})]_2$  has been determined by X-ray diffraction.

For the later transition metals, 1,4-diazadienes have been successfully employed as ligands, exhibiting a wide range of co-ordination modes.<sup>1</sup> Remarkably, their use as ancillary ligands for the early transition metals has been unexplored so far. Only a few diazadiene complexes of the Group 4 metals, formed through intramolecular C-C coupling of di-iminoacyls, are known.<sup>2</sup> In these compounds, the diazadiene is bound to the metal as an enediamide ligand, and as such they can be compared to the metallacyclopentene structures

adopted by the Group 4 metal buta-1,3-diene complexes  $\text{Cp}_2\text{M}(1,3\text{-diene})$  ( $\text{M} = \text{Zr}, \text{Hf}$ ;  $\text{Cp} = \text{C}_5\text{H}_5$ )<sup>3</sup> and  $(\eta^5\text{-C}_5\text{Me}_5)\text{M}(1,3\text{-diene})\text{Cl}$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ).<sup>4</sup> Here we report a new class of enediamide complexes of hafnium,  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Hf}(\text{Pr}^i\text{-DAB})\text{Cl}]$  ( $\text{Pr}^i\text{-DAB} = N,N'$ -di-isopropyl-1,4-diazabuta-1,3-diene), and its methyl, propynyl, acyl, and hydride derivatives.

When  $(\eta^5\text{-C}_5\text{Me}_5)\text{Hf}(2,3\text{-dimethylbuta-1,3-diene})\text{Cl}$ <sup>4</sup> is treated with free  $\text{Pr}^i\text{-DAB}$ , the diene ligand is smoothly

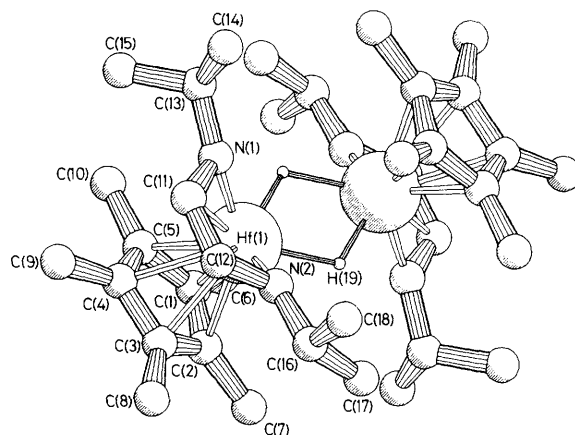


**Scheme 1.** Reagents and conditions: i, Pri-DAB, pentane, 20 °C; diene = 2,3-dimethylbuta-1,3-diene; ii, MeLi, Et<sub>2</sub>O, 0 °C; iii, MeC≡CH, [2H<sub>6</sub>]-benzene, 120 °C; iv, <sup>13</sup>C, [2H<sub>6</sub>]-benzene, 20 °C; v, H<sub>2</sub>, toluene, 100 °C.

displaced by the diazadiene, yielding the pale yellow enedi- amide complex (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Hf(Pri-DAB)Cl (1). Although an X-ray structure determination was thwarted by persistent crystal twinning, the enedi- amide character of the diazadiene ligand in (1) can be deduced from the marked upfield shift of the =CH- nuclei in <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra,<sup>†</sup> compared to diazadienes bound in a σ<sup>2</sup>-N,N'-4e fashion.<sup>‡</sup> The compound is soluble in pentane, ether, and aromatic solvents.

Complex (1) reacts with MeLi to give the methyl derivative (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Hf(Pri-DAB)Me (2). The <sup>13</sup>C n.m.r. resonance of the Hf-bound methyl group<sup>†</sup> in (2) lies at 20.7 p.p.m. higher field than in the corresponding 14e complex (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Hf(2,3-dimethylbuta-1,3-diene)Me.<sup>4</sup> This indicates that the metal centre in (2) is considerably less electron deficient, probably due to a significant amount of π-donation from the nitrogen lone pairs. Complex (2) reacts with propyne through hydrogen transfer to give methane and the alkynyl complex (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Hf(Pri-DAB)C≡CMe (3). Reaction of (2) with <sup>13</sup>CO initially gives the acyl complex (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Hf(Pri-DAB)<sup>13</sup>C(O)Me (4), identified by n.m.r.,<sup>†</sup> but this then reacts further to give an as yet unidentified compound, which is currently under investigation.

Complex (2) reacts with H<sub>2</sub> to produce the yellow hydride derivative [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Hf(Pri-DAB)(μ-H)]<sub>2</sub> (5), which is shown to be dimeric by X-ray diffraction<sup>§</sup> (Figure 1). The folded enedi- amido structure of the 'prone' [*i.e.* with the N(Pri)-groups pointed away from the (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)ligand] co-ordinated diazadiene ligand can be seen from the short C(11)-C(12) distance of 1.375(5) Å and the fold angle [between the Hf(1)-N(1)-N(2) and N(1)-C(11)-C(12)-N(2) planes] of 138.8°. The Hf-N distances in (5) are close to the 2.027(8) Å observed in (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Hf(NHMe)H<sup>5</sup>, in which a significant amount of π-donation appears to be present. The geometry of the Hf<sub>2</sub>H<sub>2</sub>-unit resembles that of the bridging arrangement in [(C<sub>5</sub>H<sub>4</sub>Me)<sub>2</sub>Zr(H)(μ-H)]<sub>2</sub>.<sup>6</sup>



**Figure 1.** Molecular structure of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Hf(Pri-DAB)(μ-H)]<sub>2</sub> (5). Selected distances (Å) and angles (°) are: Hf(1)-N(1) 2.058(4), Hf(1)-N(2) 2.075(4), Hf(1)-C(11) 2.523(5), Hf(1)-C(12) 2.510(4), C(11)-C(12) 1.375(7), N(1)-C(11) 1.390(6), N(2)-C(12) 1.389(7), Hf(1)-H(19) 2.06(5), Hf(1)-H(19A) 1.94(5), Hf(1) ··· Hf(1A) 3.3966(7), N(1)-Hf(1)-N(2) 86.4(2), Hf(1)-H(19)-Hf(1A) 64.(3), H(19)-Hf(1)-H(19A) 116.(3). The molecule contains a centre of symmetry. Suffix 'A' denotes symmetry related atom.

Based on these observations, 1,4-diazadienes appear to be useful ancillary ligands for early transition metals, allowing observation or isolation of species that are otherwise difficult to obtain in mono(pentamethylcyclopentadienyl) systems.

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<sup>†</sup> Selected spectroscopic data. <sup>1</sup>H n.m.r. (C<sub>6</sub>D<sub>6</sub>, 20 °C): (1), δ 5.35 (s, =CH-); (2), δ -0.30 (s, Hf-Me); (3), δ 1.64 (s, ≡C-Me); (4), δ 2.48 [d, <sup>2</sup>J<sub>CH</sub> 4.4 Hz, <sup>13</sup>C(O)Me]; (5), δ 8.89 (s, Hf-H). <sup>13</sup>C n.m.r. (C<sub>6</sub>D<sub>6</sub>, 20 °C): (1), δ 103.61 (d, 168.5 Hz, =CH-); (2), δ 33.32 (q, 112.3 Hz, Hf-Me); (3), δ 142.15 (s, Hf-C≡), 106.85 (s, ≡C-Me); (4), δ 343.31 (q, <sup>2</sup>J<sub>CH</sub> 4.4 Hz, <sup>13</sup>C(O)Me); i.r. (nujol, KBr): (3), 2095 cm<sup>-1</sup> (ν<sub>C≡C</sub>).

<sup>‡</sup> <sup>1</sup>H and <sup>13</sup>C n.m.r. resonances of the =CH- group in σ<sup>2</sup>-N,N' 4e bound DAB ligands around δ 8.0 and 160 p.p.m. respectively, see ref. 1b and references cited therein.

<sup>§</sup> Crystal data for (5): Hf<sub>2</sub>C<sub>36</sub>H<sub>64</sub>N<sub>4</sub>, M = 909.91, space group P $\bar{1}$ , a = 9.942(2), b = 10.667(1), c = 10.681(1) Å, α = 117.55(1), β = 103.88(1), γ = 100.64(1)°, U = 915.7(2) Å<sup>3</sup>, Z = 1, D<sub>c</sub> = 1.650 g cm<sup>-3</sup>, μ(Mo-Kα) = 56.4 cm<sup>-1</sup>. At 100 K 4764 reflections measured with I < 2.5σ(I) and corrected for absorption yielded R(F) = 0.026, R<sub>w</sub>(F) = 0.033 for 319 parameters. All hydrogen atoms were located and refined isotropically. Maximum residual electron density in final difference Fourier map: -0.95 and 0.79 e Å<sup>-3</sup> within 1.0 Å of the Hf atom. 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.