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Preliminary communication

Planar tetracoordinate carbon stabilized in a dimetallic hafnium/aluminium compound: formation and crystal structure of $Cp_2Hf[\mu\text{-}\eta^1:\eta^2\text{-}MeCC(C_6H_{11})][\mu\text{-}CC(C_6H_{11})]AlMe_2$

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Abstract

The reaction of $[Me_2AlC{\equiv}CR]_2$, **1** (R = cyclohexyl), with an equimolar quantity of Cp_2HfMe_2, **2** gave the dimetallic mixed metal complex $Cp_2Hf(\mu\text{-}\eta^1:\eta^2\text{-}MeCCR)(\mu\text{-}CCR)AlMe_2$, **3** and trimethylaluminium. An X-ray diffraction study of **3** revealed that it has a planar tetracoordinate carbon atom (C3) bridging between hafnium and aluminium. The four bond distances in the central plane to C3 are 1.280(9) [C3–C1], 1.562(8) [C3–C4], 2.091(6) [C3–Al], and 2.432(6) [C3–Hf] Å.

It is common knowledge that a tetrahedral coordination geometry is greatly favoured over other possible arrangements for carbon atoms involved in four σ-bonds [1]. However, the possibility of finding ways of obtaining stable, isolable compounds containing *e.g.* planar tetracoordinate carbon ("anti van 't Hoff/Le Bel compounds") has remained a great challenge over the years. Much effort went into trying to force all four σ-bonds to be coplanar by introduction of steric constraints but this was eventually unsuccessful [2]. The main methods of electronically stabilizing planar methane derivatives have been known for some time [3a]. Planar tetracoordinate carbon contains an electron-deficient σ-system (six electrons making a total of four bonds) and a doubly occupied p-orbital oriented normal to the σ-framework, and any suitable combination of σ-donor or π-acceptor ligands should enhance the stability. Various dimetallic methane derivatives have been calculated to have thermodynamically stable planar ground states (1,1-dilithiocyclopropane is an often-cited example) [3b]. There are even a few

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isolated molecular organometallic compounds known in which planar tetracoordinate carbon located in suitably substituted aromatic ring systems is stabilized by the combined electron donation by two σ-bonded metal centres (*e.g.* vanadium, lithium or zirconium) [4].

We have recently developed a specific way of preparing a novel class of organometallic compounds containing planar tetracoordinate carbon. These complexes contain a main group metal (Al) and a transition element (Zr) both bonded to the carbon center. The key step in our new synthesis was the addition of an Al-compound (such as $Cl-AlMe_2$ or $RC{\equiv}C-AlMe_2$) to a very reactive π-acetylene Group 4 metallocene complex generated *in situ* in the presence of the main group metal scavenger compound. By use of this fairly general synthetic approach [5] we have now prepared and structurally characterized the first mixed metal Al, Hf complex containing a central planar tetracoordinate carbon centre.

The reaction of Cp_2HfMe_2 **2** with $[Me_2AlC{\equiv}C(cyclo\text{-}C_6H_{11})]_2$ **1** in toluene at ambient temperature (20 h) gave a mixture of the novel dimetallic complex $Cp_2Hf[\mu\text{-}\eta^1:\eta^2\text{-}MeCC(cyclo\text{-}C_6H_{11})][\mu\text{-}CC(cyclo\text{-}C_6H_{11})]AlMe_2$ **3** and trimethylaluminium **4**. The latter was removed *in vacuo* and **3** was recrystallized from pentane at −30°C to give analytically pure (C,H) yellow crystals (64%), m.p. 141–143°C. The ^1H NMR spectrum of **3** [d_6-benzene] shows signals at δ 5.47 (s, 10 H, Cp), 3.00 (m, 1 H, cyclohexyl-CH), 2.66 (s, 3 H, Me), 2.29 (m, 1 H, cyclohexyl-CH), 1.87–1.03 (m, 20 H, cyclohexyl-CH_2) and −0.15 (s, 6 H, $AlMe_2$). Corresponding ^{13}C NMR signals [d_6-benzene] appear at δ 201.0 (Hf–C=), 153.6, 106.9 (2 quart.-C), 106.3 (Cp), 104.9 (quart.-C), 43.2, 32.7 (2 CH), 32.1, 31.4, 27.9, 26.9, 26.0, 25.2 (6 CH_2), 24.3 (Me) and −6.6 ($AlMe_2$). Complex **3** exhibits the typical IR bands of the bent metallocene unit at $\nu = 3094$, 1446, 1012 and 808 cm^{-1}. The bridging hydrocarbyl moieties give rise to CC stretching bands at $\nu = 2067$ (C≡C) and 1606 cm^{-1} (C=C).

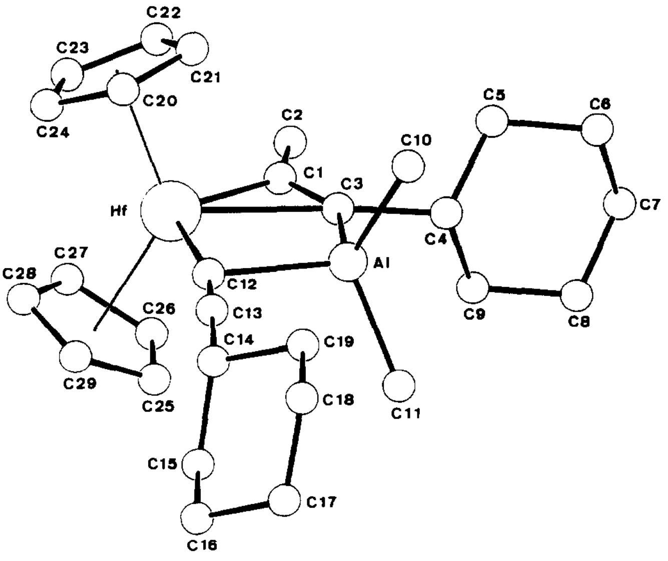

Fig. 1. Molecular structure of **3** showing the atom numbering scheme.

Table 1

Selected bond distances (Å) and angles (deg) for **3**

Hf–C1	2.120(6)	C12–Hf–C3	87.5(2)
Hf–C3	2.432(6)	C12–Hf–C1	119.3(2)
Hf–C12	2.310(6)	C3–Hf–C1	31.7(2)
Hf–C20	2.528(7)	C12–Al–C11	106.5(3)
Hf–C21	2.50(1)	C12–Al–C10	108.1(3)
Hf–C22	2.475(7)	C12–Al–C3	103.5(2)
Hf–C23	2.468(8)	C11–Al–C10	118.8(3)
Hf–C24	2.507(8)	C11–Al–C3	110.3(3)
Hf–C25	2.504(8)	C10–Al–C3	108.5(3)
Hf–C26	2.514(7)	C3–C1–C2	133.8(6)
Hf–C27	2.49(1)	C3–C1–Hf	87.7(4)
Hf–C28	2.501(8)	C2–C1–Hf	138.4(5)
Hf–C29	2.494(9)	C4–C3–C1	124.1(5)
Al–C3	2.091(6)	C4–C3–Al	92.5(3)
Al–C10	1.965(7)	C4–C3–Hf	175.0(4)
Al–C11	1.945(7)	C1–C3–Al	143.4(5)
Al–C12	2.087(6)	C1–C3–Hf	60.6(4)
C1–C2	1.53(1)	Al–C3–Hf	82.8(2)
C1–C3	1.280(9)	C13–C12–Al	104.7(5)
C3–C4	1.562(8)	C13–C12–Hf	168.9(5)
C12–C13	1.186(8)	Al–C12–Hf	86.0(2)
C13–C14	1.470(9)	C14–C13–C12	175.7(6)

The X-ray crystal structure of **3** reveals the presence of a central bicyclic ring system containing two unsaturated hydrocarbyl ligand systems bridging the hafnocene and the dimethylaluminium moieties (Fig. 1). The two metal centres (*d*(Al · · · Hf) = 3.004(2) Å) are connected through C12 (*d*(C12–Hf) = 2.310(6) Å, *d*(C12–Al) = 2.087(6) Å, angle Hf–C12–Al = 86.0(2)°) [6]. The (chair conformation) cyclohexyl-substituted alkynyl unit is nearly linear (Hf–C12–C13 168.9(5)°) with a C≡C triple bond between C12 and C13 (1.186(8) Å). The angle Al–C12–C13 is 104.7(5)°, and the relatively short distance Al · · · C13 of 2.649(6) Å indicates a bending of the moiety C12–C13 towards aluminium [7]. The dimethylaluminium unit (*d*(Al–C10) = 1.965(7) Å, *d*(Al–C11) = 1.945(7) Å, angle C10–Al–C11 = 118.8(3)°) forms a dihedral angle of 89° with the central heterometallic coplanar rings (max. deviation ± 0.02 Å).

The other bridging group can be described as an alkenyl ligand bonded η^2 to hafnium (*d*(C1–Hf) = 2.120(6) Å, *d*(C3–Hf) = 2.432(6) Å) and η^1 to aluminium (*d*(C3–Al) = 2.091(6) Å). This ligand bears a methyl substituent at C1 (*d*(C1–C2) = 1.53(1) Å) and a cyclohexyl ring (chair conformation) at C3 (*d*(C3–C4) = 1.562(8) Å). The C1–C3 double bond is rather short at 1.280(9) Å [8].

The extraordinary coordination geometry at C3 is the most remarkable structural feature of **3**. The carbon centre C3 features four bonds (to Hf, C1, C4 and Al) all lying perfectly in one plane. Bond angles around the planar tetracoordinate carbon atom C3 are 124.1(5)° (C4–C3–C1), 92.5(3)° (C4–C3–Al), 82.8(2)° (Al–C3–Hf) and 60.6(4)° (C1–C3–Hf): the sum of bonding angles at C3 is 360° [9*].

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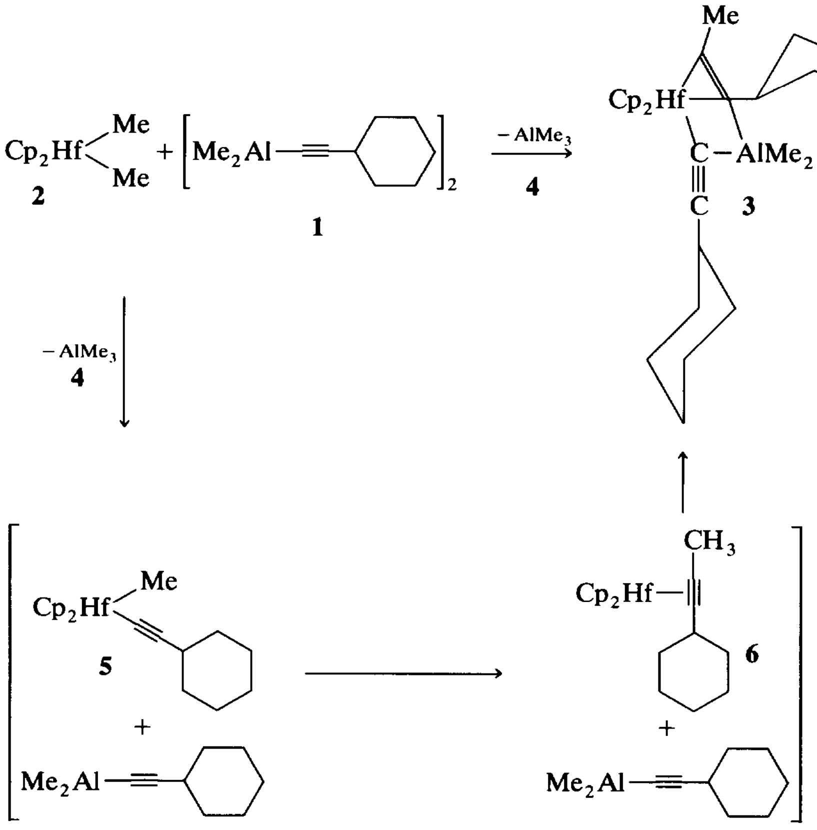
* Reference number with asterisk indicates a note in the list of references.



Scheme 1

A possible pathway to **3** is outlined in Scheme 1. $Cp_2Hf(Me)[CC(cyclo\text{-}C_6H_{11})]$ **5** and trimethylaluminium **4** are probably the initial products of the σ-metathesis reaction between Cp_2HfMe_2 **2** and a molar equivalent of dimethyl(cyclohexylethynyl)aluminium **1**. The alkynyl(methyl)hafnium compound **5** subsequently undergoes a reductive coupling reaction to give a reactive (η^2-alkyne)hafnocene complex **6**. This in turn is not stable in the presence of **1**. Addition of dimethyl(cyclohexylalkynyl)aluminium leads directly to formation of **3**. It is noteworthy that this addition to **6** does not produce a stable metallacyclopentadiene system, as commonly observed [10], but instead yields the very unusually-structured "dimetallabicyclic" complex **3** having a planar tetracoordinate carbon centre as part of one of the bridging ligand systems. That the formation of **3** appears to be thermodynamically favoured over its monocyclic metallacyclopentadiene isomer illustrates how effectively the combined action of a main group and early transition metal can serve in electronic stabilization of the "unnatural" planar geometry at tetracoordinate carbon.

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9 Crystal structure analysis of **3**: $C_{29}H_{41}AlHf$, MW = 595.1, crystal size 0.05 × 0.22 × 0.50 mm, a = 12.224(1), b = 8.403(1), c = 26.114(2) Å, β = 90.77(1)°, V = 2682.2 Å^3, d_{calc} = 1.47 g cm^{-3}, μ = 38.99 cm^{-1}, $F(000)$ = 1200 e, Z = 4, space group $P2_1/c$ (Nr. 14), Enraf–Nonius CAD4 diffractometer, λ = 0.71069 Å, 18083 measured reflections ($\pm h$, $+k$, $+l$), $[(\sin\theta)/\lambda]_{max}$ 0.74 Å^{-1}, empirical absorption correction: min = 0.760, max = 0.999, 8291 independent and 5931 observed reflections $[I > 2\sigma(I)]$, 280 refined parameters, R = 0.048, R_w = 0.039 $[w = 1/\sigma^2(F_0)]$, max. residual electron density 2.20 e Å^{-3}. The structure was solved by the heavy-atom method and the H-atom positions were calculated and kept fixed in the final least-squares refinement. Details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (Germany) giving the depository number CSD-56159, the names of the authors, and the journal citation.

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