

Half-sandwich Compounds of Zirconium(II): The Synthesis of $[\text{Zr}(\eta^6\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2]$

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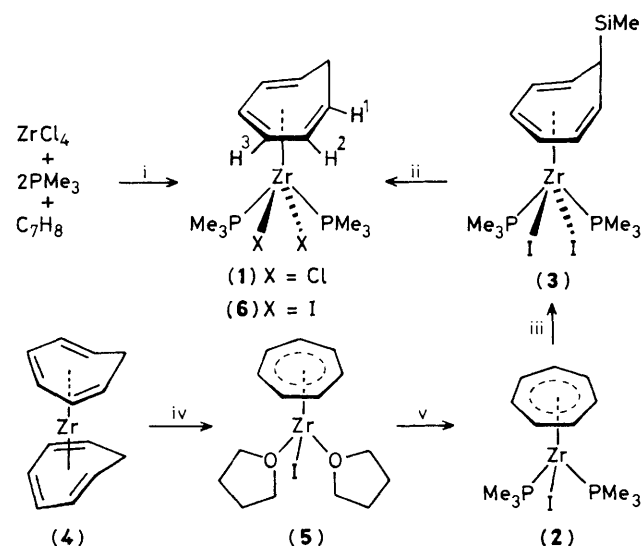
Reduction of $[\text{ZrCl}_4]$ in the presence of cycloheptatriene and PMe_3 forms $[\text{Zr}(\eta^6\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2]$ (1), and reaction of iodotrimethylsilane with $[\text{Zr}(\eta^7\text{-C}_7\text{H}_7)(\text{PMe}_3)_2\text{I}]$ (2), produced from $[\text{Zr}(\eta^6\text{-C}_7\text{H}_8)_2]$ (4) via $[\text{Zr}(\eta^7\text{-C}_7\text{H}_7)(\text{tetrahydrofuran})_2\text{I}]$ (5), forms $[\text{Zr}(\text{exo-}\eta^6\text{-C}_7\text{H}_7\text{SiMe}_3)(\text{PMe}_3)_2\text{I}]$ (3); the crystal structures of (1), (3), and (5) have been determined.

The chemistry of divalent molecular compounds of zirconium is relatively unexplored, the few examples being mainly limited to η -cyclopentadienyl compounds of the classes $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2]$ ¹ and $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_4\text{L}_4\text{X}]$.²

Here we report a convenient synthesis of a divalent

half-sandwich compound of zirconium, $[\text{Zr}(\eta^6\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2]$ (1), easily produced in multi-gram quantities. In a typical experiment $[\text{ZrCl}_4]$ (8 g, 34 mmol) in toluene was pretreated with two equivalents of trimethylphosphine (6.6 ml, 70 mmol) and the mixture was stirred with sodium amalgam (2 equiv.) in the presence of an excess of cycloheptatriene (10 ml, 96 mmol) for 24 h. Filtration followed by solvent reduction and then addition of light petroleum gave red crystals of (1) (yield 6.1 g, 44%).

Additional evidence for the structure proposed for (1) comes from the related compound $[\text{Zr}(\text{exo-}\eta^6\text{-}$



Scheme 1. Reagents and conditions: i, 2 Na/Hg at -80°C gradual warm up, stirred at room temp. for 24 h (colourless to red) (44%); ii, 100°C for 2 days (orange to green), >95% (by n.m.r.); iii, Me_3SiI in toluene for 30 min (green to orange) (81%); iv, I_2 in thf for 3 h (red to red) (17%), blue crystals; v, PMe_3 in toluene for 30 min (blue to green) (80%).

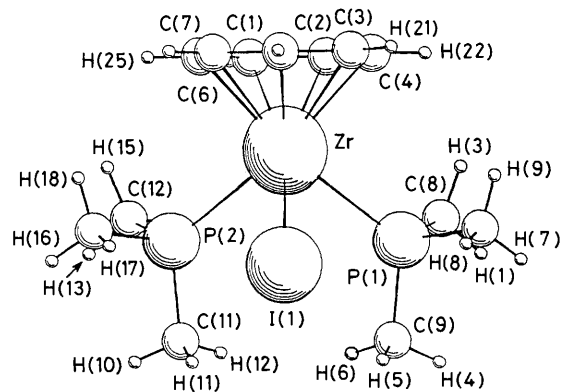


Figure 1. Molecular structure of (2). Selected bond distances (\AA): $\text{Zr}(1)\text{-I}(1)$ 2.939(1), $\text{Zr}(1)\text{-P}(1)$ 2.811(1), $\text{Zr}(1)\text{-P}(2)$ 2.807(1), $\text{Zr}(1)\text{-C}_7\text{H}_7(\text{centroid})$ 1.706, $\text{Zr}(1)\text{-C}(1\text{--}7)$, mean 2.36(1). Selected bond angles ($^\circ$): $\text{P}(1)\text{-Zr}(1)\text{-I}(1)$ 80.81(2), $\text{P}(2)\text{-Zr}(1)\text{-I}(1)$ 80.07(2), $\text{P}(2)\text{-Zr}(1)\text{-P}(1)$ 97.46(3), $\text{C}(1)\text{-Zr}(1)\text{-P}(1)$ 165.7(1), $\text{C}(1)\text{-Zr}(1)\text{-P}(2)$ 96.8(1).

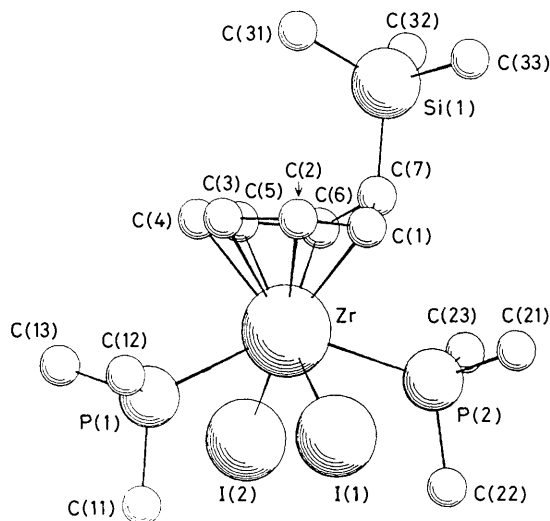


Figure 2. Molecular structure of (3). Selected bond distances (Å): Zr(1)–I(1) 2.944(1), Zr(1)–I(2) 2.936(1), Zr(1)–P(1) 2.788(2), Zr(1)–P(2) 2.819(1), Zr(1)–C(1) 2.384(5), Zr(1)–C(2) 2.463(6), Zr(1)–C(3) 2.428(6), Zr(1)–C(4) 2.426(5), Zr(1)–C(5) 2.477(5), Zr(1)–C(6) 2.423(5), Zr(1)–C(7) 2.791(5), C(1)–C(2) 1.383(8), C(2)–C(3) 1.394(9), C(3)–C(4) 1.42(1), C(4)–C(5) 1.40(1), C(5)–C(6) 1.38(1), C(6)–C(7) 1.507(7), C(1)–C(7) 1.528(7), Si(1)–C(7) 1.905(5). Selected bond angles (°): I(2)–Zr(1)–I(1) 104.17(2), P(1)–Zr(1)–I(2) 76.68(3), P(1)–Zr(1)–I(1) 77.90(4), P(2)–Zr(1)–I(1) 77.41(3), P(2)–Zr(1)–I(2) 78.87(4), P(2)–Zr(1)–P(1) 139.44(5).

$C_7H_7SiMe_3(PMe_3)_2I_2$ (3) whose crystal structure has been determined; the molecular structure is shown in Figure 1.† Compound (3) was prepared *via* the unusual route shown in Scheme 1. Thus treatment of the recently described $[Zr(\eta^6-C_7H_8)_2]$ (4)³ with iodine in tetrahydrofuran (thf) produces blue crystals of $[Zr(\eta^7-C_7H_7)(thf)_2I]$ (5) which on addition of PMe_3 yields dark green crystals of $[Zr(\eta^7-C_7H_7)(PMe_3)_2I]$ (2). The reaction of (2) with iodotrimethylsilane unexpectedly produces the *exo* substituted compound (3) in high yield. We assume that formation of (3) from (2) involves radical intermediates and note that treatment of $[Mo(\eta^7-C_7H_7)(CO)_2I]$ with iodotrimethylsilane gives the dimer $[Mo_2(\eta^7-C_7H_7)_2I_3]$.⁴ Compound (3) is thermally sensitive, and upon heating in toluene at 100 °C gave the compound (6),

† *Crystal data* for (2): $ZrC_{13}H_{25}P_2I$, $M = 461.42$, monoclinic, space group P_n , $a = 9.876(1)$, $b = 13.385(2)$, $c = 6.998(3)$ Å, $\beta = 92.79(2)^\circ$, $U = 923.9$ Å³, $D_c = 1.66$ g cm⁻³, $Z = 2$, $\mu = 23.9$ cm⁻¹, $F(000) = 425$, $R = 0.015$, $R_w = 0.017$ for 1884 observed reflections with $I > 3\sigma(I)$, $\lambda(Mo-K\alpha) = 0.71069$ Å; (3): $ZrC_{16}H_{34}I_2P_2Si$, $M = 661.50$, monoclinic, space group $P2_1/n$, $a = 11.225(2)$, $b = 26.887(5)$, $c = 8.708(2)$ Å, $\beta = 106.36(1)^\circ$, $U = 2521.8$ Å³, $D_c = 1.74$ g cm⁻³, $Z = 4$, $\mu = 30.22$ cm⁻¹, $F(000) = 1280$, $R = 0.028$, $R_w = 0.033$ for 2805 observed reflections with $I > 3\sigma(I)$, $\lambda(Mo-K\alpha) = 0.71069$ Å; (5): $ZrC_{15}H_{23}O_2I$, $M = 453.4$, orthorhombic, space group $Pbca$, $a = 8.891(5)$, $b = 16.817(6)$, $c = 22.43(1)$ Å, $U = 3354.0$ Å³, $D_c = 1.796$ g cm⁻³, $Z = 8$, $\mu = 24.64$ cm⁻¹, $F(000) = 1776$, $R = 0.027$, $R_w = 0.033$ for 2093 observed reflections with $I > 3\sigma(I)$, $\lambda(Mo-K\alpha) = 0.71069$ Å. Data were collected using an Enraf-Nonius CAD4 diffractometer ($3 \leq \theta \leq 50$). The structures were solved from Patterson and Fourier syntheses and refined by full-matrix least squares procedures, with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions. Crystallographic calculations were carried out using the Oxford CRYSTALS package.⁶ 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.

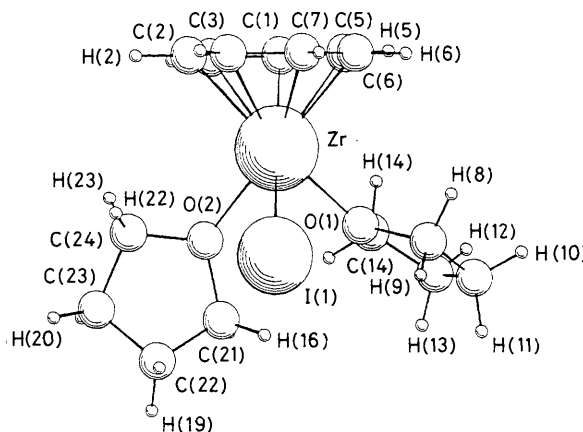


Figure 3. Molecular structure of (5). Selected bond distances (Å): Zr(1)–I(1) 3.003(1), Zr(1)–O(1) 2.321(3), Zr(1)–O(2) 2.329(3), Zr(1)–C₇H₇(centroid) 1.696, Zr(1)–C(1–7, mean) 2.34(1). Selected bond angles (°): O(1)–Zr(1)–I(1) 87.16(9), O(2)–Zr(1)–O(1) 77.8(1), O(2)–Zr(1)–O(1) 77.8(1), C(1)–Zr(1)–O(1) 159.5(2), C(1)–Zr(1)–O(2) 122.1(2).

identified by the ¹H n.m.r. spectrum which is analogous to that of (1).‡

The crystal structures of (2) and (5) have also been determined.† The molecular structures of (2) and (5) are shown in Figures 2 and 3 together with important distances and angles. The compounds (2) and (5) are the first structurally characterised $\eta^7-C_7H_7$ half-sandwich compounds of zirconium. Previously the crystal structure of $[Zr(\eta^7-C_7H_7)(\eta^5-C_5Me_5)]$ has been reported.⁵

In conclusion, we have described the facile synthesis of a new class of half-sandwich ($\eta^7-C_7H_7$)–zirconium(II) compounds which have a clear potential for the further development of low-valent zirconium chemistry.

Received, 7th March 1988; Com. 9/00994I

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‡ *Selected n.m.r. data* (coupling constants in Hz): Compound (1); $\delta_H(C_7D_8)$ 5.75 (2H, m, H²), 5.26 (2H, m, H³), 4.10 (2H, m, H¹), 1.41 [1H, dt, $J(H^{exo}H^{endo})$ 11, $J(H^1H^{endo}$ 7, H^{endo}), 1.27 [9H, d, $J(PH)$ 6, 3 P–Me], 0.99 [9H, d, $J(PH)$ 6, 3 P–Me], –0.11 [1H, m, H^{exo}]; $\delta_P(C_6D_6)$ –25.9 [1P, d, $J(PP)$ 70], –30.3 [1P, d, $J(PP)$ 70]. (2) $\delta_H(C_7D_8)$ 5.00 (7H, s, C₇H₇), 0.84 (18H, brs, 3P–Me); $\delta_P(C_7D_8)$ –50.9 [1P, s], (3) $\delta_H(C_7H_8)$ 5.59 (2H, m, H²), 5.15 (2H, m, H³), 4.34 (2H, m, H¹), 1.58 (9H, brs, 3P–Me), 1.20 [1H, brt, $J(H^1H^{endo})$ 7, H^{endo}], 1.17 [9H, brd, $J(PH)$ 7, 3P–Me], –0.27 (9H, s, 3 Si–Me); δ_P –26.5 [1P, brs], –43.7 [1P, brs]. (6) $\delta_H(C_6D_6)$ 5.73 (2H, m, H²), 5.34 (2H, m, H³), 3.94 (2H, m, H¹), 1.53 [9H, d, $J(PH)$ 6, 3P–Me], 1.25 [1H, m, H^{endo}], 1.17 [9H, d, $J(PH)$ 6, 3P–Me], 0.09 [1H, m, H^{exo}]; δ_P –28.15 [1P, d, $J(PP)$ 35], –41.45 [1P, d, $J(PP)$ 35]. Satisfactory microanalysis was obtained on all compounds, except (6).