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Divalent η-arene(bis-η-allyl) derivatives of zirconium and hafnium *

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Abstract

The synthesis of the η-diene derivatives [Hf(η-1-methylcyclohexa-1,5-diene)$(PMe_3)_2Cl_2$] and the divalent zirconium and hafnium compounds [Zr(η-C_6H_5R)(η-$C_3H_5)_2$], where M = Zr, R = H, or M = Hf, R = H, Me is described.

1. Introduction

We have recently reported diene compounds of zirconium and hafnium of the type [M(diene)$(PMe_3)_2Cl_2$] [1]. It was concluded that the diene ligands in these compounds were best described as bonding to the metal by the $\sigma^2\pi$ mode and, in consequence, the metal centre in these compounds is most appropriately described as d^0. Here we describe further reactions of these compounds that give η-arene-zirconium and -hafnium compounds. Previous examples of compounds of this type are [Zr_3Cl_6(η-C_6Me_6)]Cl [2], [Zr(η-arene)$_2(PMe_3)_2$] [3], [Zr(η-1,3,5-$^tBuC_6H_3)_2$] [4], [Zr(η-arene)$(AlCl_4)_2$] [5], [{Hf$(PMe_2Ph)_2I_2\}_2$(μ : η-arene)] [6], [Zr$(CH_2Ph)_3$(η-$C_6H_5BPh_3$)] [7] and [Zr(η-C_6H_5Me)$(PMe_3)_2Cl_2$] [1].

2. Results and discussion

The compounds [M(η-cyclohexa-1,3-diene)$(PMe_3)_2Cl_2$], (M = Zr, **1**, or Hf, **2**) were prepared by reduction of MCl_4 (M = Zr and Hf) in the presence of trimethylphosphine and cyclohexa-1,3-diene, as previously described. During an attempt to obtain improved yields of the compounds **1** and **2** it was found they were also formed when the cyclohexa-1,3-diene was replaced by cyclohexa-1,4-diene and despite the fact that an isomerisation reaction must have occurred, the yields were essentially the same. The related compound [Hf(η-1-methylcyclohexa-1,5-diene)$(PMe_3)_2Cl_2$] (**3**) was prepared in the manner used for **1** and **2** but using the diene 2-methylcyclohexa-1,4-diene. The compound **3**, and the other new compounds **4**, **5** and **6** described below, have been characterised by the analytical and spectroscopic data given in Table 1.

Treatment of the compound **1** with allylmagnesium bromide at 0°C gave dark green microcrystals of the bis-η-allyl derivative [Zr(η-C_6H_6)(η-$C_3H_5)_2$] (**4**) in 24% yield. The η-toluene compound [Hf(η-C_6H_5Me)(η-$C_3H_5)_2$] (**6**) has also been be prepared, by treatment of **3** with allylmagnesium bromide. The bis-η-allyl compounds **4**, **5** and **6** are soluble in petroleum ether; the solids and solutions rapidly decompose on exposure to air. Attempts to sublime the compounds in a vacuum led to decomposition. Repeated attempts to grow crystals suitable for X-ray diffraction studies were unsuccessful. The data in Table 1 do not permit distinction between structures in which the η-allyl groups adopt the V-up disposition shown in Scheme 1, or the opposite V-down disposition. The mechanism of the formation of the compounds **4–6** is not obvious.

The compounds are formally analogous to the "naked" nickel compound [Ni(η-$C_3H_5)_2$], in that the moiety Zr(η-arene) and the Ni atom are both 10-electron systems. However, treatment of **5–7** variously with ethene, propene and, especially, butadiene produced no evidence of reactions analogous to those of [Ni(η-$C_3H_5)_2$], and only slow decomposition was observed.

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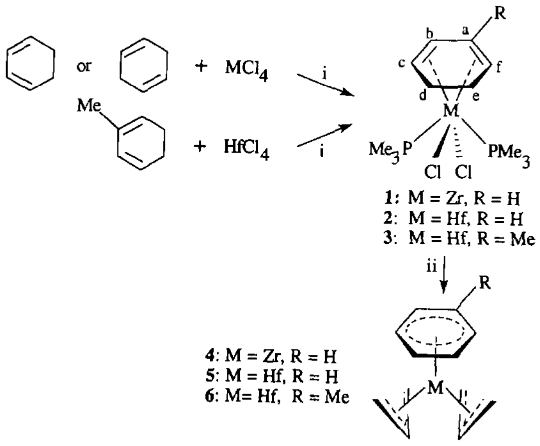

Scheme 1. (i) Na/Hg, 2PMe$_3$, 16 h, 20%–30%; (ii) allylmagnesium bromide, 0–10°C, 15 min.

The new reactions and the proposed structures are shown in the Scheme. Since the η^6-arene ligand is formally regarded as neutral, the formal oxidation state of the metal centre in the compounds **4**–**6** is two, *i.e.* the metals are divalent, d^2.

3. Experimental section

All manipulations and reactions were carried out under a dinitrogen (< 10 ppm oxygen or water) by use of standard Schlenk-vessel and vacuum-line techniques or in a dry box.

Solvents were pre-dried over activated 5 Å molecular sieves and then distilled under an atmosphere of dinitrogen from potassium (tetrahydrofuran), sodium (toluene), sodium–potassium alloy [light petroleum (b.p. 40–60°C) and diethyl ether] or phosphorus pentaoxide (dichloromethane), under dinitrogen. Deuterated solvents for NMR samples were stored in ampoules over activated molecular sieves (C_6D_6) or with sodium ([$^2H_8$] toluene) or dried over calcium hydride (CD_2Cl_2) and transfered by vacuum distillation.

The NMR spectra were recorded on a Bruker AM-300 [^{1}H (300 MHz), ^{13}C(75.43 MHz), ^{31}P (121 MHz)] and referenced internally to residual protio solvent resonances (^{1}H and ^{13}C) relative to tetramethylsilane ($\delta = 0$). Low resolution mass spectra were obtained on an AEI MS 302 mass spectrometer, updated by a data-handling system supplied by Mass Spectroscopy Services. Elemental analyses were performed by both the Analytical Laboratory in this Department and the Analytische Laboratorien (Gummersbach, Germany).

3.1. *Synthesis of [Hf(η^4-1-methyl-cyclohexa-1,5-diene)(PMe$_3$)$_2$Cl$_2$] (3)*

HfCl$_4$ (4 g, 12.5 mmol) in toluene (60 cm^3) was treated with two equivalents of PMe$_3$ (2.8 cm^3, 27 mmol) and the resulting mixture was stirred with sodium amalgam (0.6 g of Na in 30 cm^3 of Hg) in the presence of an excess of 2-methyl-1,4-cyclohexadiene (5 g, 53 mmol) for 16 h. After filtration and extraction of residue into toluene (25 cm^3) the volatiles were removed under reduced pressure. Extraction into petroleum ether (b.p. 40–60°C, 3 × 25 cm^3) gave a red

TABLE 1. Analytical and spectroscopic data

Compound [a]	NMR data [b]
3 [Hf(η^4-1-Me-cyclohexa-1,5-diene)-(PMe$_3$)$_2$Cl$_2$] [c] red C: 31.18 (31.5): H: 5.5 (5.69); Cl: 14.36 (14.3)	H^1: 6.17 (m, 1H, H$_b$); 3.2 (m, 1H, H$_{c\text{ or }f}$); 2.78 (m, 2H, H$_{d\text{ or }e\text{ endo}}$); 2.4 (s, 3H); 2.35 (m, 1H, H$_{c\text{ or }f}$); 2.25 (m, 2H, H$_{d\text{ and }e\text{ exo}}$); 1.07 (m, 18H) ^{13}C {H^1}: 125.6 (Cq$_a$); 116.5 (CH$_b$); 79.7 (CH$_{c\text{ or }f}$); 73.9 (CH$_{c\text{ or }f}$); 29.7 (CH$_{2\,d\text{ or }e}$); 28.6 (CH$_{2\,d\text{ or }e}$); 23.9 (C–*Me*) 12.9 (P–*Me*); 12.8 (P–*Me*) ^{31}P NMR: −15.9
4 [Zr(η^6-C$_6$H$_6$)(η-C$_3$H$_5$)$_2$] [e] dark green C: 56.96 (57.31); H: 6.03 (6.41)	H^1: 4.74 (tt, 2H, ^3J(H, H$_{cis}$) = 10 Hz, ^3J(H, H$_{trans}$) = 16 Hz); 3.68 (s, 6H); 3.28 (dm, 4H, ^3J(H, H$_{cis}$) = 10 Hz); 0.72 (dm, 4H, ^3J(H, H$_{trans}$) = 16 Hz) ^{13}C {H^1}: 108.7 (C–benzene); 94.3 (CH$_{allyl}$); 51.3 (CH$_2$)
5 [Hf(η^6-C$_6$H$_6$)(η-C$_3$H$_5$)$_2$] [e] purple C: 41.97 (42.55); H: 4.44 (4.76)	H^1: 4.53 (tt, 2H, ^3J(H, H$_{cis}$) = 9 Hz, ^3J(H, H$_{trans}$) = 15 Hz); 3.69 (s, 6H); 3.24 (dm, 4H, ^3J(H, H$_{cis}$) = 9 Hz); 0.63 (dm, 4H, ^3J(H, H$_{trans}$) = 15 Hz) ^{13}C: 105.2 (C-benzene, ^1J(CH) = 156 Hz); 91.7 (CH$_{allyl}$, ^1J(CH) = 176 Hz); 50.6 (CH$_2$, ^1J(CH) = 150 Hz)
6 [Hf(η^6-C$_6$H$_5$Me)(η-C$_3$H$_5$)$_2$] [f] red-purple C: 44.42 (44.26); H: 5.28 (5.14)	H^1: 4.47 (tt, 2H, ^3J(H, H$_{cis}$) = 7 Hz, ^3J(H, H$_{trans}$) = 16 Hz); 4.09 (m, 2H); 3.65 (m, 3H); 3.19 (dm, 4H, ^3J(HH*cis*) = 7 Hz); 1.0 (s, 34); 0.66 (dm, 4H, ^3J(H, H$_{trans}$) = 16 Hz) ^{13}C {H^1}; 117.4 (C$_{quat}$): 108.18; 104.56; 85.11; 83.5; 51.08 (CH$_2$); 21.1 (CH$_3$).

[a] Analytical data given as: found (calculated)%; [b] in C_6D_6. For labelling see Scheme 1; [c] MS m/z: 496 (M$^+$), 410 (M$^+$–PMe$_3$); [d] MS m/z: 252 (M$^+$); [e] MS m/z: 340 (M$^+$); [f] MS m/z 354 (M$^+$), 262 (M$^+$-toluene).

solution. The volume was reduced to *ca.* 30 cm^3 and the Schlenk vessel kept at −20°C; to give red crystals of [Hf(1-methyl-η^4-cyclohexadiene)($PMe_3)_2Cl_2$]. Yield, 1.7 g, 27%.

3.2. Synthesis of [$Zr(\eta$-$C_6H_6)(\eta$-$C_3H_5)_2$] (4)

The compound [Zr(η^4-cyclohexadiene)(PMe_3)Cl_2] (4 mmol) in Et_2O (15 cm^3) was added to a stirred solution of allymagnesium bromide (8.4 mmol in Et_2O) at 0°C. The mixture instantly became deep red-purple and a pale precipitate separated. After 15 min stirring the temperature was allowed to rise to 10°C. Further stirring and higher temperatures result in lower yields. After removal of the volatiles under reduced pressure, extraction with petroleum ether (b.p. 40–60°C) gave a red solution, which on slow cooling gave deep green microcrystals of the analytically-pure product in 21% yield. The analogues of **4**, namely **5** and **6**, were prepared in an essentially identical manner. The yields were 37%, **5** and 21%, **6**.

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References

1 G.M. Diamond, M.L.H. Green, N.M. Walker, J.A.K. Howard and S.A. Mason, *J. Chem. Soc., Dalton Trans.*, (1992) 2641.

2 E.O. Fischer and F. Röhrscheid, *J. Organomet. Chem.*, *6* (1966) 53; F. Stollmaier and U. Thewalt, *J. Organomet. Chem.*, *208* (1981), 327.

3 F.G.N. Cloke and M.L.H. Green, *J. Chem. Soc., Chem. Commun.*, (1979) 127.

4 F.G.N. Cloke, M.F. Lappert, G.A. Lawless and A.C. Swain, *J. Chem. Soc., Chem. Commun.*, (1987) 1667.

5 F. Calderazzo, P. Pallavicini and G. Pamalomi, *J. Chem. Soc., Dalton Trans.*, (1990) 1813.

6 F.A. Cotton, P.A. Kibala and W.A. Wojtczak, *J. Am. Chem. Soc.*, *113* (1991) 1462.

7 M. Bochmann, G. Kargar and A.J. Jaggar, *J. Chem. Soc., Chem. Commun.*, (1990) 1038.