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Preliminary communication

## Convenient one-pot synthesis of half-sandwich $\eta$ -cycloheptatrienyl and $\eta$ -toluene derivatives of the metals titanium and zirconium; crystal structure of $[\text{Zr}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{PMe}_3)_2\text{Cl}_2]$ \*

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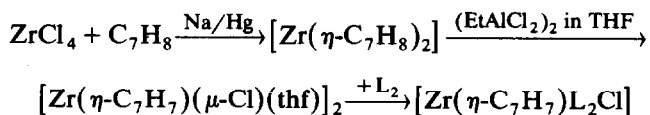
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### Abstract

The compounds  $[\text{M}(\eta^7\text{-C}_7\text{H}_7)\text{L}_2\text{Cl}]$  ( $\text{M} = \text{Ti}$ ;  $\text{L}_2 = (\text{PMe}_3)_2$ ,  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ ,  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ .  $\text{M} = \text{Zr}$ ;  $\text{L}_2 = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ ) and the  $\eta^6$ -arene derivative  $[\text{Zr}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{PMe}_3)_2\text{Cl}_2]$  have been prepared in a one-pot reduction of  $\text{MCl}_4$  in the presence of  $\text{L}_2$  and an excess of cycloheptatriene or toluene, respectively. The crystal structure of  $[\text{Zr}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{PMe}_3)_2\text{Cl}_2]$  has been determined.

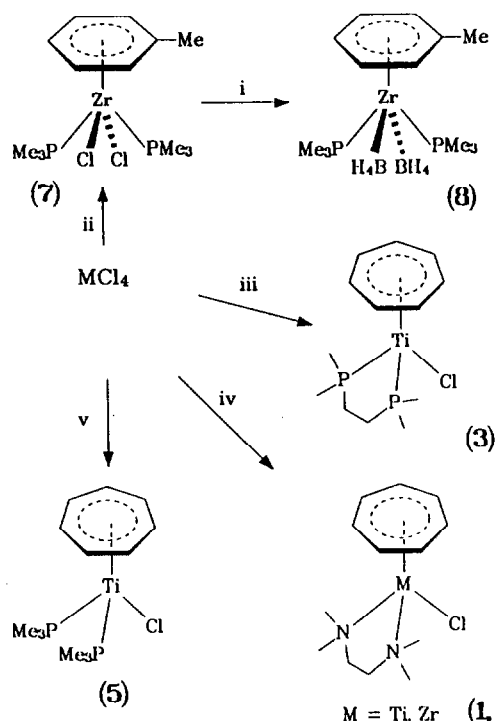
Recently we reported the synthesis of the compounds  $[\text{M}(\eta\text{-C}_7\text{H}_7)\text{L}_2\text{Cl}]$ , where  $\text{M} = \text{Ti}$  [1] or  $\text{Zr}$  [2], and  $\text{L}_2 = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$  (tmada) (1 or 2),  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$  (dmpe) (3 or 4), and  $(\text{PMe}_3)_2$  (5 or 6), via multi-step reaction sequences. Thus for compounds 2, 4 and the iodo analogue of 6 three steps are required [2]; e.g. for 2 and 4:



In the case of 1, 3 and 5 the starting material is bis( $\eta$ -toluene)titanium which is difficult to prepare without using the specialised metal vapour synthesis route [1].

Here we report that the compounds 1, 2, 3 and 5 may be readily prepared directly from  $\text{MCl}_4$ ,  $\text{M} = \text{Ti}$  or  $\text{Zr}$ , in one-pot reactions. Thus  $\text{MCl}_4$  ( $\text{M} = \text{Ti}$ ,  $\text{Zr}$ ) in toluene at  $-78^\circ\text{C}$  was treated with one equivalent of  $\text{L}_2$  ( $\text{M} = \text{Ti}$ ,  $\text{L}_2 = (\text{PMe}_3)_2$ ,  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ,  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ ;  $\text{M} = \text{Zr}$ ,  $\text{L}_2 = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ ) and then with an excess of cycloheptatriene (ca. > 5 equiv.) and sodium amalgam (2 equiv.). The mixtures were stirred at r.t. for 16 hours, then volatiles were removed

\* Dedicated to Professor Peter L. Pauson on the occasion of this retirement.



Scheme 1. Reagents and conditions: (i)  $\text{LiBH}_4$  in THF, 5 min, > 80%. (ii) (M = Zr),  $\text{PMe}_3$  (2 equiv.), Na/K (excess) in toluene at r.t. for 12 h, 5%. (iii)  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$  (1 equiv.), Na/Hg (2 equiv.), excess cycloheptatriene in toluene at r.t. for 16 h (44%). (iv) (For M = Ti or Zr),  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$  (1 equiv.), Na/Hg (2 equiv.) in cycloheptatriene at r.t. for 16 h (27% for Ti, 36% for Zr). (v)  $\text{PMe}_3$  (2 equiv.), Na/Hg (2 equiv.) and excess cycloheptatriene in toluene at r.t. for 16 h (10%).

and the residue extracted into toluene. Filtration followed by concentration and cooling to  $-78^\circ\text{C}$  gave the crystalline compounds 1, 2, 3 and 5. Typically the reactions gave yields for 1, 2, 3 and 5 of 10–44% (see Scheme 1). Thus the half sandwich compounds 1, 2, 3 and 5 are now very readily available and are clearly likely to be useful starting materials.

It seemed likely that the syntheses of 1, 2, 3 and 5 proceeded by initial formation of intermediates containing a  $\eta^6$ -cycloheptatriene ligand, followed by migration of *endo*-hydrogen from the  $\text{C}_7$ -ring to the metal. We, therefore, investigated the reduction of  $\text{ZrCl}_4$  in the presence of toluene and  $\text{PMe}_3$ .

In a typical experiment  $\text{ZrCl}_4$  (4 g) was treated with trimethylphosphine (2 equiv.) in toluene ( $100\text{ cm}^3$ ), and this mixture was added to Na/K alloy at ambient

\* Selected NMR data (coupling constants in Hz); Compound 7:  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ ) 4.67 [1 H, tt,  $J(\text{H}_{\text{meta}}-\text{H}_{\text{para}})$  7.8,  $J(\text{H}_{\text{ortho}}-\text{H}_{\text{para}})$  1.7,  $\text{H}_{\text{para}}$ ], 3.50 (2 H, m,  $\text{H}_{\text{meta}}$ ), 3.26 (2H, m,  $\text{H}_{\text{ortho}}$ ), 1.12 [18 H, d,  $J(\text{P}-\text{H})$  7, 3P-Me], 1.10 (3 H, s, Me).  $\delta_{\text{P}}$  ( $\text{C}_6\text{D}_6$ ) -19.2  $\delta_{\text{C}}$  ( $^{13}\text{C}\{^1\text{H}\}$ ,  $\text{C}_6\text{D}_6$ ) 117.9 (s,  $\text{C}_{\text{para}}$ ), 95.4 (s,  $\text{C}_{\text{ortho}}$  or  $\text{C}_{\text{para}}$ ), 94.6 (s,  $\text{C}_{\text{ortho}}$  or  $\text{C}_{\text{para}}$ ), 21.8 (s,  $\text{CH}_3$ ), 13.9 [t,  $J(\text{P}-\text{C})$  7, P-Me]. Compound 8:  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ ) 4.36 [1 H, tt,  $J(\text{H}_{\text{meta}}-\text{H}_{\text{para}})$  7.6,  $J(\text{H}_{\text{ortho}}-\text{H}_{\text{para}})$  1.6,  $\text{H}_{\text{para}}$ ], 3.81 (2 H, m,  $\text{H}_{\text{meta}}$ ), 3.64 (2H, m,  $\text{H}_{\text{ortho}}$ ), 1.20 (3 H, s, Me) 1.13 [18 H, d,  $J(\text{P}-\text{H})$  6, 3P-Me], 0.25 [8 H, br q,  $J(^{11}\text{B}-\text{H})$  83, 8BH].  $\delta_{\text{P}}$  ( $\text{C}_6\text{D}_6$ ) -18.4.  $\delta_{\text{C}}$  ( $\text{C}_6\text{D}_6$ ) 113.7 [d,  $J(\text{CH})$  147  $\text{C}_{\text{para}}$ ], 93.7 [d,  $J(\text{CH})$  171,  $\text{C}_{\text{ortho}}$  or  $\text{C}_{\text{para}}$ ], 92.1 [d,  $J(\text{CH})$  164,  $\text{C}_{\text{ortho}}$  or  $\text{C}_{\text{para}}$ ], 22.5 [d,  $J(\text{CH})$  127,  $\text{CH}_3$ ], 15.6 [qt,  $J(\text{C}-\text{H})$  126,  $J(\text{P}-\text{C})$  8, P-Me].  $\delta_{\text{B}}$  ( $\text{C}_6\text{D}_6$ ) -23.6 [quin,  $J(\text{BH})$  83].

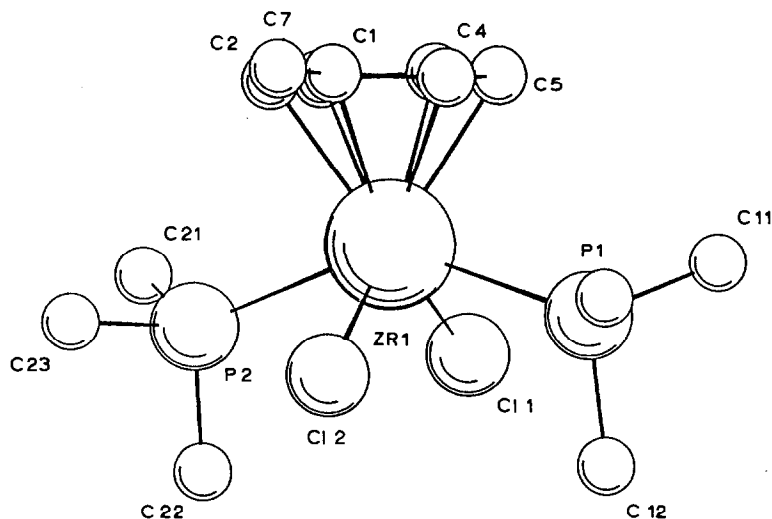


Fig. 1. Molecular structure of the complex 7; only one molecule is shown. Selected bond lengths (Å): Zr(1)–Cl(1) 2.526(2), Zr(1)–Cl(2) 2.496(3), Zr(1)–P(1) 2.760(3), Zr(1)–P(2) 2.756(3), Zr(1)–C(1) 2.523(7), Zr(1)–C(2) 2.417(8), Zr(1)–C(3), 2.41(1), Zr(1)–C(4) 2.40(1), Zr(1)–C(5) 2.403(9), Zr(1)–C(6) 2.410(8), C(1)–C(2) 1.39(1), C(1)–C(6) 1.37(2), C(1)–C(7) 1.51(1), C(2)–C(3) 1.42(2), C(3)–C(4) 1.37(3), C(4)–C(5) 1.30(2), C(5)–C(6) 1.39(2). Selected bond angles (°) Cl(2)–Zr(1)–Cl(1) 109.40(9), P(1)–Zr(1)–Cl(1) 80.71(8), P(1)–Zr(1)–Cl(2) 77.1(1), P(2)–Zr(1)–Cl(1) 80.04(9), P(2)–Zr(1)–Cl(2) 78.0(1), P(2)–Zr(1)–P(1) 141.14(8).

temperature under dinitrogen and stirred for 7 h. The solvent was removed in *in vacuo* and the residue extracted into petroleum ether (b.p. 40–60 °C). The extract was concentrated and cooled to –78 °C to give air-sensitive, green crystals of  $[\text{Zr}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{PMe}_3)_2\text{Cl}_2]$  (ca. 300 mg, 5%) (7) \*\*. The crystal structure of 7 has been determined; the molecular structure is shown in Fig. 1 \*\* along with selected bond distances and angles. Compound 7 crystallises in the space group  $P2_1$  with two independent molecules in the unique part of the unit cell, the main difference between these being a slight rotation of the toluene ring. The molecular structure shows marked similarities to that reported for the triene compound  $[\text{Zr}(\text{exo-}\eta^6\text{-C}_7\text{H}_7\text{SiMe}_3)(\text{PMe}_3)_2\text{I}_2]$  [2] and both compounds have a square-based pyramidal arrangement of the  $(\text{PMe}_3)_2\text{Cl}_2$  ligands.

Compound 7 is a rare example of an  $\eta$ -arene derivative of zirconium. Previous examples are the compounds  $[\text{Zr}_3\text{Cl}_6(\eta^6\text{-C}_6\text{Me}_6)_3]\text{X}_n$  ( $\text{X} = \text{Cl}$  or  $\text{PF}_6$ ) (a bridged

\*\* Crystal data for 1:  $\text{C}_{13}\text{H}_{26}\text{Cl}_2\text{P}_2\text{Zr}$ ,  $M = 406.4$ , monoclinic, space group  $P2_1$ ,  $a$  13.527(5),  $b$  11.338(5),  $c$  12.922(6) Å,  $\beta$  93.37(3)°,  $U$  1978.5 Å<sup>3</sup>,  $Z = 4$ ,  $D_c$  1.36 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 9.65$  cm<sup>-1</sup>, crystal size ca. 0.05 × 0.4 × 0.6. Data were collected on an Enraf–Nonius CAD4 diffractometer using Mo-K $\alpha$  radiation. Empirical absorption correction was applied and structure refinement carried out using 2994 observed reflections with  $I > 3\sigma(I)$  from 3433 independent reflections measured. The structure was solved by Patterson and Fourier methods. The hydrogen atoms were placed in calculated positions. Crystallographic calculations were carried out using the Oxford CRYSTALS package [8]. Full matrix least square refinement of 325 least square parameters has led to final agreement factors of  $R = 0.0335$  and  $R_w = 0.0433$ . The absolute structure was not determined. Atomic co-ordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

trinuclear structure,  $n = 1$  or  $2$ ) [3],  $[\text{Zr}_3\text{Cl}_6(\eta^6\text{-C}_6\text{Me}_6)][\text{Al}_2\text{Cl}_7]_2$  [4],  $[\text{Zr}(\text{arene})(\text{AlX}_4)_2]$  [5],  $[\text{Zr}(\text{CH}_2\text{Ph})_3][\text{BPh}_4]$  [6] and  $[\text{Zr}(\eta^6\text{-1,3,5-}^t\text{Bu}_3\text{C}_6\text{H}_3)_2]$  [7].

Treatment of **7** with lithium borohydride gives air-sensitive brown crystals in high yield which the  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$  and  $^{31}\text{P}$  NMR suggest to be the bis-borohydrido derivative  $[\text{Zr}(\eta\text{-C}_6\text{H}_5\text{Me})(\text{PMe}_3)_2(\text{BH}_4)_2]$  (**8**). The  $^1\text{H}$  NMR spectrum \* shows that **8** is fluxional since only one band is observed for the eight hydrogens of the two  $\text{BH}_4$  groups, even at 183 K.

In conclusion, we have described greatly improved syntheses of the potentially useful synthons **1**, **2**, **3** and **5** and a simple direct route to the novel and reactive, divalent zirconium  $\eta$ -toluene compound **7**.

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