Synthesis, Crystal Structure and Reactions of Zerovalent 16-Electron Bis(η-cycloheptatriene)zirconium†

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Reduction of $ZrCl_4$ with sodium amalgam in the presence of cycloheptatriene gives the crystallographically identified $[Zr(\eta^6-C_7H_8)_2]$ **1** which exhibits a non-parallel arrangement of the cycloheptatrienyl ligands. This reacts with PMe_3 or 1,2-bis(dimethylphosphino)ethane (dmpe) to yield $[Zr(\eta^7-C_7H_7)(\eta^5-C_7H_9)(PMe_3)]$ **2** and $[\{Zr(\eta^7-C_7H_7)(\eta^5-C_7H_9)\}_2(dmpe)]$ **3** respectively. Treatment of compound **1** with $(AlEt_2Cl)_2$ in tetrahydrofuran (thf) yields $[\{Zr(\eta^7-C_7H_7)(thf)(\mu-Cl)\}_2]$ **4** which reacts with *N,N,N′,N′*-tetramethylethylenediamine, PMe_3, dmpe and 1,2-dimethoxyethane to produce $[Zr(\eta^7-C_7H_7)(Me_2NCH_2CH_2NMe_2)Cl]$ **5**, $[Zr(\eta^7-C_7H_7)(PMe_3)_2Cl]$ **6**, $[Zr(\eta^7-C_7H_7)(dmpe)Cl]$ **7** and $[Zr(\eta^7-C_7H_7)(MeOCH_2CH_2OMe)Cl]$ **8**, respectively. The electronic structures of **1** and $[Zr(\eta^7-C_7H_7)(\eta^5-C_7H_9)]$ **11** have been investigated by photoelectron spectroscopy and extended-Hückel molecular-orbital calculations.

Few low-valent compounds of zirconium had been described until recently. The bis η^6-arene compounds $[Zr(\eta^6-C_6H_3Bu^t_3-1,3,5)_2]$[1] and $[Zr(\eta^6-C_6H_5Me)_2(PMe_3)]$[2] were prepared *via* zirconium atoms. Other zerovalent compounds include $[Zr(\eta^4-C_4H_4)_2(dmpe)]$[3] [dmpe = 1,2-bis(dimethylphosphino)ethane], $[NEt_4][Zr(\eta^5-C_5H_5)(CO)_4]$,[4] and $[Zr(CO)_4\{MeC(CH_2PMe_2)_3\}]$.[5]

Relatively few cycloheptatriene compounds of the Group 4 metals have been reported, and the only compounds containing two seven-membered rings are $[M(\eta^7-C_7H_7)(\eta^5-C_7H_9)]$ (M = Ti, Zr or Hf).[6,7] Timms and Turney[8] proposed the formation of the bis(triene) compound $[Ti(\eta^6-C_7H_8)_2]$ **9** as a likely intermediate in the reaction between titanium atoms and cycloheptatriene giving $[Ti(\eta^7-C_7H_7)(\eta^5-C_7H_9)]$ **10** but no evidence was presented for the formation of this compound. Also, the synthesis of $[Zr(\eta^7-C_7H_7)(\eta^5-C_7H_9)]$ **11** from zirconium atoms and cycloheptatriene, by Green and coworkers, gave no indication of a bis(triene) compound. However bis(cycloheptatriene) compounds of other metals have been made by metal-vapour synthesis. Thus the reaction between molybdenum atoms and cycloheptatriene was originally reported by Timms and Turney[8] to give only $[Mo(\eta^7-C_7H_7)(\eta^5-C_7H_9)]$. However, a re-examination of this reaction, by Green *et al.*,[9] including a low-temperature isolation procedure, showed that the thermally sensitive green bis(triene) compound $[Mo(\eta^6-C_7H_8)_2]$ was formed in good yields. This compound proved to be unstable over long periods of time and decomposed cleanly *via* hydrogen migration to the more stable $[Mo(\eta^7-C_7H_7)(\eta^5-C_7H_9)]$. Studies of the reaction kinetics and crossover experiments indicated the migration reaction was unimolecular.

Here we report a one-pot, high-yield synthesis of the 16-electron bis(η^6- cycloheptatriene)zirconium compound $[Zr(\eta^6-C_7H_8)_2]$ **1** which is a reactive precursor of new organometallic compounds of zirconium. A preliminary communication of part of this work has appeared.[10]

Results and Discussion

Reduction of $ZrCl_4$ together with cycloheptatriene in tetrahydrofuran (thf) using sodium amalgam at < -10 °C (Scheme 1) gives compound **1** in *ca.* 40% yield (typically 20 g of $ZrCl_4$ give 8.5 g of compound **1**). The analytical and spectroscopic data for this compound and for other new compounds described below are given in Table 1 and are not discussed further unless interpretation is not straightforward. When the above reaction is carried out at room temperature an inseparable mixture of compound **1** and the previously described compound **11** is formed. The stability of pure compound **1** to hydrogen migration in the absence of a Lewis base is remarkable in comparison to those of the related titanium and molybdenum compounds. No significant conversion of compound **1** into **11** was observed at 100 °C in toluene over 48 h, and compound **1** may be sublimed without decomposition at 60 °C at 10^{-5} mmHg. However, under the conditions used for measuring the photoelectron spectrum, conversion of compound **1** into **11** was observed. The synthesis of compound **11** has previously been reported by Green and coworkers,[7] using metal-vapour synthesis techniques. We have found an alternative route to this product namely the sodium amalgam reduction of zirconium tetrachloride in a tetrahydrofuran solution of cycloheptatriene at room temperature. The product **11** was isolated as thermally stable, red crystals.

The crystal structure of compound **1** has been determined and shows an unusual non-parallel arrangement of the two triene ligands with a dihedral angle between the best planes of the two C_7H_8 rings of 25.6°. The molecular structure is shown in Fig. 1 and selected data are summarized in Tables 2 and 3.

Comparison of the structure of compound **1** with that of $[Mo(\eta^6-C_7H_8)(CO)_3]$ shows that the latter has shorter metal–carbon bonds (mean 2.37 Å) for the triene carbons than compound **1** (mean 2.42 Å).[11] The metal to methylene carbon atom distance is longer in $[Mo(\eta^6-C_7H_8)(CO)_3]$ (2.96 Å) than in compound **1** (2.76 Å) indicating a decreased deviation from a planar arrangement in this molecule.

This bent arrangement of the trienes is surprising when it is contrasted with the normal parallel arrangement of arene rings in the related bis(arene) compounds. Only two structurally characterised bent bis(arene) compounds are known, $[Nb(\eta^6-C_6H_5Me)_2(PMe_3)]PF_6$ (142.3°) and $[Hf(\eta^6-C_6H_5Me)_2(SnMe_3)_2]$ (138.9°).[12,13]

Another point of interest is shown in the top view of compound **1**. This indicates the staggered nature of the η^6-C_7H_8 rings; with respect to an eclipsed arrangement, one ring is rotated 42.5° relative to the other.

Reduction of $TiCl_4$ with magnesium turnings in the presence of cycloheptatriene gave a green crystalline product which the

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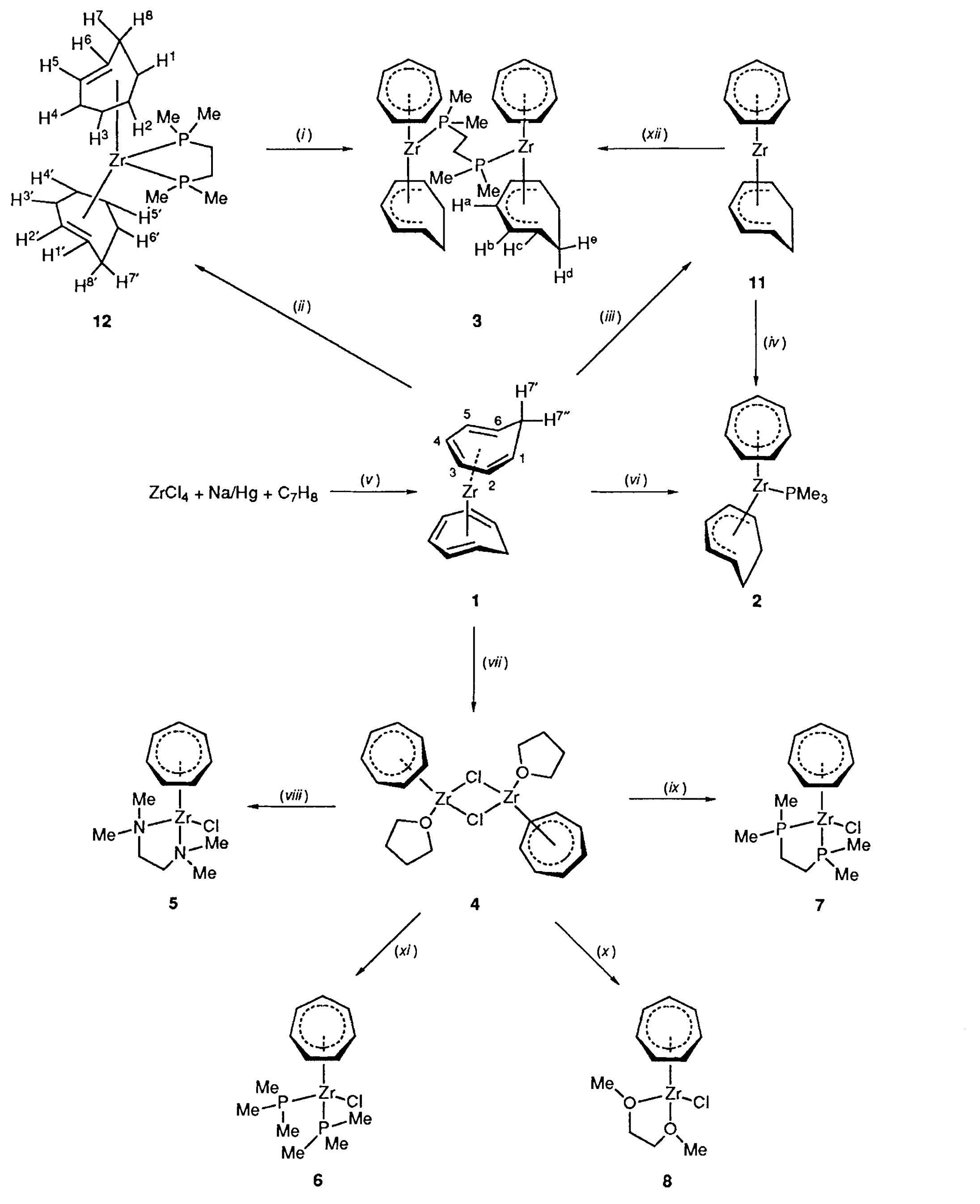
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI units employed: atm = 101 325 Pa, mmHg ≈ 133 Pa, eV ≈ 1.60×10^{-19} J.



Scheme 1 *Reagents and conditions:* (*i*) in toluene at r.t. for 12 h (yield 40%); (*ii*) dmpe in toluene at −10 °C (65%); (*iii*) in toluene under CO (4 atm) (>90%); (*iv*) PMe_3 in toluene for 2 h at r.t. (90%); (*v*) gradual warming from −78 °C over 3 h in thf (44%); (*vi*) PMe_3, r.t., 12 h (38%); (*vii*) $(AlEt_2Cl)_2$ in thf for 1 week (46%); (*viii*) tmen for 12 h in toluene (86%); (*ix*) dmpe in toluene for 12 h (54%); (*x*) dme in toluene for 15 h (29%); (*xi*) PMe_3 in toluene for 1.5 h (90%); (*xii*) dmpe in toluene for 12 h (52%)

^1H NMR spectrum shows to be a *ca.* 8:2 mixture of the bis(triene) compound **9** and the previously described compound **10**. Solutions of compound **9** readily decompose to **10** and it was not possible to isolate pure **9**; longer reaction times (*ca.* 12 h) gave compound **10** as the only product. This reaction is closely analogous to the previous route to compound **10** using $MgPr^iBr$ as the reducing agent.[6] The ^1H NMR spectrum assigned to compound **9** is closely related to that of the crystallographically characterised zirconium analogue **1**.

All attempts to prepare $[Hf(\eta^6\text{-}C_7H_8)_2]$ by reductive methods produced only an orange oil, the ^1H NMR spectrum of which indicated the presence of only a small amount of the desired product. It appears that the main problem in this synthesis is the inability of sodium amalgam to reduce hafnium(IV) to hafnium(0) whilst stronger reducing agents react with cycloheptatriene.

The reaction between compound **1** and carbon monoxide, $[Sn_2Me_6]$, or *N,N,N′,N′*-tetramethylethylenediamine (tmen) produced only compound **11**, in high yields. However, compound **1** reacts with trimethylphosphine to give **2**, a thermally sensitive trimethylphosphine adduct of **11**. The related reaction of compound **1** with dmpe gave the thermally sensitive compound **12**, which is rapidly converted into **3** at room temperature (r.t.). The compound **3** can also be directly prepared by treatment of **11** with dmpe.

The reaction of compound **1** with $(AlEt_2Cl)_2$ in thf at r.t. gives insoluble black crystals, which the limited available data (Table 1) suggest to be the compound $[\{Zr(\eta^7\text{-}C_7H_7)(thf)(\mu\text{-}Cl)\}_2]$ **4**. The titanium analogue of compound **4** has been described and has an extensive chemistry.[14] The chemical reactions of compound **4** also lead to a potentially rich chemistry of the $Zr(\eta\text{-}C_7H_7)$ system and provide support for

Table 1 Analytical and spectroscopic data[a]

Compound	Colour	NMR data
1 C, 61.0 (61.0); H, 5.8 (5.85)	Black	^{1}H (C_6D_6): 5.9 (m, 4 H, H$^{2\text{ or }5}$, H$^{3\text{ or }4}$), 5.5 [ddd, 2 H, *J*(H$^{2\text{ or }5}$, H$^{7'}$) 2, *J*(H$^{5\text{ or }2}$, H$^{6\text{ or }1}$) 9, *J*(H$^{2\text{ or }5}$, H$^{3\text{ or }4}$) 10, H$^{2\text{ or }5}$], 5.1 (m, 2 H, H$^{3\text{ or }4}$), 4.7 (m, 2 H, H$^{1\text{ or }6}$), 3.1 (m, 2 H, H$^{1\text{ or }6}$), 2.7 [ddd, 2 H, *J*(H$^{7'}$, H$^{7''}$) 12, *J*(H$^{7''}$, H$^{1\text{ or }6}$) 8, *J*(H$^{7''}$, H$^{1\text{ or }6}$) 2, H$^{7''}$], 1.3 [br d, 2 H, *J*(H$^{7'}$, H$^{7''}$) 12, H$^{7'}$] ^{13}C (C_6D_6): 119.7 [d, *J*(CH) 154, C$^{2\text{ or }5}$], 119.2 [d, *J*(CH) 159, C$^{2\text{ or }5}$ or C$^{3\text{ or }4}$], 98.2 [d, *J*(CH) 162, C$^{2\text{ or }5}$ or C$^{3\text{ or }4}$], 96.8 [d, *J*(CH) 163, C$^{3\text{ or }4}$], 77.6 [d, *J*(CH) 160, C$^{1\text{ or }6}$], 67.2 [d, *J*(CH) 165, C$^{1\text{ or }6}$], 32.2 [t, *J*(CH) 132, CH_2]
2 C, 53.1 (58.1); H, 6.6 (7.2)	Red	^{1}H (C_6D_6, 295 K): 5.3 (m, 4 H, H^{b,c}), 4.8 (s, 7 H, H^{1}), 4.3 [m, 1 H, *J*(H^{a}H^{b}) 4, H^{a}], 2.0 (m, 4 H, H$^{d\text{ or }e}$), 0.5 [d, 9 H, *J*(PH) 3, 3PCH_3] ^{31}P-{^{1}H} (C_6D_6): −49.5 ^{13}C-{^{1}H} (C_6D_6): 109.2 (C^{b} or C^{c}), 101.7 (C^{b} or C^{c}), 89.5 (C^{a}), 80.4 (C_7H_7), 36.3 (CH_2), 17.0 [d, *J*(PC) 11, PCH_3]
3 C, 55.9 (58.2); H, 6.7 (6.9)	Red	^{1}H (C_6D_6): 5.4 [dd, 4 H, *J*(H^{b}H^{a}) 7, *J*(H^{b}H^{c}) 11, H^{b}], 5.2 (m, 4 H, H^{c}), 4.9 [d, 14 H, *J*(PH) 0.6, C_7H_7], 4.25 [dtt, 2 H, *J*(PH) 1.3, *J*(H^{a}H^{c}) 1.8, *J*(H^{a}H^{b}) 7.5, H^{a}], 1.9 (m, 8 H, H^{d,c}), 1.1 (m, 4 H, PCH_2), 0.6 (s, 12 H, PCH_3) ^{31}P-{^{1}H} (C_6D_6): −43.52 (br s) ^{13}C-{^{1}H} (C_6D_6): 113.3 (C^{b} or C^{c}), 102.1 (C^{b} or C^{c}), 92.9 (C^{a}), 81.2 (C_7H_7), 36.7 (C^{d,c}), 27.4 (2PCH_2), 14.1 (4PCH_3)
4 C, 45.3 (45.6); H, 5.1 (5.2); Cl, 12.1 (12.2)	Black	^{1}H^{b} (C_4D_8O): 5.11 (s, C_7H_7), 5.10 (s, C_7H_7)
5 C, 46.5 (46.7); H, 6.8 (6.9); N, 8.4 (8.3)	Blue	^{1}H (C_6D_6): 5.26 (s, 7 H, C_7H_7), 2.2 (s, 6 H, NCH_3), 1.8 (m, 2 H, NCH_2), 1.7 (s, 6 H, NCH_3), 1.2 (m, 2 H, NCH_2) ^{13}C (C_6D_6): 84.4 [d, *J*(CH) 165, C_7H_7], 58.1 [t, *J*(CH) 139, NCH_2], 51.0 [q, *J*(CH) 137, NCH_3], 49.2 [q, *J*(CH) 135, NCH_3]
6 C, 32.4 (31.4); H, 4.7 (5.1)	Purple	^{1}H ($CD_3C_6D_5$): 5.1 (s, 7 H, C_7H_7), 0.8 [d, 18 H, *J*(PH) 5, 6PCH_3] ^{31}P-{^{1}H} ($CD_3C_6D_5$): −53.0 (s) ^{13}C ($CD_3C_6D_5$): 83.5 [d, *J*(CH) 167, C_7H_7], 16.1 [dq, *J*(CH) 124, *J*(PC) 8, PCH_3]
7 C, 42.1 (42.4); H, 6.1 (6.3); Cl, 9.8 (9.6)	Turquoise	^{1}H ($CD_3C_6D_5$, 295 K): 5.3 (s, 7 H, C_7H_7), 0.7 (br m, 16 H, dmpe) ($CD_3C_6D_5$, 243 K):[c] 5.3 (s, 7 H, C_7H_7), 0.86 (br s, *ca.* 8 H, PCH_3 and PCH_2), 0.51 (br s, *ca.* 8 H, PCH_3 and PCH_2) ^{31}P-{^{1}H} ($CD_3C_6D_5$, 303 K): −37.2 ^{13}C ($CD_3C_6D_5$): 83.0 [d, *J*(CH) 162, C_7H_7], 27.2 [t, *J*(PH) 20, PCH_2], 11.9 (br s, PCH_3)
8 C, 42.7 (42.9); H, 5.45 (5.6)	Purple	^{1}H (CD_2Cl_2): 5.4 (s, 7 H, C_7H_7), 3.8 (s, 4 H, 2OCH_2), 3.6 (s, 6 H, 2OCH_3)
9	Green	^{1}H (C_6D_6): 6.1 (br t, 2 H, H$^{2\text{ or }5}$), 5.8 (m, 2 H, H$^{3\text{ or }4}$), 5.3 (m, 2 H, H$^{1\text{ or }6}$), 4.8 (m, 2 H, H$^{1\text{ or }6}$), 4.7 (tt, 2 H, H$^{2\text{ or }5}$), 2.7 (m, 4 H, H$^{7''}$ H$^{3\text{ or }4}$), 1.6 (br d, 2 H, H$^{7'}$)
12	Orange	^{1}H ($CD_3C_6D_5$, 253 K): 6.5 (br t, 1 H, H$^{1'}$), 6.0 (br t, 1 H, H^{5}), 5.7 (br q, 1 H, H^{3}), 5.5 (t, 1 H, H$^{2'}$), 5.2 (m, 1 H, H^{6}), 4.7 (m, 2 H, H$^{3'}$, H$^{4'}$), 4.1 (m, 1 H, H^{2}), 3.3 (m, 1 H, H$^{7\text{ or }8}$), 3.0 (m, 1 H, H$^{7\text{ or }8}$), 2.7 (t, 1 H, H^{4}), 2.6 (br t, 1 H, H$^{5'}$), 2.4 (m, 1 H, H^{1}), 1.7 (m, 1 H, H$^{6'}$), 1.2 (m, 1 H, H$^{7'}$), 1.0 [d, 3 H, *J*(PH) 5, PCH_3], 0.9 (br m, 4 H, PCH_2), 0.7 [d, 3 H, *J*(PH) 5, PCH_3], 0.5 [d, 3 H, *J*(PH) 5, PCH_3], 0.5 (m, 1 H, H$^{8'}$), 0.2 [d, 3 H, *J*(PH) 5, PCH_3] ^{31}P-{^{1}H} ($CD_3C_6D_5$, 243 K): 2.7 [d, *J*(PP) 32], −15.2 [d, *J*(PP) 32] ^{31}P-{^{1}H}^{d} ($CD_3C_6D_5$, 243 K of minor isomer): 6.3 [d, *J*(PP), 31], −14.7 [d, *J*(PP), 32]
12	Orange	^{13}C^{e} (C_4H_8O–C_4D_8O, 270 K): 131.7 [d, *J*(CH) 145, CH], 128.8 [d, *J*(CH) 162, CH], 128.0 [d, *J*(CH) 165, CH], 125.2 [d, *J*(CH) *ca.* 160, CH], 125.1 [d, *J*(CH) *ca.* 160, CH], 125.0 [d, *J*(CH) *ca.* 160, CH], 115.4 [d, *J*(CH) *ca.* 153, CH], 110.6 [d, *J*(CH) 161, CH], 107.4 [d, *J*(CH) 156, CH], 103.3 [d, *J*(CH) 157, CH], 100.6 [d, *J*(CH) 154, CH], 99.6 [d, *J*(CH) 156, CH], 33.9 [t, *J*(CH) 144, CH_2], 20.8 [q, *J*(CH) 126, PCH_3] ^{13}C-{^{1}H}: 15.1 [d, *J*(PC) 12, PCH_3] 14.5 [dd, *J*(PC) 12, 2, PCH_2], 12.3 [d, *J*(PC) 9, PCH_3], 12.1 [dd, *J*(PC) 6, 3, PCH_2]

[a] Analytical data (%) given as Found (Calc.). Unless otherwise stated: ^{1}H NMR at 300 MHz, ^{31}P at 101 MHz, and ^{13}C at 75 MHz. [b] These peaks were observed to be present in the ratio 1:3 in agreement with an equilibrium of the type proposed previously. [c] The exact position of the methylenes could not be determined. [d] The presence of two minor isomers was indicated in the ^{31}P NMR spectrum at 243 K in the ratio 90:8: < 2. [e] One CH_2 and one PCH_3 obscured either by coincidental overlap or by the solvent resonances.

Table 2 Selected bond distances (Å) and angles (°) for compound **1** with estimated standard deviations in parentheses

Zr-C(1)	2.376(6)	Zr-C(11)	2.413(6)
Zr-C(2)	2.474(5)	Zr-C(12)	2.448(5)
Zr-C(3)	2.419(5)	Zr-C(13)	2.394(5)
Zr-C(4)	2.397(5)	Zr-C(14)	2.433(5)
Zr-C(5)	2.436(6)	Zr-C(15)	2.449(5)
Zr-C(6)	2.436(6)	Zr-C(16)	2.376(5)
Zr-C(7)	2.761(6)	Zr-C(17)	2.761(6)
C(1)-C(2)	1.434(8)	C(11)-C(12)	1.376(8)
C(2)-C(3)	1.387(9)	C(12)-C(13)	1.404(8)
C(3)-C(4)	1.419(8)	C(13)-C(14)	1.436(8)
C(4)-C(5)	1.429(8)	C(14)-C(15)	1.399(8)
C(5)-C(6)	1.378(8)	C(15)-C(16)	1.410(8)
C(6)-C(7)	1.471(9)	C(16)-C(17)	1.506(8)
C(7)-C(1)	1.496(8)	C(17)-C(11)	1.526(7)

C(1)-C(2)-C(3)	127.0(6)	C(5)-C(6)-C(7)	127.2(5)
C(2)-C(3)-C(4)	130.2(5)	C(6)-C(7)-C(8)	118.8(5)
C(3)-C(4)-C(5)	128.6(6)	C(7)-C(1)-C(2)	121.6(6)
C(4)-C(5)-C(6)	126.9(6)		

Best plane [C(1)-C(6)]-best plane [C(11)-C(16)] 25.6

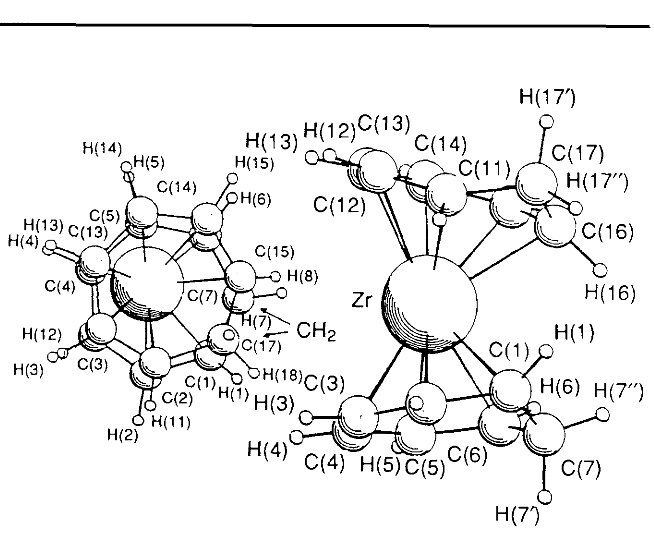


Fig. 1 Molecular structure of compound **1**

the proposed structure of compound **4**. For example, treatment of compound **4** with dmpe, tmen or 1,2-dimethoxyethane (dme)

Table 3 Atomic coordinates (× 10^4) for all non-hydrogen atoms of $[Zr(\eta^6\text{-}C_7H_8)_2]$

Atom	*X/a*	*Y/b*	*Z/c*
Zr	184.3(5)	2014.4(4)	3159.1(4)
C(1)	1599(7)	2154(6)	1696(5)
C(2)	2912(6)	2084(6)	2744(5)
C(3)	3013(6)	1334(5)	3666(5)
C(4)	1988(7)	385(5)	3779(5)
C(5)	574(7)	−66(5)	2945(6)
C(6)	−125(7)	360(5)	1849(5)
C(7)	673(8)	1094(5)	1151(5)
C(11)	327(8)	4112(5)	3237(5)
C(12)	158(7)	3777(5)	4300(5)
C(13)	−990(6)	2980(5)	4518(4)
C(14)	−2339(6)	2398(5)	3722(5)
C(15)	−2789(6)	2408(5)	2512(5)
C(16)	−1975(6)	2989(5)	1788(4)
C(17)	−1074(7)	4124(5)	2121(5)

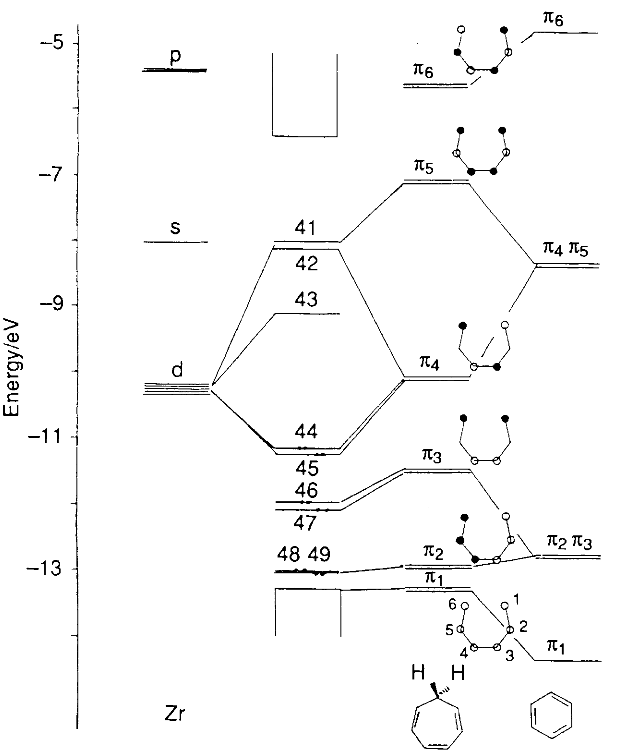


Fig. 2 Molecular orbital diagram for compound **1**

gives a turquoise compound **7**, a blue compound **5** or a purple compound **8**, respectively, in high yields.

Bonding in $[Zr(\eta^6\text{-}C_7H_8)_2]$ *and* $[Zr(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$. An examination of the bonding in compound **1** and its variation with the angle between the rings was undertaken using charge-iterative extended-Hückel molecular-orbital calculations and photoelectron spectroscopic investigations.

The molecular orbital diagram obtained from the calculations on compound **1** is shown Fig. 2 which also illustrates how the frontier molecular orbitals can be derived from those of benzene. The nature of the π orbitals of cycloheptatriene can clearly be seen from this comparison. When the six π levels of cycloheptatriene are compared with those of benzene it is evident that on opening the ring linkage between C^1 and C^6 those orbitals which are bonding across C^1 and C^6 are destabilised and those which are antibonding between C^1 and C^6 are stabilised. These shifts result in the highest occupied molecular orbital (HOMO) π_3 being higher in energy in cycloheptatriene than in benzene and the lowest unoccupied molecular orbital (LUMO) π_4 being lower

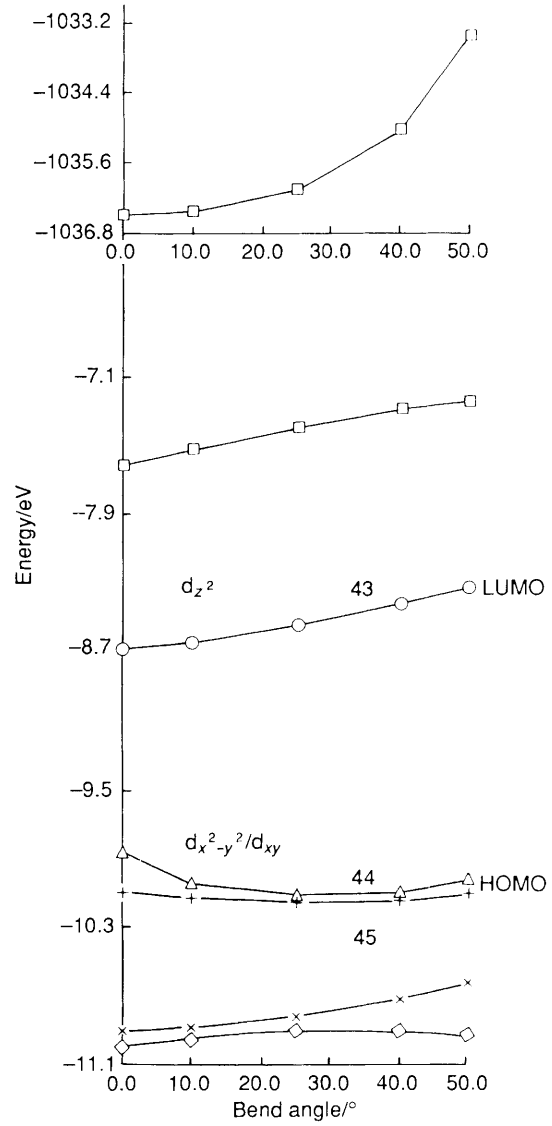


Fig. 3 Effect of bending on the orbital energies of compound **1**

in energy than in benzene. Cycloheptatriene is thus set up to be both a better donor and a better acceptor than benzene.

Orbital 43, the LUMO, is essentially a d_{z^2} orbital. Orbitals 44 and 45 are hybrid orbitals which contain a large percentage of ring character, the $d_{x^2-y^2}$ and d_{xy} orbitals mixing strongly with the two π_4 from the two rings.

A small contribution of d_{xz} is also present. Although in a d^4, zero-oxidation-state formalism, these orbitals can be considered as metal-to-ligand back bonding, they have, in the calculation, a greater percentage of ring than metal character.

The effects of bending the cycloheptatriene rings are shown in Fig. 3. The HOMO (44) and $HOMO^{-1}$ (45) of compound **1** exhibit a stabilisation in energy on bending with a minimum energy at a similar angle to that obtained from the crystal structure, although they predict a slight destabilisation in the total energy for the system. No similar stabilisation is obtained for any of the orbitals in $[Zr(\eta^6\text{-}C_6H_6)_2]$.

We now consider the origin of the staggered structure. In the hypothetical arrangement where the molecule has C_{2v} symmetry, *i.e.* the rings are eclipsed, combinations of π_4 transform as b_2 and a_2, but d_{xy} and $d_{x^2-y^2}$ transform as b_2 and a_1, so only one of the d orbitals is of the correct symmetry to back-donate to the ligand. When the symmetry is lowered to C_2, *i.e.* on staggering the rings, then both orbitals can back-donate, as illustrated.

Measurement of the photoelectron spectrum of compound **1**

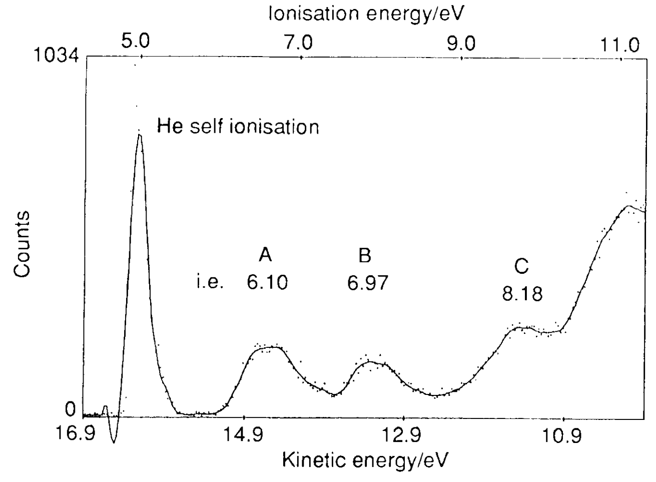


Fig. 4 He I photoelectron spectrum of compound **1**

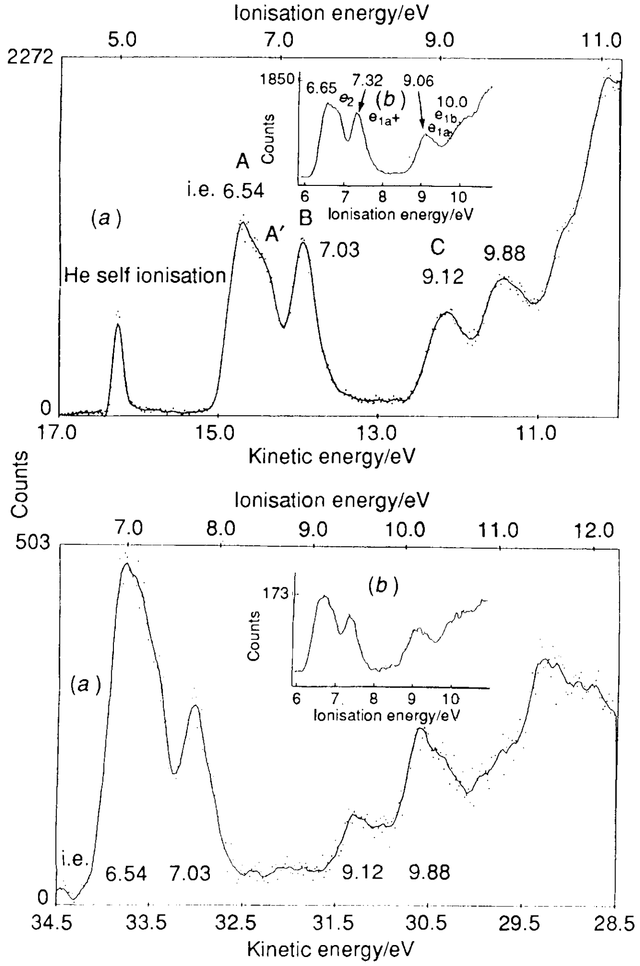
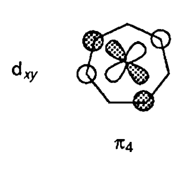
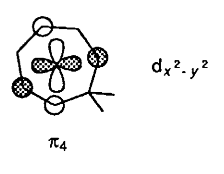


Fig. 5 He I (top) and He II (bottom) photoelectron spectra of compounds **11**(*a*) and **10**(*b*) (inset)

was complicated by the fact that between the temperatures of 74 and 160 °C the spectrum changed. At the higher temperature the spectrum was that of compound **11** so it was presumed that isomerisation was taking place and that the spectrum at lower temperature was that of compound **1**. As long as the temperature was held constant at 67 °C the spectrum remained





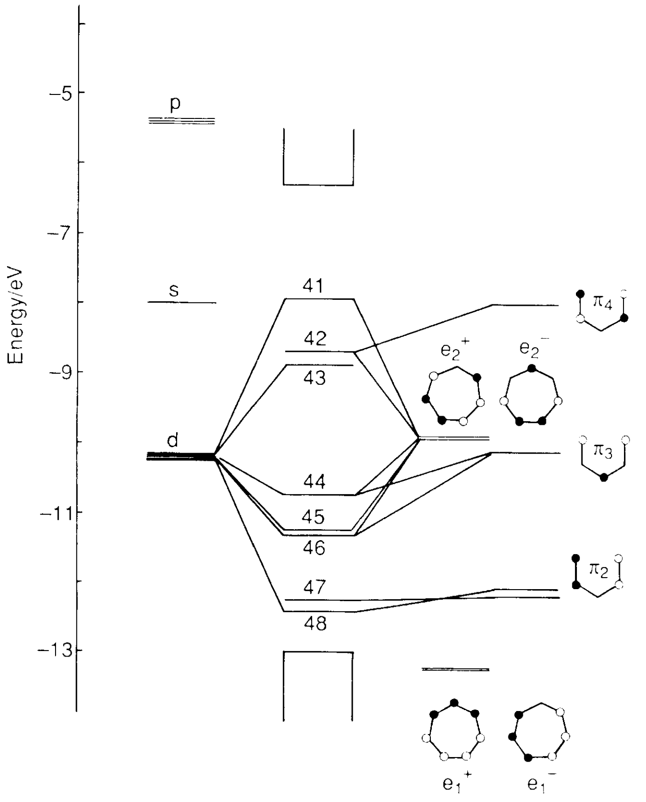


Fig. 6 Molecular orbital diagram of compound **11**

stable, but collection of data with reasonable signal-to-noise ratio with He I radiation took several hours, so a He II spectrum was not obtained.

The He I spectrum obtained is given in Fig. 4. The band at 16.23 eV is a He(1s)$^{-1}$ ionisation. Band A is assigned to orbitals 44 and 45 which are predominatly π_4 in character, B to orbitals 46 and 47 which originate from the π_3 orbitals, and C to orbitals 48 and 49 which are predominatly π_2. The 2 : 2 : 2 orbital pattern found in the calculation is thus reflected in the photoelectron spectrum. Lack of He II data in this case prevents an analysis of the d content of the molecular orbital.

[Zr(η^7-C_7H_7)(η^5-C_7H_9)]: *Extended-Hückel Calculations and Photoelectron Spectrum.*—The crystal structure of this compound has not been determined. Recent structural work by Rogers and Teuben[15] indicates that the larger zirconium will fit better than titanium onto a η^7-C_7H_7 ring.

The molecular orbital diagram for the compound **11** is shown in Fig. 6 (in an unbent arrangement) and is obviously closely related to those of compound **1** The HOMO and the HOMO^{-1} have only limited metal character like those of compound **1**.

Photoelectron spectra of compound **11** were obtained in order to examine the character of the important molecular orbitals. Previous work by Davies *et al.*[14] examined the photoelectron spectra of [Ti(η^7-C_7H_7)(η^5-C_7H_9)] **10** and assigned the bands. The He I spectra, Fig. 5, of **10** and **11** are remarkably similar both in band shape and in ionisation energies.

Empirically one can compare the band intensities of the He I spectrum with those of the He II spectrum, making use of the observation that the photoelectron cross-sections of metal d orbitals and ligand molecular orbitals differ significantly. Bands associated with ionisations from molecular orbitals of metal d character are considerably enhanced in the He II spectrum relative to those which originate from ligand orbitals.

In the photoelectron spectrum of compound **11** it is clear that band A has appreciable d character and has a slight high-energy shoulder, A′. Examination in detail suggests that the order of

Table 4 Parameters used in extended-Hückel calculations

Orbital		H_{ii}/eV	ζ_1	ζ_2
Zr	4d*	−9.53	1.82	1.776
	5s	−9.34		
	5p	−5.81		
C(1)	2s	−19.98	1.62	1.62
	2p	−10.19		
C(2)	2s	−20.23	1.62	1.62
	2p	−10.43		
C(3)	2s	−19.90	1.62	1.62
	2p	−10.10		
C(4)	2s	−20.01	1.62	1.62
	2p	−10.21		
C(5)	2s	−20.25	1.62	1.62
	2p	−10.45		
C(6)	2s	−19.78	1.62	1.62
	2p	−9.98		
C(7)	2s	−20.33	1.62	1.62
	2p	−10.53		
C(11)	2s	−19.82	1.62	1.62
	2p	−10.02		
C(12)	2s	−20.26	1.62	1.62
	2p	−10.46		
C(13)	2s	−19.95	1.62	1.62
	2p	−10.15		
C(14)	2s	−19.93	1.62	1.62
	2p	−10.13		
C(15)	2s	−20.30	1.62	1.62
	2p	−10.49		
C(16)	2s	−19.86	1.62	1.62
	2p	−10.06		
C(17)	2s	−20.26	1.62	1.62
	2p	−10.46		

* $C_1^a = 0.622$, $C_1^b = 0.578$

the bands differs from the predicted molecular-oribtal order. The orbitals with a high metal content are 45 and 46 and so A and A′ can be assigned as 45 and 46 and band B is assigned to orbital 44, the HOMO of the calculation. The HOMO is predominantly ligand in character, mostly comprised of the top π level of C_7H_9. From a detailed study of other pentadienyl compounds π_3 has an ionisation energy of around 7–8 eV, π_2 9–10 eV, and π_1 10–11 eV. These are in agreement with the assignment of C to orbital 48(π_2) and D to 50 and 51(π_1).[16]

The reactions and structures proposed for the new compounds are shown in Scheme 1.

Experimental

All manipulations were performed using standard Schlenk-line techniques 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 over-pressure of dinitrogen, and filtered using cannulae modified to be fitted with glass-fibre discs. 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 predried 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), diethyl ether, pentane]. Deuteriated solvents for NMR spectroscopy were stored in Young's ampoules over activated molecular sieves (CD_2Cl_2) or sodium–potassium alloy (benzene, toluene) and transferred by pipette in an inert-atmosphere glove-box to the NMR tubes which were subsequently sealed at high vacuum (10^{-5} mmHg). 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). Solid-state [cross-polarization magic angle spinning (CPMAS)] ^{13}C and ^{31}P NMR spectra were performed on a Brüker CXP 200 instrument, equipped with an Andrews-type MAS probe, and high-power proton decoupler. All chemical shifts are quoted in δ (ppm) and coupling constants 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.

Photoelectron spectra were recorded on a P.E.S. Laboratories 0078 spectrometer using a heated inlet system, and calibrated using the ionisation potentials of He, N_2 and Xe. Figs. 4 and 5 show the experimental spectra as points; the solid line is a least-squares fit to these points. The He I spectra of compounds **1** and **11** were obtained at 67 and 100 °C respectively. The parameters used in the extended-Hückel calculation are summarised in Table 4.

Microanalyses were performed by Analytische Laboratorien, Elbach, Germany.

Crystallography.—Crystal data for compound **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, $\beta = 105.63(3)°$, $U = 1115$ Å^3, $Z = 4$, $D_c = 1.64$ g cm^{-3}, μ(Mo-Kα) = 9.32, $F(000) = 560$ crystal size *ca.* 0.2 × 0.2 × 0.8 mm.

A black crystal of compound **1** was mounted in a Lindemann tube (0.7 mm) under dinitrogen and sealed with a small flame. This was transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer. Data were collected ($2\theta_{max} = 50$ °C) using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å) and ω–2θ scan mode. Unit-cell parameters were calculated from the setting angles of 25 accurately centred reflections. Negligible fluctuation was observed for three intensity standards measured repeatedly at 2-h intervals. An empirical absorption correction was applied and the data were corrected for Lorentz and polarisation effects. The location of the zirconium was determined using SHELXS,[17] and the other non-hydrogen atoms were determined from subsequent difference maps. Refinement was carried out using 1266 observed reflections [$I > 3\sigma(I)$] from 2914 independent reflections measured. The hydrogen atoms were placed in calculated positions and refined riding on their supporting atoms with thermal parameter 1.3 times that of the carbon atom. Full-matrix least-squares refinement of 52 least-squares parameters led to final agreement factors of $R = 0.0381$ and $R' = 0.0444$ [Chebyshev weighting scheme (parameters: 5.37, −1.17, 3.98)[18]]. All calculations were performed using the CRYSTALS suite of programs[19] on the VAX11/750 computer in the Chemical Crystallography Laboratory, Oxford.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Bis(η^6-cycloheptatriene)zirconium **1**.—Cold thf (700 cm^3, −30 °C) was added to $ZrCl_4$ (20 g, 86 mmol) at −196 °C and allowed to warm gradually to −20 °C. The mixture was slurried onto sodium amalgam (10 g of sodium in *ca.* 100 cm^3 of Hg), maintained at −78 °C, and stirred rapidly using an overhead mechanical stirrer for 15 min. Freshly distilled cycloheptatriene (50 cm^3, 0.482 mol) was added and, maintaining rapid stirring at all times, the reaction mixture allowed to warm to −20 °C over 1 h and to 10 °C in another 2 h during which time the mixture changed from a murky grey to deep red. Stirring was stopped and the thf removed *in vacuo* without heating above 20 °C. The red-brown sludge was extracted with light petroleum (b.p. 40–60 °C, 6 × 500 cm^3) and fritted through 7 cm of Celite. The solution was cooled to −78 °C producing black crystals of compound **1** (8.5 g, 37%); further reduction of solvent volume to 100 cm^3 produces only 0.5 g of less-pure product.

Reactions of Compound **1**.—*With* CO. (*a*) A stirred toluene solution (20 cm^3) of compound **1** (100 mg, 0.4 mmol) was placed under 2 atm of CO. Over 2 d the initially dark red-brown solution lightened. The solvent was removed under reduced pressure to give a red solid which proved to be compound **11**; yield >90 mg (>90%).

(*b*) A stirred toluene solution (50 cm^3) of compound **1** (280 mg, 1 mmol) was placed under 8 atm of CO. Overnight the dark red-brown solution turned red. The solvent was removed under reduced pressure leaving a red solid which proved to be compound **11**; yield *ca.* 280 mg (> 90%).

With tmen. The ligand tmen (0.5 cm^3, 3.3 mmol) was added to a toluene solution (20 cm^3) of compound **1** (*ca.* 100 mg, 0.4 mmol) and the mixture was stirred for 8 h, the solution lightening in colour as the reaction proceeded. Removal of solvent at reduced pressure gave compound **11** (*ca.* 100 mg, >90%).

With [Sn$_2$Me$_6$]. No change was observed when [Sn$_2$Me$_6$] (*ca.* 0.2 g) was added to compound **1** (0.2 g, 0.73 mmol) in toluene (20 cm^3) and stirred for 12 h at ambient temperature. The solution was then heated at 60 °C for 5 h; removal of solvent *in vacuo* gave a red solid which was dried under reduced pressure. The ^{1}H NMR spectrum of the solid showed that the only organometallic product present was compound **11**. Yield (*ca.* 0.2 g, >90%).

(η^5-*Cycloheptadienyl*)(η^7-*cycloheptatrienyl*)(*trimethylphosphine*)*zirconium* **2**.—(*a*) Trimethylphosphine (*ca.* 2 cm^3, 20 mmol) was added to a stirred solution of compound **1** (1 g, 3.6 mmol) in toluene (120 cm^3), the mixture stirred for 10 min and allowed to stand overnight at r.t. The solution was filtered, reduced in volume to *ca.* 50 cm^3, and cooled to −80 °C yielding red crystals of compound **2** (480 mg, 38%).

(*b*) A sample of [Zr(η^7-C$_7$H$_7$)(η^5-C$_7$H$_9$)] **11** in C$_6$D$_6$ treated with PMe$_3$ (excess) was monitored by ^{1}H NMR spectroscopy over a period of 48 h and was observed to undergo clean conversion into compound **2**. Yield (>90%).

Preparation of [{Zr(η^7-C$_7$H$_7$)(η^5-C$_7$H$_9$)}$_2$(dmpe)] **3**.—(*a*) The ligand dmpe (0.12 cm^3, 0.73 mmol) was added to a toluene solution (50 cm^3) of compound **11** and the mixture was left to stand for 12 h. Gradually small red crystals were deposited which were separated by filtration and dried under reduced pressure giving compound **3** (160 mg, 52%).

(*b*) A sample of [Zr(η^4-C$_7$H$_8$)$_2$(dmpe)] **12** in C$_6$D$_6$ was monitored by ^{1}H NMR spectroscopy over a period of 48 h and was observed to undergo conversion into compound **3** (*ca.* 40%) but accompanied by a small amount of decomposition.

Bis[(μ-*chloro*)(η^7-*cycloheptatrienyl*)(*tetrahydrofuran*)*zirconium*] **4**.—The compound (AlEt$_2$Cl)$_2$ (3.5 cm^3, 26 mmol) was added to a cold (*ca.* −100 °C) solution of compound **1** (6 g, 22 mmol) in thf (100 cm^3). This mixture was stirred rapidly for 30 min and allowed to stand at r.t. for 2 weeks. Slowly, over this time, black microcrystals of compound **4** were deposited (2.63 g) and after another 3 weeks 0.31 g was deposited; total yield (46%). The mother-liquor was evaporated to dryness under reduced pressure giving a red-brown oily solid which was extracted into toluene (50 cm^3) giving a deep red solution. This was placed at −78 °C and red crystals of compound **11** were deposited over 20 h. Yield 2 g (33%).

Chloro(η^7-*cycloheptatrienyl*)(N,N,N′,N′-*tetramethylethylenediamine*)*zirconium* **5**.—A stirred suspension of compound **4** (1 g, 1.7 mmol) in toluene (80 cm^3) was treated with a solution of tmen (*ca.* 3 cm^3) in toluene. A rapid colour change occurred from colourless to blue. The reaction was stirred for 14 h to ensure completion. The volatile components were then removed under reduced pressure to leave a blue solid. This was extracted into hot toluene (20 cm^3, 80 °C), filtered, and cooled to r.t. over 12 h. The mother-liquor was decanted leaving blue crystals of compound **5** which were dried *in vacuo* (0.792 mg). A second crop was obtained from the supernatant at −20 °C (195 mg). Yield 0.987 g (86%).

Chloro(η^7-*cycloheptatrienyl*)*bis*(*trimethylphosphine*)*zirconium* **6**.—A stirred suspension of compound **4** (40 mg, 0.07 mmol) in toluene (20 cm^3) was treated with a solution of PMe$_3$ (0.4 cm^3) in toluene. A rapid colour change occurred from colourless to purple and the reaction was stirred for 1.5 h. The volatile components were then removed under reduced pressure to leave a purple solid. This was extracted into toluene (20 cm^3), filtered, and cooled to −20 °C. Purple crystals of compound **6** were obtained (42 mg, 90%).

[1,2-*Bis*(*dimethylphosphino*)*ethane*]*chloro*(η^7-*cycloheptatrienyl*)*zirconium* **7**.—A stirred suspension of compound **4** (80 mg, 0.137 mmol) in toluene (20 cm^3) was treated with a solution of dmpe (0.3 cm^3) in toluene. A rapid colour change was observed, from colourless to turquoise. The reaction was stirred for 12 h to ensure completion. The volatile components were then removed under reduced pressure to leave a turquoise solid. This was extracted into hot toluene (20 cm^3, 80 °C), filtered, and cooled to r.t. Turquoise crystals of compound **7** were obtained (140 mg, 54%).

Chloro(η^7-*cycloheptatrienyl*)(1,2-*dimethoxyethane*)*zirconium* **8**.—A stirred suspension of compound **4** (400 mg, 1.7 mmol) in toluene (50 cm^3) was treated with dme (2.5 cm^3) as a toluene solution. A rapid colour change from colourless to purple occurred. The reaction was stirred for 15 h to ensure completion. The volatile components were then removed under reduced pressure to leave a purple solid. This was dissolved in CH$_2$Cl$_2$ (*ca.* 5 cm^3), filtered, and cooled at −80 °C for 20 h, giving purple needles. The supernatant solution was decanted leaving 80 mg of compound **8**; reduction of the volume of the solution gave another 200 mg. Yield 280 mg (29%). When a sample of **8** was left in dichloromethane at r.t. for 12 h decomposition to a flocculent brown precipitate occurred.

Bis(η^6-*cycloheptatriene*)*titanium* **9**.—Cold thf (50 cm^3, −30 °C) was added to TiCl$_4$ (2.3 cm^3, 20 mmol) at −196 °C and allowed to warm gradually to −20 °C. This mixture was slurried onto a stirred suspension of magnesium turnings (3 g, 0.123 mmol) in thf (20 cm^3), and to this freshly distilled cycloheptatriene (15 cm^3, 0.150 mol) was added with rapid stirring at all times. The reaction mixture was allowed to warm to r.t. over 2 h, the solution gradually taking on a green colour. Stirring was stopped and the thf removed *in vacuo* without heating above 20 °C. The resulting green sludge was extracted with light petroleum (b.p. 40–60 °C, 6 × 500 cm^3), filtered, and the solvent reduced *in vacuo* to *ca.* 40 cm^3. The solution was cooled to −78 °C producing green microcrystals of a 1:4 mixture of compounds **10** and **9** (800 mg, 18%).

(η^5-*Cycloheptadienyl*)(η^7-*cycloheptatrienyl*)*zirconium* **11**.—Cold thf (30 cm^3, −30 °C) was added to ZrCl$_4$ (2 g, 8.6 mmol) at −196 °C and allowed to warm gradually to r.t. This was slurried onto a stirred suspension of sodium amalgam (0.97 g of Na, *ca.* 50 cm^3 of Hg) in thf (50 cm^3), and to this freshly distilled cycloheptatriene (*ca.* 10 cm^3, 0.098 mol) was added with rapid stirring at all times. After 1 h the mixture had darkened considerably to a murky brown colour which gradually gained a red colouration, on stirring for 10 h. Stirring was stopped and the thf removed *in vacuo* without heating above 20 °C. The green sludge was extracted with light petroleum (b.p. 40–60 °C, 200 cm^3), filtered, and reduced *in vacuo* to *ca.* 20 cm^3. The solution was cooled to −78 °C giving red microcrystals of compound **11** (1.1 g, 44%).

[1,2-Bis(dimethylphosphino)ethane]bis(η^4-cycloheptatriene)-zirconium **12**.—The ligand dmpe (0.12 cm^3, 0.73 mmol) was added to a stirred suspension of compound **1** (200 mg, 0.73 mmol) in light petroleum (b.p. 40–60 °C, 40 cm^3). Immediately orange microcrystals began to deposit. After stirring for 4 h the solution was filtered and the residue extracted with light petroleum (b.p. 40–60 °C, 2 × 30 cm^3) and once with toluene (10 cm^3). The extracts were combined and cooled to -80 °C, giving an orange powder which was recrystallised from toluene at -20 °C to give orange crystals. These were separated by filtration and dried under reduced pressure giving pure compound **12** (201 mg, 65%).

Acknowledgements

We thank the SERC and ICI for a CASE award (to N. M. W.) and Dr. John Kelland (ICI, Wilton) for helpful discussions.

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Received 30*th July* 1990; *Paper* 0/03471A