Half-sandwich η-Cycloheptatri-ene and -enyl Derivatives of Titanium and Zirconium

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Treatment of $[Zr(\eta^6\text{-}C_7H_8)_2]$ **1** in tetrahydrofuran with iodine gives $[Zr(\eta\text{-}C_7H_7)(thf)_2I]$ **2** which reacts with PMe_3 forming $[Zr(\eta\text{-}C_7H_7)(PMe_3)_2I]$ **3**. The latter reacts with iodotrimethylsilane to give the *exo*-trimethylsilylcycloheptatriene compound $[Zr\{exo\text{-}\eta^6\text{-}C_7H_7(SiMe_3)\}(PMe_3)_2I_2]$ **4**. Thermolysis of **4** gives $[Zr(\eta^6\text{-}C_7H_8)(PMe_3)_2I_2]$ **5**. The compounds $[M(\eta\text{-}C_7H_7)L_2Cl]$ [M = Ti, $L_2 = (PMe_3)_2$ **6**, $Me_2NCH_2CH_2NMe_2$ **7** or $Me_2PCH_2CH_2PMe_2$ **8**; M = Zr, $L_2 = Me_2NCH_2CH_2NMe_2$ **9**] have been prepared in one-pot reactions.

We have been interested to develop the chemistry of C_7-ring compounds of the early transition metals and have recently described η-cycloheptatri-ene and -enyl derivatives of titanium,[1] zirconium,[2,3] hafnium[4] and niobium.[5] Here we report further studies on half-sandwich C_7-ring compounds of these metals. Part of this work has been communicated.[3,6]

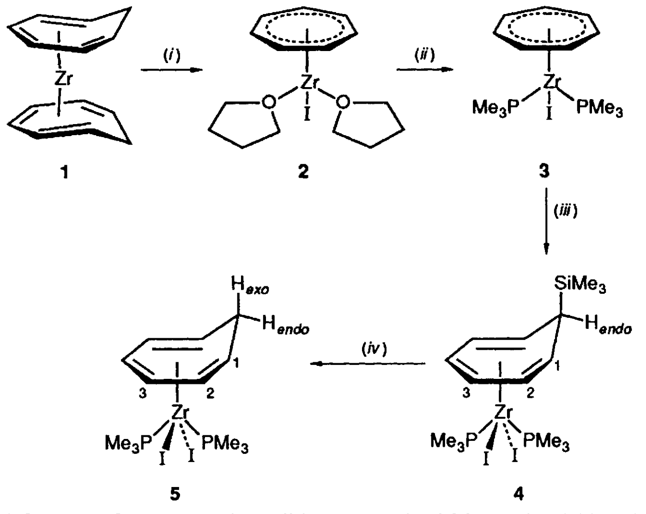
Results and Discussion

Treatment of the recently described compound $[Zr(\eta^6\text{-}C_7H_8)_2]$[2] **1** with iodine in tetrahydrofuran (thf) gave, after recrystallisation from thf, large blue crystals of $[Zr(\eta\text{-}C_7H_7)(thf)_2I]$ **2**. The data characterising **2**, and all other new compounds described in this work, are given in Table 1 and will not be further discussed. The reactions and proposed structures of the new compounds are given in Schemes 1 and 2. Compound **2** is insoluble in hydrocarbon solvents and reacts with chlorinated solvents to give insoluble flocculent material. Its crystal structure has been described previously.[3] The Zr–O bond length is 0.134 Å longer than the Ti–O bond found in $[\{Ti(\eta\text{-}C_7H_7)(thf)Cl\}_2]$ [2.187(1) Å].[1]

Addition of PMe_3 to a toluene suspension of compound **2** gave a deep green solution from which large air-sensitive, green crystals of $[Zr(\eta\text{-}C_7H_7)(PMe_3)_2I]$ **3** were isolated. Toluene solutions of compound **3** were stable to 80 °C. The crystal structure has also been reported.[3] The carbon atoms of the $\eta^7\text{-}C_7H_7$ groups in both compounds **2** and **3** are coplanar within experimental error. The $\eta^7\text{-}C_7H_7$ rings can be described as essentially regular heptagons with C–C bond distances in the range 1.38(1)–1.46(1) (mean 1.41 Å) for **2** and 1.40(1)–1.42(1) (mean 1.41 Å) for **3** and internal ring angles 127.0(6)–130.0(6) (mean 128.3°) for **2** and 127.7(3)–129.1(3) (mean 128.6°) for **3**.[3]

The zirconium–carbon bond distances in compounds **2** and **3** (Table 2) are similar and compare well with those in $[Zr(\eta\text{-}C_7H_7)(\eta\text{-}C_5Me_5)]$ [2.332(3) Å].[10] They are longer than in related $Mo(\eta\text{-}C_7H_7)$ compounds, *e.g.* for $[Mo(\eta\text{-}C_7H_7)(thf)I_2]$ [Mo–C_7(mean)[7] 2.25 Å] and for $[Mo(acac)(H_2O)(\eta\text{-}C_7H_7)]^+$ (acac = acetylacetonate) [mean 2.265(15) Å].[11] There is a marked increase in the zirconium–iodine bond length with a decrease in the formal oxidation state of the metal (Table 2). Furthermore, the Zr–I bonds are considerably longer than those found in related $[Mo(\eta\text{-}C_7H_7)(thf)I_2]$ (2.810 Å).[7]

Stone and co-workers[12] have described a reaction between $[Mo(\eta\text{-}C_7H_7)(CO)_2I]$ and iodotrimethylsilane which gave the dinuclear compound $[Mo_2(\eta\text{-}C_7H_7)_2(\mu\text{-}I_3)]$. We have investigated the corresponding reaction between iodotrimethylsilane and $[Zr(\eta\text{-}C_7H_7)(PMe_3)_2I]$ **3** and observed a rapid reaction leading to the isolation of orange crystals of $[Zr\{exo\text{-}\eta^6\text{-}C_7H_7(SiMe_3)\}(PMe_3)_2I_2]$ **4** in 81% yield, the crystal structure of which has been determined.[3]



Scheme 1 Reagents and conditions: (*i*) I_2 in thf for 12 h (yield); (*ii*) PMe_3 in toluene for 1 h; (*iii*) $SiMe_3I$ in toluene for 30 min; (*iv*) 100 °C for 100 h in toluene (yield > 95% by NMR spectroscopy)

There are two previous compounds which contain a trimethylsilyl-substituted C_7 ligand, namely $[Ru_2(SiMe_3)\{\mu\text{-}\eta^3{:}\eta^4\text{-}C_7H_6(SiMe_3)(CO)_5]$[13] and $[Ru(SiMe_3)\{\eta^5\text{-}C_7H_7\text{-}(C_6F_5)(SiMe_3)\}(CO)_2]$.[14] The first structure has a Si–C(ring) distance of 1.876(12) Å which compares well with that for **4**. In compound **4** the $C_7H_7(SiMe_3)$ ring has a 'boat' structure, with the $SiMe_3$ group in a quasi-axial position; this is similar to the structure of $C_7H_7(SnPh_3)$.[15] The mean C–C distance (of adjacent triene carbons) for $C_7H_7(SnPh_3)$ is 1.356 Å, which when compared with the mean C–C in compound **4** indicates that only a very small change occurs on co-ordination of a substituted cycloheptatriene. Prolonged heating of compound **4** in toluene at 100 °C for 100 h gives the green cycloheptatriene complex $[Zr(\eta^6\text{-}C_7H_8)(PMe_3)_2I_2]$ **5**. When perdeuteriotoluene was used as solvent there was no observable incorporation of deuterium into **5**. We have recently described a one-step synthesis of the chloride analogue of **5** from $ZrCl_4$.[4]

Half-sandwich compounds in the class $[Ti(\eta\text{-}C_7H_7)L_2Cl]$, where $L_2 = (PMe_3)_2$, $Me_2PCH_2CH_2PMe_2$ or $Me_2NCH_2CH_2NMe_2$, have been prepared previously using the dimer $[\{Ti(\eta\text{-}C_7H_7)(\mu\text{-}Cl)(C_4H_8O)\}_2]$[1] which is itself derived from bis(η-toluene)titanium. Here we report one-pot syntheses of these and a related zirconium compound which are considerably more

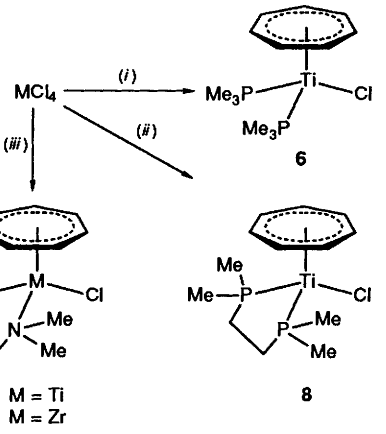
Table 1 Analytical and spectroscopic data[a]

Compound	Colour	NMR data
2 C, 39.5 (39.7); H, 4.9 (5.1)	Blue	
3 C, 33.7 (33.8); H, 5.3 (5.5); I, 27.6 (27.5)	Green	$\delta_H{}^b$ 5.00 (s, 7 H, C_7H_7), 0.84 (br s, 18 H, P–CH_3) $\delta_P{}^b$ −50.9 (s) $\delta_C{}^h$ 84.0 (s, C_7H_7), 16.9 [d, *J*(P–C) 11, P–CH_3]
4 C, 28.9, (29.0); H, 5.1 (5.1); I, 38.55 (38.3)	Bronze	$\delta_H{}^b$ 5.59 (m, 2 H, H^2), 5.15 (m, 2 H, H^3), 4.34 (m, 2 H, H^1), 1.58 (br s, 9 H, P–CH_3), 1.20 [br t, 1 H, *J*(H^1–H_{endo}) 7, H_{endo}], 1.17 [br d, 9 H, *J*(P–H) 7, P–CH_3], −0.27 (s, 9 H, Si–CH_3) $\delta_P{}^b$ −26.5 (br s, 1 P), −43.7 (br s, 1 P) $\delta_C{}^b$ 118.6 [d, *J*(C–H) 163, C^2], 99.1 [dt, *J*(C–H) 163, *J*(P–C) 11, C^3], 86.8 [d, *J*(C–H) 166, C^1], 26.5 [d, *J*(C–H) 119, Si–CH], 17.4 [dq, *J*(C–H) 125, *J*(P–C) 16, P–CH], 16.0 [dq, *J*(C–H) 125, *J*(P–C) 16, P–CH_3], −2.0 [q, *J*(C–H) 119, Si–CH_3]
5	Green	$\delta_H{}^c$ 5.73 (m, 2 H, H^2), 5.34 (m, 2 H, H^3), 3.94 (m, 2 H, H^1), 1.53 [d, 9 H, *J*(P–H) 9, 3 P–CH_3], 1.25 (m, 1 H, H_{endo}), 1.17 [d, 9 H, *J*(P–H) 6, 3P–CH_3], 0.09 (m, 1 H, H_{exo}) $\delta_P{}^c$ −28.15 [d, 1 P, *J*(P–P) 35], −41.45 [d, 1 P, *J*(P–P) 35]
6 C, 47.6 (47.8); H, 7.6 (7.7)	Dark red	$\delta_H{}^c$ (200 MHz) 5.56 (s, 7 H, C_7H_7), 0.79 [d, 18 H, *J*(P–H) 4, P–CH_3]
7 [1,2]	Red-brown	$\delta_H{}^c$ (200 MHz) 5.8 (s, 7 H, C_7H_7), 2.0 (br s, 12 H, N–CH_3), 1.4 (br s, 4 H, N–CH_2)
8 [1,2]	Bronze	$\delta_H{}^c$ 5.59 [t, 7 H, *J*(P–H) 2, C_7H_7], 0.82 (br s, 12 H, P–CH_3), 0.76 (br m, 4 H, P–CH_2)
9 [1,2] C, 46.6 (46.7); H, 6.8 (6.9)	Blue[d]	$\delta_H{}^c$ 5.39 (s, 7 H, C_7H_7), 2.25 (s, 6 H, N–CH_3), 1.80 (m, 2 H, N–CH_2), 1.64 (s, 6 H, N–CH_3), 1.17 (m, 2 H, N–CH_2)

[a] Unless otherwise stated: ^1H at 300 MHz, ^{31}P at 120 MHz, ^{13}C at 75 MHz. Coupling constants in Hz. Analytical data (%) given as: Found (Calc.). [b] In [$^2H_8$]toluene. [c] In C_6D_6. [d] N, 8.3 (8.4); Cl, 10.7 (10.6)%.

Table 2 Comparison of M–C_7 and M–I bond lengths

Compound	M–C_7(mean)/Å	M–I/Å	Ref.
[Mo(η-C_7H_7)(thf)I_2]	2.25	2.81	7
[Zr(η-C_5H_5)$_2I_2$]	—	2.83	8
[Zr(η^6-$C_7H_7SiMe_3$)(PMe_3)$_2I_2$]	—	2.94	3
[Zr(η-C_7H_7)(PMe_3)$_2$I]	2.36	2.94	3
[Zr(η-C_7H_7)(thf)$_2$I]	2.34	3.00	3
[Ti(η-C_7H_7)(η-C_5H_5)]	2.19	—	9



Scheme 2 Reagents and conditions: (*i*) M = Ti, L_2 = $(PMe_3)_2$, Na/Hg (2 equivalents) in toluene at r.t. for 16 h; (*ii*) M = Ti, L_2 = $Me_2PCH_2CH_2PMe_2$, Na/Hg (2 equivalents), C_7H_8 in toluene at r.t. for 16 h; (*iii*) L_2 = $Me_2NCH_2CH_2NMe_2$, Na/Hg in toluene

convenient. In a typical experiment MCl_4 (M = Ti or Zr) in toluene was pretreated at −78 °C with 1 equivalent of L_2 [for example M = Ti, L_2 = $(PMe_3)_2$; M = Zr, L_2 = $Me_2NCH_2CH_2NMe_2$] and the mixture was stirred with sodium amalgam (2 equivalents) in the presence of an excess of cycloheptatriene (*ca.* >5 equivalents). Filtration followed by further extraction with more toluene yielded crystals at −78 °C of [M(η-C_7H_7)L_2Cl] [M = Ti, L_2 = $(PMe_3)_2$ **6**, $Me_2NCH_2CH_2NMe_2$ **7** or $Me_2PCH_2CH_2PMe_2$ **8**; M = Zr, L_2 = $Me_2NCH_2CH_2NMe_2$ **9**.

In conclusion, it seems likely that the formation of compound **4** from **3** involves a radical process but, as for the conversion of **4** into **5**, the mechanism is not intuitively obvious. Many of these new divalent zirconium and titanium compounds are likely to be useful starting compounds for the further development of the relatively unexplored low-valent chemistry of these elements.

Experimental

All manipulations were performed using standard vacuum-line and Schlenk-vessel techniques either under an atmosphere of dinitrogen, which had been purified by passage over MnO catalyst and 4 Å molecular sieves, or in an inert-atmosphere dry-box.

Solvents and solutions were generally transferred through stainless-steel cannulae using an overpressure of dinitrogen, and filtered using cannulae modified to be fitted with glass-fibre disks. All solvents were thoroughly deoxygenated before use by repeated evacuation followed by admission of dinitrogen, or by bubbling dinitrogen through them for 20 min. All glassware was pre-dried by heating at 240 °C in an oven before use.

Solvents were pre-dried by standing over molecular sieves followed by distillation from sodium (toluene), potassium–benzophenone (tetrahydrofuran) or sodium–potassium alloy [light petroleum (b.p. 40–60 °C)]. Deuteriated solvents for NMR spectroscopy were stored over sodium–potassium alloy (C_6D_6, [$^2H_8$]toluene). The NMR samples were sealed under vacuum (10^{-5} mmHg, *ca.* 1.3 × 10^{-3} Pa). Celite 545 filtration aid (Koch-Light) was pre-dried at 240 °C before use.

The NMR spectra were referenced internally using the residual solvent (^1H) and solvent (^{13}C) resonances relative to tetramethylsilane (δ = 0), or externally using trimethyl phosphate [$PO(OMe)_3$] in D_2O (^{31}P). All chemical shifts are quoted in δ (ppm) and coupling constants are in Hz. Infrared spectra were recorded on a Perkin-Elmer 1510 FT interferometer or a Perkin-Elmer 457 grating spectrometer, on which spectra below 400 cm^{-1} were obtained. Microanalyses were performed by Analytische Laboratorien, Elbach, Germany.

(η-*Cycloheptatrienyl*)*iodobis*(*tetrahydrofuran*)*zirconium* **2**.—A solution of I_2 (1.9 g, 7.5 mmol) in thf (30 cm^3) was added slowly to a stirred thf solution (50 cm^3) of [Zr(η^6-C_7H_8)$_2$] **1** (2.0 g, 7.3 mmol). This mixture was stirred for 12 h then the solvent was removed under reduced pressure. The residual red oil was washed with toluene leaving a green-grey solid which was recrystallised from thf (20 cm^3) at −78 °C to give large blue crystals of compound **2**. Yield 500 mg, 17%.

(η-*Cycloheptatrienyl*)*iodobis*(*trimethylphosphine*)*zirconium* **3**.—An excess of trimethylphosphine (*ca.* 1 cm^3) was added to a stirred suspension of compound **2** (400 mg, 0.52 mmol) in toluene (60 cm^3) and stirring was continued for 1 h. The toluene solution was concentrated (to *ca.* 20 cm^3) and the resulting blue-green solution was warmed to 60 °C and then filtered. On cooling to room temperature (r.t.) over 3 h green crystals separated. The solution was cooled to -20 °C over 12 h, then the supernatant solution was decanted leaving green crystals of **3** which were dried *in vacuo*. Yield 320 mg, 79%.

Diiodobis(trimethylphosphine)(η^6-exo-7-*trimethylsilylcyclohepta*-1,3,5-*triene)zirconium* **4**.—A toluene solution of compound **3** (500 mg, 1.08 mmol) was treated with iodotrimethylsilane (*ca.* 1 cm^3) immediately producing an orange colour. The mixture was allowed to stand for 30 min at ambient temperature and then the volatiles were removed under reduced pressure. The residual yellow oil was extracted into a 10% toluene, 90% light petroleum (b.p. 40–60 °C, 60 cm^3) mixture and the extract was filtered and cooled to -20 °C for 12 h giving orange-brown crystals of compound **4**. Yield 580 mg, 81%.

(η^6-*Cyclohepta*-1,3,5-*triene)diiodobis(trimethylphosphine)zirconium* **5**.—A solution of compound **4** in [$^2H_8$]toluene (3 cm^3) was heated at 100 °C for 100 h. The volatiles were removed *in vacuo* and the resulting green oil was extracted into light petroleum (b.p. 40–60 °C, 10 cm^3). The extract was filtered and cooled to -20 °C giving green crystals of compound **5** (*ca.* 100 mg).

Chloro(η-*cycloheptatrienyl)bis(trimethylphosphine)titanium* **6**.—A solution of $TiCl_4$ (2 cm^3, 3.46 g, 18 mmol) in toluene (80 cm^3) was treated with 2 equivalents of trimethylphosphine (2.8 cm^3, 36 mmol) and the mixture was added to sodium amalgam (2 equivalents) at -78 °C. Excess of cycloheptatriene (20 cm^3, 192 mmol) was added and the mixture was allowed to warm slowly to room temperature and was stirred for 16 h. Filtration followed by concentration of the filtrate (to *ca.* 20 cm^3) and cooling to -20 °C gave very dark red needles of compound **6** (0.20 g). Further concentration of the filtrate (to 15 cm^3) followed by addition of trimethylphosphine (2 cm^3) and light petroleum (20 cm^3) and cooling to -20 °C gave two further crops of crystals of **6**. Total yield 0.60 g, 10%.

Chloro(η-*cycloheptatrienyl*)(N,N,N′,N′-*tetramethylethane*-1,2-*diamine)titanium* **7**.—A solution of $TiCl_4$ (2 cm^3, 3.64 g, 18 mmol) in toluene (80 cm^3) was treated with 1 equivalent of *N,N,N′,N′*-tetramethylethane-1,2-diamine (tmen) (2.7 cm^3, 18 mmol) and the mixture was added to sodium amalgam (2 equivalents) at -78 °C. Excess of cycloheptatriene (20 cm^3, 192 mmol) was added and the mixture allowed to warm slowly to r.t. and was stirred for 2 h. Filtration followed by concentration of the filtrate and cooling to -20 °C gave red-brown crystals of compound **7**. Yield 1.4 g, 27%.

[1,2-*Bis(dimethylphosphino)ethane*]*chloro*(η-*cycloheptatrienyl)titanium* **8**.—A solution of [$TiCl_4$(dmpe)] (dmpe = $Me_2PCH_2CH_2PMe_2$) (1.5 g, 6.4 mmol) in toluene (80 cm^3) was added to sodium amalgam (2 equivalents) at -78 °C. Excess of cycloheptatriene (10 cm^3, 96 mmol) was added and the mixture allowed to warm slowly to room temperature and was stirred for 16 h. In this time the colour changed from orange *via* green and blue to red. Filtration followed by cooling the filtrate to -20 °C gave, after 1 week, 0.32 g of bronze-coloured needles of compound **8**. Concentration of the solution to 20 cm^3 and addition of light petroleum (20 cm^3) gave 0.59 g of **8**. Total yield 0.91 g, 44%.

Chloro(η-*cycloheptatrienyl*)(N,N,N′,N′-*tetramethylethane*-1,2-*diamine)zirconium* **9**.—A suspension of $ZrCl_4$ (4.0 g, 17 mmol) in toluene (80 cm^3) was treated with 2 equivalents of tmen (5.2 cm^3, 34 mmol) and the mixture was added to sodium amalgam (2 equivalents) at -78 °C. Excess of cycloheptatriene (10 cm^3, 96 mmol) was added and the mixture stirred while slowly warming to room temperature and then for 18 h. Filtration followed by cooling to -20 °C gave blue crystals of compound **9** (1.05 g). The mercury residues from the reduction were stirred with toluene (80 cm^3) at *ca.* 100 °C for 15 min. Filtration of the hot mixture followed by cooling the filtrate to -20 °C yielded 0.53 g of **9**. Concentration of the solution followed by cooling to -20 °C gave 0.46 g of **9** after 1 week. Total yield 2.04 g, 36%.

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