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Preliminary communication

SYNTHESIS OF d^2 η-CYCLOHEPTATRIENYL-η-CYCLOHEPTADIENYL-ZIRCONIUM AND -HAFNIUM USING THE METAL VAPOURS

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Summary

Cocondensation of cycloheptatriene with zirconium or hafnium vapours gives, after vacuum pyrolysis of the reaction mixture the diamagnetic d^2 compounds $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$.

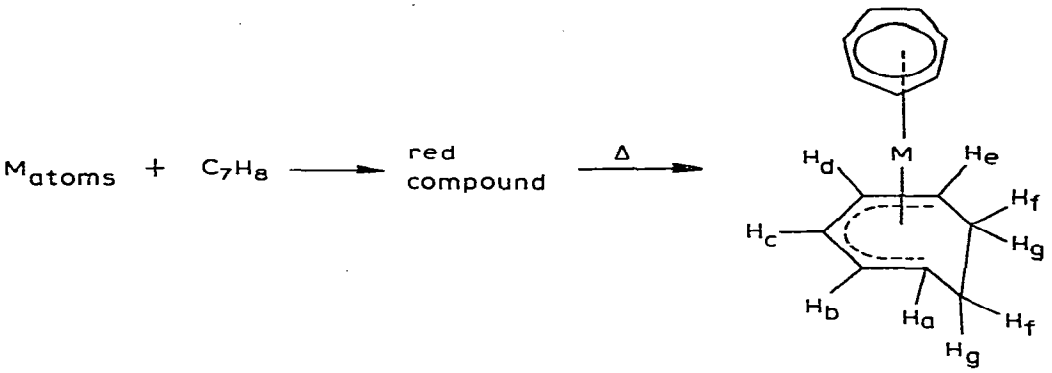
The divalent titanium compound $[Ti(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ has been prepared by cocondensation of titanium vapour with cycloheptatriene [1]. Divalent (d^2) compounds of zirconium and hafnium are rare and since we now have the facility to vaporise zirconium and hafnium [2] we set out to prepare the compounds $[M(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9]$ (I, M = Zr or Hf).

Hafnium (2700 °C) or zirconium (2750 °C) were evaporated from the water-cooled hearth of an electron-gun operating at a positive potential and the vapours were cocondensed with an excess of cycloheptatriene vapour at 77 K. Typically, 2.2 g of hafnium, from a premelted 10 g ingot, were evaporated over 4 h into 80 cm^3 of cycloheptatriene. After removal of the excess cycloheptatriene there remained a deep red oily residue. Prolonged cooling of a petroleum-ether (30—40°C) solution of this residue gave after several weeks a homogeneous red solid. The ^1H NMR spectrum (at 300 MHz) was extremely complex but showed that none of the compounds I were present. Microanalysis and a preliminary interpretation of the ^1H NMR spectrum suggests a stoichiometry such as $M(C_7H_8)_3$. Found: C, 54.21; H, 5.0. $C_{21}H_{24}Hf$ calcd.: C, 55.3; H, 5.3%.

Vacuum pyrolysis of the red residues at 120—160°C gave red sublimates which could be recrystallised from petroleum-ether (30—40°C) at −78°C giving the pure compounds I. Overall the yields were 15—20% based on metal entering the reaction zone in the cocondensation experiment.

The data characterising compounds I are given in Table 1. The ^1H NMR spectra, in particular, confirm the structure given in the diagram.

Compounds I are stable up to 150°C but are instantaneously decomposed by traces of either water or oxygen.



(I)

M = Hf, Zr

TABLE 1

ANALYTICAL AND PHYSICAL DATA OF COMPOUNDS I

Compound	Colour	Analysis (Found (calcd.) (%))		M/e
		C	H	
$Zr(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)$	Red-purple	61.2 (60.9)	5.3 (5.85)	274 $C_{14}H_{16}Zr^+$
$Hf(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)$	Orange-red	45.95 (46.35)	4.4 (4.45)	364 $C_{14}H_{16}Hf^+$

^{1}H NMR data[a, b]

5.69, 2, ddd ($J(H_aH_b)$ 11, $J(H_bH_c)$ 8, $J(H_bH_?)$ 1). H_bH_d; 5.27, 7, s, η-C_7H_7; 5.14, 2, complex, H_aH_e; 4.20; 1, tt ($J(H_cH_b)$ 8, $J(H_cH_a)$ 2) H_c; 2.22, 2, complex $2H_f$ or $2H_g$; 1.77, 2, complex, $2H_g$ or $2H_f$. I, M = Zr

5.77, 2, dd ($J(H_aH_b)$ 11.5, $J(H_bH_c)$ 8), H_bH_d; 5.10, 7, s, η-C_7H_7; 4.93, 2, complex, H_aH_e; 4.50, 1, tt ($J(H_cH_b)$ 8, $J(H_cH_a)$ 2) H_c; 2.22, 2, complex, $2H_f$ or $2H_g$; 1.70, 2, complex, $2H_g$ or $2H_f$. II, M = Hf

[a] Given as: δ, relative intensity, multiplicity (J given in Hz), assignment. Measured on a Bruker spectrograph at 300 MHz in C_6D_6. [b] ^{13}C NMR (C_6D_6): 118, 102.8 ($C_{b,d}$, $C_{a,e}$ or $C_{a,e}$ $C_{b,d}$); 82.5 (C_7H_7). 37.5 (CH_2CH_2), one band is absent; it may coincide with solvent.

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References

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