

Synthesis, Crystal Structure and Reactions of Zerovalent 16-electron Bis- η -cycloheptatrienezirconium

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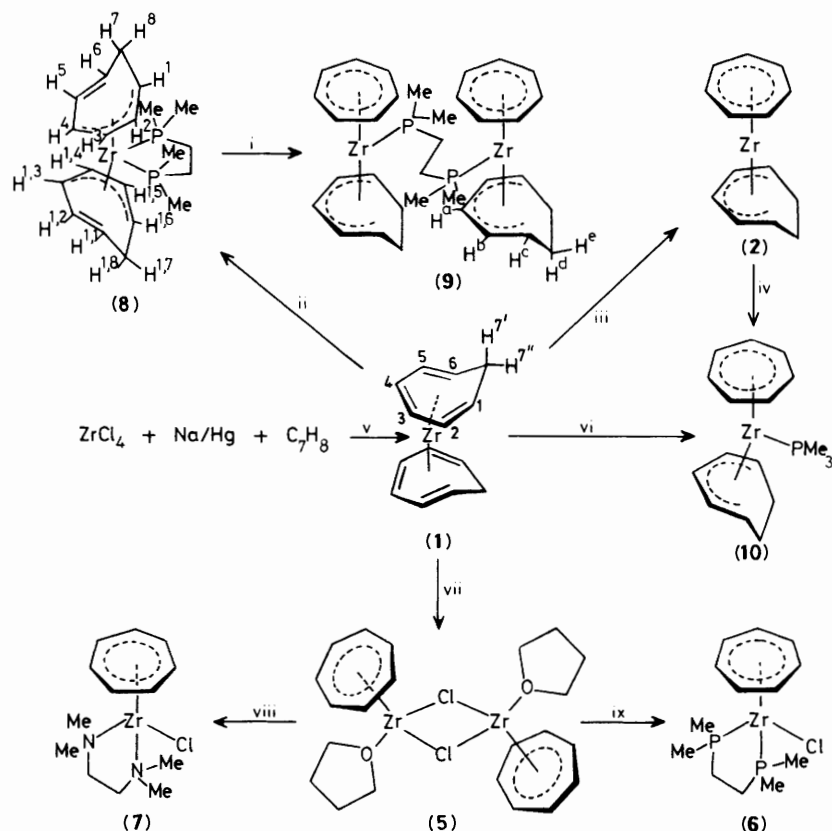
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Reduction of $ZrCl_4$ with sodium amalgam in the presence of cycloheptatriene gives $[Zr(\eta\text{-}C_7H_8)_2]$ which is a precursor to the compounds $[Zr(\eta\text{-}C_7H_7)(Me_2NCH_2CH_2NMe_2)Cl]$ and $[\{Zr(\eta\text{-}C_7H_7)(thf)\}_2(\mu\text{-}Cl)_2]$ (thf = tetrahydrofuran).

Zerovalent compounds of zirconium have only been described recently. The bis- η^6 -arene compounds $[Zr(1,3,5\text{-}C_6H_3Bu^t_3)_2]^1$ and $[Zr(\eta^6\text{-}C_6H_5Me)_2(PMe)_3]^2$ were prepared *via* zirconium atoms. Other zerovalent compounds include $[Zr(\text{butadiene})_2(\text{dmpe})]^3$ (dmpe = dimethylphosphinoethane),

$[Et_4N][(\eta^5\text{-}C_5H_5)Zr(CO)_4]^4$ and $[Zr(CO)_4\{1,1,1\text{-tris(dimethylphosphinomethyl)ethane}\}]^5$.

Here we report a one-pot high-yield synthesis of a 16-electron bis- η^6 -cycloheptatriene zirconium $[Zr(\eta^6\text{-}C_7H_8)_2]$ (1), which is a reactive precursor towards new organometallic



Scheme 1. Reagents and conditions: i, in toluene at room temp. for 12 h (40%); ii, dmpe in toluene at -10°C (>90%); iii, in toluene under CO (4 atm) (>90%); iv, PMe_3 in toluene for 2 h at room temp. (>90%); v, gradual warming from -78°C over 3 h in thf (45%); vi, PMe_3 , room temp., 12 h (>90%); vii, $[\text{Et}_2\text{AlCl}]_2$ in thf for 1 week (45%); viii, tmeda for 12 h in toluene (>90%); ix, dmpe for 12 h in toluene (>90%).

compounds of zirconium. Selected data characterising (1) and other new compounds are summarised in the footnote.[†] Reduction of ZrCl_4 in tetrahydrofuran (thf) using sodium amalgam at -10°C with cycloheptatriene under dinitrogen,

[†] Selected *n.m.r.* data (coupling constants in Hz; ^1H in C_6D_6). Compound (1): ^1H δ 5.9 (m, 4H, H^2 , H^3), 5.5 (ddd, 2H, $J_{5,7} 2$, $J_{5,6} 9$, $J_{5,4} 10$, H^5), 5.1 (m, 2H, H^4), 4.7 (m, 2H, H^1), 3.1 (m, 2H, H^4), 2.7 (ddd, 2H, $J_{7,7'} 12$, $J_{7',1} 8$, $J_{7',6} 2$, 2H, $\text{H}^{7'}$, H^{17}), 1.3 (br. d, H^7). Assignments supported by COSY45 and ^{13}C - ^1H shift correlation; elemental C, H analysis.

Compound (3): ^1H δ 6.1 (br. t, 1H, H^1), 5.8 (m, 1H, H^2), 5.3 (m, 1H, H^6), 4.8 (m, 1H, H^1), 4.7 (tt, 1H, H^5), 2.7 (m, 2H, $\text{H}^{7'}$, H^4), 1.6 (br. d, 1H, H^7). Assignments confirmed by COSY45.

Compound (5): supported by C, H, and Cl elemental analysis.

Compound (6): ^1H δ 5.3 (s, 7H, $\eta\text{-C}_7\text{H}_7$), 0.7 (br.m, 16H, dmpe), also supported by C, H, and Cl elemental analysis.

Compound (7): ^1H δ 5.26 (s, 7H, $\eta\text{-C}_7\text{H}_7$), 2.2 (s, 6H, CH_3N), 1.8 (m, 2H, CH_2N), 1.7 (s, 6H, CH_3N), 1.2 (m, 2H, CH_2N), also supported by C, H, and N elemental analysis.

Compound (8): ^1H δ 6.5 (br. t, 1H, $\text{H}^{1,1}$), 6.0 (br. t, 1H, H^2), 5.7 (br. q, 1H, H^4), 5.5 (t, 1H, $\text{H}^{1,2}$), 5.2 (m, 1H, H^1), 4.7 (m, 2H, $\text{H}^{1,3}$, $\text{H}^{1,4}$), 4.1 (m, 1H, H^5), 3.3 (m, 1H, H^7 or H^8), 3.0 (m, 1H, H^8 or H^7), 2.7 (t, 1H, H^3), 2.6 (br. t, 1H, $\text{H}^{1,1}$), 2.4 (m, 1H, H^6), 1.7 (m, 1H, $\text{H}^{1,6}$), 1.2 (m, 1H, $\text{H}^{1,7}$), 1.0 (d, 3H, $J_{\text{P,H}} 5$, PCH_3), 0.9 (br. m, 4H, PCH_2), 0.7 (d, 3H, $J_{\text{P,H}} 5$, PCH_3), 0.5 (d, 3H, $J_{\text{P,H}} 5$, PCH_3), 0.5 (m, 1H, H^8) and 0.2 (d, 3H, $J_{\text{P,H}} 5$, PCH_3); ^{31}P (thf) δ 2.7 (d, $J_{\text{P,P}} 32$), -15.4 (d, $J_{\text{P,P}} 32$), thermally unstable.

Compound (9): ^1H δ 5.4 (dd, 2H, $J_{\text{b,a}} 7$, $J_{\text{b,c}} 11$, H^b), 5.2 (m, 2H, H^c), 4.9 (d, 2H, $J_{\text{P,H}} 0.6$, H^c), 4.25 (dtt, 1H, $J_{\text{a-d,e}} 1.3$, $J_{\text{a-c,e}} 1.8$, $J_{\text{a,b}} 7.5$, H^a), 1.9 (m, 4H, $\text{H}^{\text{d,e}}$), 1.1 (m, 4H, CH_2P), 0.6 (s, 6H, $\text{CH}_3\text{-P}$); supported by C and H elemental analysis.

Compound (10): δ 5.3 (m, 4H, H^a), 4.8 (s, 7H, C_7H_7), 4.3 (p, $J_{\text{b,a}} 4$, H^b), 2.0 (m, 4H, $\text{H}^{\text{c,e}}$), 0.5 (d, 9H, $J_{\text{P,H}} 3$, P-CH_3), thermally unstable.

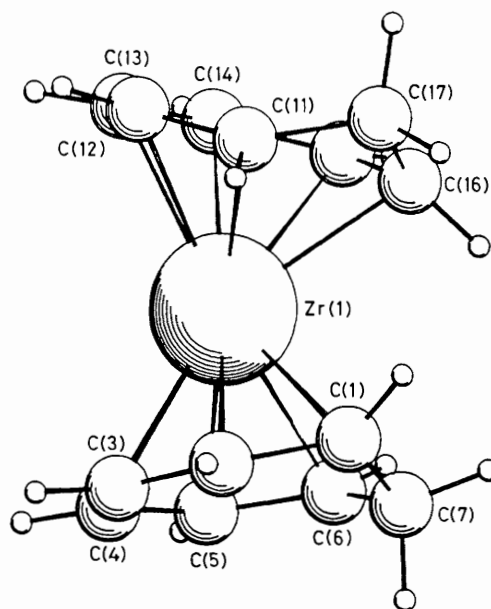


Figure 1. Crystal structure of (1). Selected bond distances (\AA): $\text{Zr-C}(1)$ 2.376(6), $\text{Zr-C}(2)$ 2.474(5), $\text{Zr-C}(3)$ 2.419(5), $\text{Zr-C}(4)$ 2.397(5), $\text{Zr-C}(5)$ 2.436(6), $\text{Zr-C}(6)$ 2.436(6), $\text{Zr-C}(7)$ 2.761(6), $\text{Zr-C}(11)$ 2.413(6), $\text{Zr-C}(12)$ 2.448(5), $\text{Zr-C}(13)$ 2.394(5), $\text{Zr-C}(14)$ 2.433(5), $\text{Zr-C}(15)$ 2.449(5), $\text{Zr-C}(16)$ 2.376(5), and $\text{Zr-C}(17)$ 2.761(6). Selected bond angles ($^{\circ}$): $\text{C}(1)\text{-C}(2)\text{-C}(3)$ 127.0(6), $\text{C}(2)\text{-C}(3)\text{-C}(4)$ 130.2(5), $\text{C}(3)\text{-C}(4)\text{-C}(5)$ 128.6(6), $\text{C}(4)\text{-C}(5)\text{-C}(6)$ 126.9(6), $\text{C}(5)\text{-C}(6)\text{-C}(7)$ 127.2(5), $\text{C}(6)\text{-C}(7)\text{-C}(8)$ 118.8(5), and $\text{C}(7)\text{-C}(1)\text{-C}(2)$ 121.6(6). Angle between best plane of $\text{C}(1)\text{-C}(6)$ to best plane of $\text{C}(11)\text{-C}(16)$ 25.6° .

with subsequent removal of volatile material, followed by extraction into light petroleum gives (1) in ca. 40% yield [typically 20 g of $ZrCl_4$ gives 8.5 g of (1)]. When the above reaction is carried out at room temperature an inseparable mixture of $[Zr(\eta^6-C_7H_8)_2]$ (1) and the previously described $[Zr(\eta^7-C_7H_7)(\eta^5-C_7H_9)]$ (2) is formed.

The crystal structure of (1) has been determined[‡] and shows an unusual bent arrangement with the dihedral angle between the best planes of the two C_7H_8 rings being 25.6° . The molecular structure of (1) and selected data are given in Figure 1.

Reduction of $TiCl_4$ in C_7H_8 with magnesium turnings gives a green crystalline product which the 1H n.m.r. spectrum shows to be a ca. 4:1 mixture of $[Ti(\eta^6-C_7H_8)_2]$ (3) and the previously described $[Ti(\eta^7-C_7H_7)(\eta^5-C_7H_9)]$ ⁶ (4). Solutions of (3) readily decompose to give (4) and it was not possible to isolate pure (3).

The reaction of (1) with $[AlEt_2Cl]_2$ in thf at room temperature gives insoluble black crystals, which the limited

data available suggest to be the compound $[(Zr(\eta^7-C_7H_7)(thf)_2(\mu-Cl)_2)]$ (5). The titanium analogue of (5) has been described and has an extensive chemistry.⁷ Preliminary studies of the chemical reactions of (5) which are given in Scheme 1, show that (5) can also lead to a potentially rich chemistry of the $Zr(\eta-C_7H_7)$ system and provide support for the proposed structure of (5). For example treatment of (5) with dmpe or tetramethylethylenediamine (tmeda) gives the turquoise compound (6) or the blue compound (7) respectively, in high yields. Further evidence that (1) is likely to be an excellent synthon for new zirconium chemistry arises from the reactions with tertiary phosphines giving (8), (9), and (10) as shown in Scheme 1.

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[‡] Crystal data for (1): $C_{14}H_{16}Zr$, $M = 275.5$, monoclinic, space group $P2_1/n$, $a = 8.400(4)$, $b = 11.486(6)$, $c = 11.999(3)$ Å, $\beta = 105.64(2)^\circ$, $U = 1115$ Å³, $Z = 4$, $D_c = 1.64$ g cm⁻³, $\mu(Mo-K_\alpha) = 9.32$ cm⁻¹, crystal size ca. $0.2 \times 0.2 \times 0.8$. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo- K_α radiation. Empirical absorption correction was applied and structure refinement and solution carried out using 1266 observed reflections with $I > 3\sigma(I)$ from 2914 independent reflections measured. The structure was solved by Patterson and Fourier methods. The hydrogen atoms were placed in calculated positions. Full-matrix least-squares refinement of 52 least square parameters has led to final agreement factors of $R = 0.0381$ and $R_w = 0.0444$. 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.