ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 605 (2000) 45–54

Journal of Organometallic Chemistry

Synthesis of racemic chiral-at-metal complexes of the Group 4 metals

Nathaniel W. Alcock, Howard J. Clase, David J. Duncalf, Suzanne L. Hart, Andrew McCamley, Peter J. McCormack, Paul C. Taylor *

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK

Received 14 February 2000; accepted 16 April 2000

Abstract

A protocol for asymmetric synthesis of chiral-at-metal complexes is described, but enantiomerically-enriched products can not be isolated due to formation of complexes between the Group 4 metallocene products and the borane by-products. An efficient method for synthesis of racemic chiral-at-metal metallocenes, through lithium chloride catalysed ligand redistribution reactions, is described. Sterically-hindered racemic chiral-at-metal complexes are prepared by nucleophilic substitution of prochiral dichlorides.

Keywords: Titanocene; Zirconocene; Hafnocene

1. Introduction

Chiral complexes of Group 4 metals, both racemic and enantiomerically enriched, have found numerous applications as catalysts for stereoregular polymerisations and catalysts and reagents for asymmetric synthesis [1,2]. The majority of these complexes are chiral due to the presence of one or more centres of chirality in one or more of the ligands. A further group of complexes are chiral due to conformational restrictions, notably the so-called ebi and ebthi metallocenes [2]. Our interest lies in a third, little studied class of chiral complexes of Group 4 metals such as **1** [3], where the metal atom is the sole centre of chirality. These complexes belong to a general class of metal complexes which may be described as 'chiral-at-metal'.

Prominent among the chiral Group 4 complexes which are employed as catalysts are metallocene dichlorides and dialkyls. The chiral monochloro monoalkyl metallocenes **2**–**6b**–**e** were thus potential targets, as were the related monochloro monothiophenolato complexes **2**–**6f**. Three strategies for synthesis of racemic compounds **2**–**6b**–**f** from the prochiral dichlorides **2**–**6a** were considered: (i) direct nucleophilic displacement of chloride from compounds **2**–**6a**; (ii) ligand redistribution reactions between dichlorides **2**–**6a** and dialkyl or dithiophenolato compounds **7**–**11b**–**f**; (iii) transmetalation reactions from boron compounds. The last method was of particular interest to us as it offers an opportunity for asymmetric synthesis of non-racemic complexes.

Herein we first describe the preparation of the prochiral metallocene dichloride starting materials. The limitations of the direct nucleophilic displacement method ((i) above) are then discussed, followed by the conversion of the dichlorides to some of the dialkyl and dithiophenolato substrates **7**–**11b**–**f** for the ligand redistribution and transmetalation methods.

2. Results and discussion

2.1. Synthesis of mixed-ring metallocene dichlorides

All useful syntheses of mixed-ring transition metal complexes involve the stepwise introduction of the two rings to the metal centre [4]. The more synthetically versatile sequence, given that we aimed to have an unsubstituted Cp ligand in all our targets, is to intro-

* Corresponding author. Fax: +44-2476-524112.
E-mail address: p.c.taylor@warwick.ac.uk (P.C. Taylor).

0022-328X/00/$ - see front matter
PII: S0022-328X(00)00253-9

duce Cp in the first step followed by the required substituted ring. Fortunately, for the zirconium and hafnium series, this was also the higher yielding process (Scheme 1). Hence, zirconium and hafnium chlorides reacted with $CpSnBu_3$, according to Abel's procedure [4], to yield the half-sandwich intermediates. Displacement of a second chloride ligand with lithium indenide or Cp′Li led smoothly to the prochiral mixed-ring complexes **4**–**6a**. The tetramethylcyclopentadienyl zirconocene analogue $Me_4C_5HCpZrCl_2$ was also prepared and is included in Section 4.

Unfortunately, the procedure in Scheme 1 was not synthetically useful in our hands for the titanium analogues. Our failure to isolate the target complexes is consistent with Grubbs' observation that the second step leads to ring-exchange by-products (Cp_2TiCl_2 and Ind_2TiCl_2) in the indenyl case [5]. Therefore, it was necessary to introduce the substituted ring first, via the tributyltin reagent [4], followed by reaction with lithium cyclopentadienide (Scheme 2).

2.2. Chiral-at-metal compounds by nucleophilic displacement of chloride ligands

A conceptually simple method for preparation of racemic compounds **2**–**6b**–**f** is nucleophilic displacement of one of the chlorides of a metallocene dichloride by a nucleophile X^- (using a Grignard reagent, organolithium reagent or thiophenolate) (Scheme 3) [6]. However, in our experience this reaction is synthetically useful only in cases where the nucleophile is very sterically demanding; otherwise contamination with the disubstituted product is inevitable. Hence, reaction of dichlorides **2a**, **3a** and **6a** with one equivalent of trimethylsilylmethyl magnesium chloride or its lithium analogue, in diethyl ether at low temperature, led smoothly to the racemic chiral products **2d**, **3d** and **6d**.

That steric hindrance is significant in this reaction is indicated by the fact that in the cases of **2** and **6**, the bis(trimethylsilylmethyl) product could not be prepared, even with an excess of the nucleophile. Indeed, as we have previously reported [7], the crystallographic and ^{1}H-NMR data for compounds **2d** and **3d** give good evidence for a strong steric interaction between the trimethylsilyl group and the cyclopentadienyl substitutent.

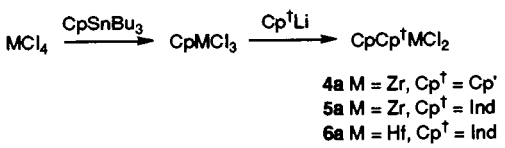
In short, synthesis of the target chiral-at-metal complexes by simple nucleophilic displacement of a chloride ligand is only useful when there is significant steric hindrance to addition of a second equivalent of the nucleophile.

2.3. Synthesis of dialkyl- and dithiophenolato-mixed-ring metallocenes

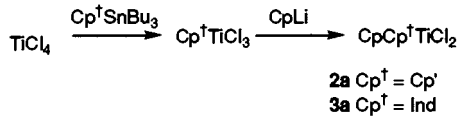
Our remaining synthetic strategies required the preparation of dialkyl and diphenylthiolato precursors **7**–**11b**–**f**. As anticipated [6], we encountered few problems with the simple substitution of the two chloride ligands of **2**–**6a**. Nucleophilic displacement of both chloride ligands of complexes **2**–**6a** was possible using a range of organolithium and Grignard reagents. With thiophenol it was possible to carry out chloride displacement reactions directly in the presence of non-nucleophilic organic bases, but reaction with preformed lithium thiophenolate gave better yields.

The new dimethyl, bis(trimethylsilylmethyl) and diphenyl complexes were prepared by the reaction of 2.2–2.4 mol equivalents of the corresponding lithium or Grignard reagent with the dichloride analogue. These nucleophilic displacement reactions were quite solvent dependent, with reactions in diethyl ether generally higher yielding than reactions in thf. The attempted syntheses of the dibenzyl complexes **4**–**6c** were unsuccessful. It is known that many Group 4 metallocene dibenzyl complexes, which have substituted cyclopentadienyl rings, are oils, which makes their isolation difficult [8]. However, we were able to isolate the titanium analogues **2c** and **3c**. Indeed, compound **2c** proved to be an interesting carbonyl benzylidenation reagent [9].

The reactions of **2**–**6a** with 2.2 mol equivalents of LiSPh led to the formation of the dithiophenolates **7**–**11f** in good yield. The low temperature crystal structures of **7f** and **9f** are shown in Fig. 1. Although the structures are unsurprising per se, there is an intriguing difference between the titanium and zirconium analogues as regards the orientations of the thiophenyl groups relative to the *t*-butyl substituent. It may be that



Scheme 1.



Scheme 2.

Scheme 3.

crystal packing favours the conformation found in the zirconium compound, but that this arrangement requires too much steric crowding in the tighter coordination sphere of titanium. Selected bond lengths and angles for **7f** and **9f** are given in Table 1.

The low-temperature crystal structure of **10e** is shown in Fig. 2 and selected bond lengths and angles are given in Table 2. The complex is one of a small number of crystallographically-characterised compounds containing a phenyl ring η^1-bound to zirconium [10]. The phenyl rings are η^1-bound to the zirconium atom with metal-carbon bond lengths of 2.286(5) and 2.289(4) Å which are not significantly different. It is

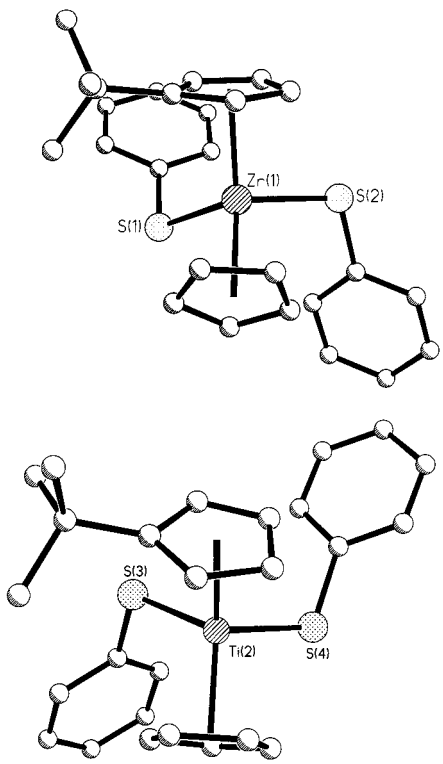


Fig. 1. Low temperature crystal structures of **7f** and **9f**.

Table 1
Selected bond lengths (Å) and bond angles (°) for **7f** and **9f**

7f		**9f**	
Ti–S(1)	2.414(2)	Zr–S(1)	2.5159(5)
Ti–S(2)	2.461(2)	Zr–S(2)	2.5198(5)
Ti–C(1)	2.427(7)	Zr–C(1)	2.586(2)
Ti–C(2)	2.363(7)	Zr–C(2)	2.517(2)
Ti–C(3)	2.318(7)	Zr–C(3)	2.466(2)
Ti–C(4)	2.412(7)	Zr–C(4)	2.497(2)
Ti–C(5)	2.483(7)	Zr–C(5)	2.547(2)
Ti–C(10)	2.361(7)	Zr–C(10)	2.516(2)
Ti–C(11)	2.393(7)	Zr–C(11)	2.534(2)
Ti–C(12)	2.400(7)	Zr–C(12)	2.519(2)
Ti–C(13)	2.392(7)	Zr–C(13)	2.470(2)
Ti–C(14)	2.376(7)	Zr–C(14)	2.488(2)
S(1)–Ti–S(2)	96.41	S(1)–Zr–S(2)	101.28(2)

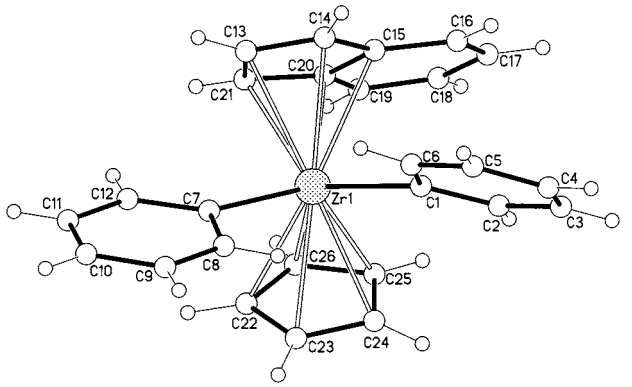


Fig. 2. Low temperature crystal structure of **10e**.

Table 2
Selected bond lengths (Å) and bond angles (°) for **10e**

Zr–Ph			
Zr–C(1)	2.289(4)	C(7)–Zr–C(7)	103.09(16)
Zr–C(7)	2.286(5)		
Zr–Indenyl			
Zr–C(13)	2.520(4)		
Zr–C(14)	2.527(4)		
Zr–C(15)	2.589(4)		
Zr–C(20)	2.569(4)		
Zr–C(21)	2.478(4)		
Zr–C_5H_5			
Zr–C(10)	2.525(5)		
Zr–C(11)	2.551(5)		
Zr–C(12)	2.527(4)		
Zr–C(13)	2.481(4)		
Zr–C(14)	2.493(5)		

Scheme 4.

interesting that the C–Zr–C bond angle in **10e** is rather large [10], presumably due to the two phenyl groups being forced into the same plane to avoid unfavourable interactions with the Cp and indenyl rings.

2.4. Chiral-at-metal compounds by ligand redistribution

In principle, mixing one equivalent of a dialkyl or diphenylthiolato compound **7**–**11b**–**f** with one equivalent of its dichloro precursor **2**–**6a** can lead to the target complexes by ligand redistribution (Scheme 4). This reaction has no by-product, which should make purification of the product simpler. Synthetically useful ligand redistribution reactions have been reported for mixtures of Cp_2TiCl_2 with Cp_2TiMe_2 and with Cp_2TiPh_2 [11]. The analogous reactions of Cp_2ZrCl_2 with Cp_2ZrMe_2 and with Cp_2ZrPh_2 proved much too

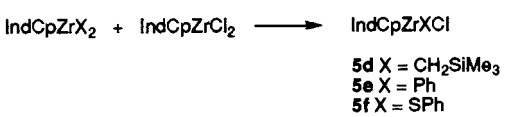
slow to be preparatively important [12]. Rapid ligand redistribution was noted between Cp_2ZrCl_2 and Cp_2ZrBr_2 [12,13].

As expected [11], the ligand redistribution reactions of the prochiral titanium compounds **7c** and **7f** with the dichloride **2a** proceeded smoothly to furnish the racemic chiral targets **2c** and **2f** in good yields and purity. However, contrary to expectations [12], rapid reaction was also observed for some alkyl zirconocene analogues. As we have previously communicated [14], these anomalously fast reactions could be linked to the presence of lithium chloride as an impurity. We thus added a small amount of lithium chloride to all the redistribution reactions which had previously been slow and, indeed, preparatively useful reaction times (less than 1 day) were observed in all cases. Pleasingly, three racemic chiral zirconocenes **5d–f** could be prepared in this manner (Scheme 5). The role of the lithium chloride in these reactions remains unclear.

In summary, the target chiral metallocene compounds can be prepared racemically by ligand redistribution reactions. For zirconium derivatives, the presence of lithium chloride is necessary for a synthetically useful procedure.

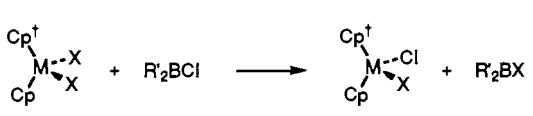
2.5. Chiral-at-metal compounds by transmetalation

Our target chiral-at-metal complexes could in principle be prepared by reaction of prochiral dialkyl or dithiophenolato metallocenes **7–11** with one equivalent of a chloride source. Although reactions of this type have been reported [6], the problems discussed in the nucleophilic displacement section above pertain here too and mixtures of mono- and di-substituted compounds result. Nevertheless, we were keen to proceed to the targets from complexes **7–11** using an external chloride source, since we wished to attempt to induce asymmetry in the process.



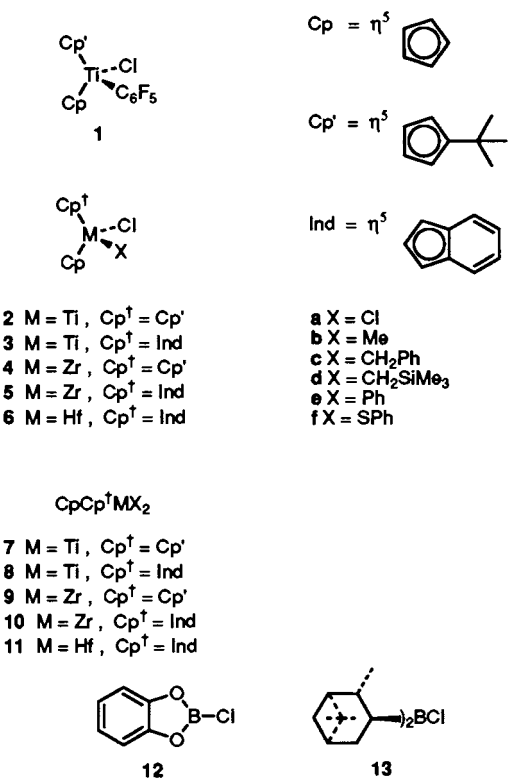
Scheme 5.

Scheme 6.



Scheme 7.

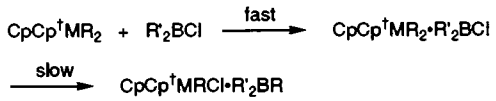
We therefore decided to adapt a procedure developed by Cole for transmetalation from zirconium to boron [15]. Cole's group found that monoalkyl- and monoalkenyl-zirconocene chlorides, prepared by hydrozirconation of alkenes and alkynes respectively, react with chloroboranes to yield the corresponding alkyl or alkenyl boranes (Scheme 6). A chloride ligand is transferred concomitantly from boron to zirconium. We reasoned that the parallel reaction of a dialkylmetallocene with a boron halide would proceed even more readily to yield chiral-at-metal products (Scheme 7). This transmetalation procedure was particularly attractive since enantiomerically enriched boron halides are readily available, thus providing an opportunity for asymmetric induction.



Model reactions of titanocenes **7c** and **7f** with achiral chlorocatecholborane **12** were followed by ^{1}H-NMR spectroscopy. It was clear, by comparison with authentic samples, that clean transmetalation had occurred to yield the racemic chiral products **2c** and **2f**.

Finally, we attempted reaction of titanocenes **7c** and **7f** and zirconocenes **10d–f** with the commercially available, enantiomerically-enriched chloroborane DIP-Cl (**13**). Again, ^{1}H-NMR spectroscopy showed that in all five cases the chiral complexes **2c**, **2f** and **5d–f** were the major products and we thus proceeded to a preparative scale, with the aim of isolating the, hopefully, enantiomerically-enriched chiral-at-metal metallocenes.

As expected, the preparative scale reactions led smoothly to mixtures of the chiral-at-metal product and



Scheme 8.

the by-product DIP-X ($X = CH_2Ph$, CH_2SiMe_3, Ph, SPh). However, we were most disappointed to find that despite numerous attempts, it was not possible to isolate the metallocenes free of the chiral DIP-X by-product and we were thus unable to determine to what extent, if any, asymmetric induction had occurred. It is conceivable that this problem is due to formation of a complex between the product and by-product. Indeed, kinetic studies [16] show these reactions to be first order, which is consistent with initial fast reaction of the reactants to form a complex, followed by slow, unimolecular reorganisation to a product complex (Scheme 8). We were unable to isolate and characterise any such complex and the fact that in some cases some of the DIP-X by-product could be separated by extraction into pentane argues against its existence in the crude product. Nevertheless, the extraction of DIP-X was remarkably difficult and always incomplete.

It is unfortunate that we were not able to judge the success or otherwise of our asymmetric synthesis of chiral-at-metal complexes, but we hope that the protocol developed here may be of use in the preparation of other chiral-at-metal targets in enantiomerically enriched form.

3. Conclusions

A protocol for asymmetric synthesis of chiral-at-metal complexes has been established, but it is not synthetically useful for our particular target molecules due, we propose, to formation of complexes between the metallocene products and the borane by-products. A very practical and efficient method for synthesis of racemic chiral-at-metal metallocenes, through lithium chloride catalysed ligand redistribution between prochiral metallocene dichlorides and their dialkyl or dithiophenolato derivatives, has been developed. Sterically-hindered racemic chiral-at-metal complexes are most readily prepared by simple nucleophilic substitution of one chloride of prochiral dichlorides.

4. Experimental

4.1. General

All manipulations of air- and moisture-sensitive materials were carried out using standard vacuum and Schlenk techniques under an atmosphere of argon, or in a dry box under an atmosphere of nitrogen. All solvents were purified and dried by refluxing over a drying agent, followed by distillation under a nitrogen atmosphere. The following compounds were prepared according to literature methods, or simple modifications thereof: $C_5H_5MCl_3$, $^tBuC_5H_4MCl_3$ and $C_9H_7MCl_3$ [4]; **2a**, **3a**, **8b**, **8c** and **8f** [4,7]. NMR spectra were recorded using Bruker ACF-250 and AC-400 spectrometers. Spectra were referenced using the resonances of residual protons in the deuterated solvents.

4.2. $[Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H^t_4Bu)Cl_2]$ (**4a**)

To a suspension of $CpZrCl_3DME$ (5.00 g, 14.2 mmol) in 3:1 toluene–diethyl ether (70 cm^3) at $-78°C$ was added a suspension of $LiC_5H^t_4Bu$ (1.92 g, 15.0 mmol) in diethyl ether (50 cm^3). A pale yellow suspension resulted and this mixture was stirred and allowed to warm to ambient temperature over 12 h. Work-up as for **5a** yielded 2.62 g (53%) of pale yellow micro-crystalline **4a**. M.p. 152–154°C. Found (calculated for $C_{14}H_{18}Cl_2Zr$): C, 47.56 (48.26); H, 5.24 (5.21)%. ^{1}H-NMR ($CDCl_3$): δ 6.36 (5H, s, C_5H_5), 6.34 (2H, m, C_5H_4), 6.22 (2H, m, C_5H_4), 1.30 (9H, s, ^{t}Bu). ^{13}C-NMR: δ 142.41 (C_q of C_5H_4), 114.50 (C_5H_5), 113.69 (C_5H_4), 111.89 (C_5H_4), 33.28 (CMe_3), 31.28 (CMe_3). MS (m/z): 345/347 $[M-1]^+$.

4.3. $[Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)Cl_2]$ (**5a**)

To a suspension of $CpZrCl_3DME$ (10 g, 28.3 mmol) in 3:1 toluene–diethyl ether (100 cm^3) at $-78°C$ was added a freshly prepared solution of LiC_9H_7 (3.59 g, 29.5 mmol) in diethyl ether (50 cm^3). An orange–red suspension resulted and this mixture was stirred and allowed to warm to ambient temperature over 8 h. After 8 h a bright yellow suspension was obtained. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 (80 cm^3). The resulting suspension was cooled to $-10°C$ for 1 h and filtered cold. The filtrate was reduced in volume to 40 cm^3 and pentane (15 cm^3) was added to yield a bright yellow solution. This solution was cooled to $-18°C$ for 12 h to yield bright yellow micro-crystalline **5a** upon filtration. A further crop of **5a** could be obtained from the filtrate by concentrating the filtrate and diluting with pentane yielding (8.05 g, 83%) of **5a**. M.p. 146–148°C. Found (calculated for $C_{14}H_{12}Cl_2Zr$), C, 48.08 (49.11); H, 3.60 (3.53)%. ^{1}H-NMR (C_6D_6): δ 7.35 (2H, m, C_9H_7), 6.90 (2H, m, C_9H_7), 6.48 (1H, t, C_9H_7), 6.06 (2H, d, C_9H_7), 5.76 (5H, s, C_5H_5). ^{13}C-NMR: δ 126.00 (C_q of C_9H_7), 125.64 (C_9H_7), 125.17 (C_9H_7), 123.85 (C_a of C_9H_7), 115.85 (C_5H_5), 102.52 (C_b of C_9H_7). MS (m/z, + CI(ammonia)): 358/360 $[M + NH_4^+]$.

4.4. $[Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_{13})Cl_2]$

To a suspension of $CpZrCl_3DME$ (5 g, 14.17 mmol) in thf (70 cm^3) at −78°C was added a solution of LiC_5HMe_4 (1.92 g, 15.00 mmol) in thf (30 cm^3). A pale yellow suspension resulted and this mixture was stirred and allowed to warm to ambient temperature over 1 h and heated to 50°C for 4 h. After 5 h a deep orange coloured solution was obtained. The solvent was removed under reduced pressure and the residue extracted with CH_2Cl_2 (50 cm^3). To the resulting suspension was added dry activated charcoal (0.5 g) and the mixture was stirred and cooled to 0°C for 1 h. The suspension was filtered and the pale yelow filtrate reduced in volume by one half. Pentane (10 cm^3) was added and the solution was cooled to −18°C for 48 h. Cream coloured micro-crystalline product (3.35 g, 68%) was isolated upon filtration. M.p. 185–188°C. Found (calculated for $C_{14}H_{18}Cl_2Zr$): C, 47.75 (48.26); H, 5.37 (5.21)%. ^{1}H-NMR ($CDCl_3$): δ 6.35 (5H, s, C_5H_5), 5.96 (1H, s, CH), 2.01 (6H, s, CH_3), 1.99 (6H, s, CH_3). ^{13}C-NMR: δ 130.20 (C_q of C_9H_{13}), 122.79 ($C_{q'}$ of C_9H_{13}), 115.70 (C_5H_5), 111.69 (CH of C_9H_{13}), 14.60 (Me_a), 12.42(Me_b). MS (m/z): 346/348 [M^+], 310 (M^+ − HCl), 281/283 ($M^+ - C_5H_5$).

4.5. $[Hf(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)Cl_2]$ (**6a**)

To a suspension of $CpHfCl_3DME$ (5.00 g, 11.3 mmol) in 3:1 toluene–diethyl ether (70 cm^3) at −78°C was added a solution of LiC_9H_7 (1.46 g, 12.0 mmol) in diethyl ether (50 cm^3). A cream–yellow suspension resulted and this mixture was stirred and allowed to warm to ambient temperature over 15 h. After 15 h a cream–yellow suspension was obtained. Work-up as for **5a** yielded (3.32 g, 68%) of pale yellow micro-crystalline **6a**. M.p. 158–160°C. Found (calculated for $C_{14}H_{12}Cl_2Hf$): C, 38.80 (39.14); H, 2.84 (2.82)%. ^{1}H-NMR ($CDCl_3$): δ 7.67 (2H, m, C_9H_7), 7.28 (2H, m, C_9H_7), 6.90 (1H, t, C_9H_7), 6.40 (2H, d, C_9H_7), 6.06 (5H, s, C_5H_5). ^{13}C-NMR: δ 126.13 (C_9H_7), 125.51 (C_9H_7), 124.25 (C_a of C_9H_7), 114.97 (C_5H_5), 100.54 (C_b of C_9H_7), not observed (C_q of C_9H_7).

4.6. $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H'_4Bu)Me_2]$ (**7b**)

To a solution of **2a** (0.2 g, 0.65 mmol) in diethyl ether (30 cm^3) at −40°C was added dropwise with stirring MeMgBr (0.45 cm^3 of 3 M solution in diethyl ether). The mixture was stirred for 5 h, allowed to warm to room temperature (r.t.) and the solvent was removed in vacuo. The resulting residue was extracted with toluene (15 cm^3) and filtered. Concentrating the solution and cooling to −30°C yielded ca. 0.09 g (52%) of yellow powder **7b**. It was not possible to obtain elemental analysis as the product rapidly decomposed when at r.t. ^{1}H-NMR (C_6D_6): δ 5.82 (5H, s, C_5H_5), 5.77 (2H, m, C_5H_4), 5.74 (2H, m, C_5H_4), 1.03 (9H, s, ^{t}Bu), 0.19 (6H, s, Me). ^{13}C-NMR: δ 138.76 (C_q), 113.50 (C_5H_4), 113.29 (C_5H_5), 110.15 (C_5H_4), 45.57 (Me), 31.06 (CMe_3), 27.28 ($C(CH_3)_3$).

4.7. $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H'_4Bu)(CH_2Ph)_2]$ (**7c**)

To a solution of **2a** (1 g, 0.65 mmol) in diethyl ether (30 cm^3) at −40°C was added dropwise with stirring $PhCH_2MgBr$ (6.6 cm^3 of a 1 M solution in diethyl ether). Work-up as for **7b** yielded ca. 0.08 g (60%) of a brown powder of **7c.** M.p. 41°C (dec.). Found(calculated for $C_{28}H_{32}Ti$): C, 79.06 (80.56); H, 7.01 (7.97)%. ^{1}H-NMR (C_6D_6): δ 7.26 (4H, m, C_6H_5), 6.98 (2H, m, C_6H_5), 6.90 (4H, m, C_6H_5), 5.96 (2H, m, C_5H_4), 5.75 (5H, s, C_5H_5), 5.67 (2H, m, C_5H_4), 2.22 (2H, d, $J = 9.3$ Hz, CH_2), 1.91 (2H, d, $J = 9.3$ Hz, CH_2), 0.94 (9H, s, ^{t}Bu). ^{13}C-NMR: δ 154.03 (C_q of C_6H_5), 139.22 (C_q of C_5H_4), 125.53 (C_6H_5), 121.53 (C_6H_5), 115.38 (C_5H_5), 114.87 (C_5H_4), 113.71 (C_5H_4), 100.34 (C_6H_5), 73.73 (CH_2), 32.50 ($C(Me)_3$), 31.14 ($C(CH_3)_3$).

4.8. $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H'_4Bu)(SPh)_2]$ (**7f**)

To a solution of **2a** (0.2 g, 0.66 mmol) in thf (30 cm^3) at −40°C was added dropwise with stirring LiSPh (1.32 cm^3 of a 1 M solution in thf). The mixture was stirred for 5 h, allowed to warm to r.t. and the solvent was removed in vacuo. The resulting residue was extracted with petroleum ether (15 cm^3) and filtered. Concentrating the solution (20 cm^3) and cooling to −30°C yielded ca. 0.18 g (64%) of purple crystals of **7f**. M.p. 88°C (dec.). Found (calculated for $C_{26}H_{28}S_2Ti$): C, 67.10 (67.27); H, 6.21 (6.59)%]. ^{1}H-NMR (C_6D_6): δ 7.95 (4H, m, C_6H_5), 7.18 (4H, m, C_6H_5), 7.01 (2H, m, C_6H_5), 5.93 (2H, m, C_5H_4), 5.85 (5H, s, C_5H_5), 5.81 (2H, m, C_5H_4), 1.16 (9H, s, ^{t}Bu). ^{13}C-NMR: δ 149.95 (C_q of C_6H_5), 140.01 (C_q of C_5H_4), 132.34 (C_6H_5), 128.95 (C_6H_5), 125.05 (C_6H_5), 112.85 (C_5H_5), 112.65 (C_5H_4), 111.50 (C_5H_4), 33.14 ($C(Me)_3$), 31.50 ($C(CH_3)_3$).

4.9. $[Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H'_4Bu)(SPh)_2]$ (**9f**)

To a vigorously stirred suspension of **4a** (2.00 g, 5.74 mmol) in diethyl ether (40 cm^3) at −78°C was added LiSPh (12.6 cm^3 of a 1 M thf solution) dropwise over a period of 30 min. The mixture became yellow in colour. Work-up proceeded as in **10f** except that after filtration the toluene solution was concentrated to 10 cm^3 and layered with 15 cm^3 of pentane. Upon standing at r.t. for 72 h, 1.73 g (61%) of large yellow crystals of **9f** were obtained. M.p. 132–134°C. Found (calculated for $C_{26}H_{28}S_2Zr$): C, 62.71 (62.98); H, 5.71 (5.69)%. ^{1}H-NMR (C_6D_6): 7.93 (4H, m, Ph), 7.16 (4H, m, Ph), 6.99 (2H, m, Ph), 5.89 (2H, m, C_5H_4), 5.85 (5H, s, C_5H_5),

5.72 (2H, m, C_5H_4), 1.14 (9H, s, ^{t}Bu). ^{13}C-NMR: δ 146.12 (C_q of Ph), 140.10 (C_q of C_5H_4), 132.83 (Ph), 128.24 (Ph), 124.90 (Ph), 111.46 (C_5H_5) 111.11 (C_5H_4), 109.29 (C_5H_4), 32.60 (CMe_3), 31.53 (CMe_3).

4.10. [Zr(η^5-C_5H_5)(η^5-C_9H_7)Me_2] (**10b**)

To a vigorously stirred suspension of **5a** (2.00 g, 5.84 mmol) in diethyl ether (40 cm^3) at −78°C was added MeMgCl (12.8 cm^3 of a 1 M diethyl ether solution, 12.8 mmol) dropwise over a period of 30 min. The suspension changed from a bright yellow to a pale cream colour. Work-up as for **10e** yielded pale yellow microcrystalline **10b** (0.72 g, 41%). M.p. 72–74°C. Found (calculated for $C_{16}H_{18}Zr$): C, 64.56 (63.74); H, 5.37 (5.98)%. ^{1}H-NMR (C_6D_6): δ 7.31 (2H, m, C_9H_7), 6.97 (2H, m, C_9H_7), 5.94 (2H, d, C_9H_7), 5.83 (1H, t, C_9H_7), 5.64 (5H, s, C_5H_5), −0.43 (6H, s, Zr–*Me*). ^{13}C-NMR: δ 124.58 (C_9H_7), 124.02 (C_9H_7), 113.42 (C_a of C_9H_7), 112.66 (C_q of C_9H_7), 110.20 (C_5H_5), 98.67 (C_b of C_9H_7), 32.66 (Zr–*Me*).

4.11. [Zr (η^5-C_5H_5)(η^5-C_9H_7)(CH_2SiMe_3)$_2$] (**10d**)

To a vigorously stirred suspension of **5a** (2.00 g, 5.84 mmol) in diethyl ether (60 cm^3) at −78°C was added $LiCH_2SiMe_3$ (13.0 cm^3 of a 1 M pentane solution, 13.0 mmol) dropwise over a period of 1 h. The suspension changed from a bright yellow to a pale cream–yellow colour. The mixture was stirred for a further 12 h and the solvent was removed under reduced pressure to yield a waxy residue. This residue was extracted with warm pentane (3×40 cm^3) and the extracts were filtered through a short pad of Celite to yield a pale yellow solution. The solvent was removed under reduced pressure and the resulting solid residue was dissolved in warm diethyl ether. This solution was cooled to −18°C for 5 days. Product **10d** was isolated as a pale yellow powder from this solution (0.72 g, 41%). M.p. 54–56°C. ^{1}H-NMR (C_6D_6): δ 7.38 (2H, m, C_9H_7), 6.98 (2H, m, C_9H_7), 6.06 (2H, d, C_9H_7), 5.79 (5H, s, C_5H_5), 5.74 (1H, t, C_9H_7), 0.18 (18H, s, CH_2SiMe_3), −0.49 (4H, AB, CH_2SiMe_3. ^{13}C-NMR: δ 124.67 (C_9H_7), 124.23 (C_9H_7), 112.51 (C_9H_7), 112.24 (C_9H_7), 109.49 (C_5H_5), 97.81 (C_9H_7), 47.43 (CH_2SiMe_3), 3.42 (CH_2SiMe_3). MS (m/z): 429 [$M^+ - CH_3$], 357 [$M^+ - CH_2SiMe_3$].

4.12. [Zr(η^5-C_5H_5)(η^5-C_9H_7)Ph_2] (**10e**)

To a vigorously stirred suspension of **5a** (2.00 g, 5.84 mmol) in diethyl ether (40 cm^3) at −78°C was added PhMgCl (6.5 cm^3 of a 2 M thf solution) dropwise over a period of 30 min. The suspension changed from a bright yellow to a pale grey colour. The mixture was stirred in the absence of light for a further 10 h and allowed to warm to ambient temperature over that time. The solvent was removed under reduced pressure and dry activated charcoal (0.5 g) was added to the resulting residue. The mixture was extracted with toluene (30 cm^3), stirred for a further hour, and filtered. The pale yellow filtrate obtained was concentrated to 15 cm^3, pentane (10 cm^3) was added and the solution was cooled to −18°C for 24 h. Pale yellow crystals were obtained and these were washed with pentane to yield **10e** (1.42 g, 57%). M.p. 177°C (dec.). ^{1}H-NMR (C_6D_6): δ 7.35 (4H, m, Ph), 7.26 (4H, m, Ph), 7.18 (2H, m, Ph), 7.03 (2H, m, C_9H_7), 6.74 (2H, m, C_9H_7), 6.68 (1H, t, C_9H_7), 6.15 (2H, d, C_9H_7), 5.47 (5H, s, C_5H_5). ^{13}C-NMR: δ 184.27 (C_q of Ph), 135.67 (Ph), 126.34 (Ph), 125.39 (Ph), 125.20 (C_9H_7), 123.66 (C_9H_7) 122.32 (C_a of C_9H_7), 121.51 (C_q of C_9H_7), 113.60 (C_5H_5), 102.04 (C_b of C_9H_7). MS (m/z, +CI(ammonia)): 365 [$M + NH_4^+ - C_6H_6$], 348 [$M + H^+ - C_6H_6$], 233.

4.13. [Zr(η^5-C_5H_5)(η^5-C_9H_7)(SPh)$_2$] (**10f**)

To a vigorously stirred suspension of **5a** (3.00 g, 8.76 mmol) in diethyl ether (40 cm^3) at −78°C was added LiSPh (19.3 cm^3 of a 1 M thf solution) dropwise over a period of 30 min. The mixture became dark yellow in colour. The mixture was stirred for 10 h and allowed to warm to warm to ambient temperature over this period. The solvent was removed under reduced pressure and the resulting residue was extracted with toluene (30 cm^3) and filtered. The solvent was removed under reduced pressure from the dark yellow filtrate to yield a foaming solid which was cooled to −196°C and crushed to yield a yellow powder. Diethyl ether (20 cm^3) was added to yield a yellow solution, the solution was warmed to 35°C and pentane (5 cm^3) was added. The resulting solution was slowly cooled to −18°C for 48 h yielding 2.78 g (65%) of **10f** as a yellow powder. M.p. 119–121°C. ^{1}H-NMR (C_6D_6): δ 7.93 (4H, m, Ph), 7.25 (2H, m, C_9H_7), 7.15 (4H, m, Ph), 6.99 (2H, m, Ph), 6.77 (2H, m, C_9H_7), 6.41 (1H, t, C_9H_7), 6.17 (2H, d, C_9H_7), 5.47 (5H, s, C_5H_5). ^{13}C-NMR: 145.41 (C_q of Ph), 132.76 (Ph), 128.30 (Ph), 125.05 (Ph), 124.74 (C_9H_7), 124.55 (C_9H_7) 122.88 (C_a of C_9H_7), 121.93 (C_q of C_9H_7), 113.01 (C_5H_5), 100.46 (C_b of C_9H_7). MS (m/z): 379 [$M^+ - SPh$].

4.14. [Hf (η^5-C_5H_5)(η^5-C_9H_7)Ph_2] (**11e**)

To a vigorously stirred suspension of **6a** (1.50 g, 3.49 mmol) in diethyl ether (30 cm^3) at −78°C was added PhMgCl (4.18 cm^3 of a 2 M thf solution) dropwise over a period of 30 min. The suspension changed from a yellow to a pale grey colour. The mixture was stirred in the absence of light for a further 15 h and allowed to warm to ambient temperature over that time. Work-up as for **10e** yielded 0.73 g (40%) of cream coloured

crystals. M.p. 180°C (dec.). Found (calculated for $C_{24}H_{22}Hf$): C, 60.76 (60.88); H, 4.31 (4.32)%. ^{1}H-NMR (C_6D_6): 7.43 (4H, m, Ph), 7.34 (4H, m, Ph), 7.19 (2H, m, Ph), 7.05 (2H, m, C_9H_7), 6.77 (2H, m, C_9H_7), 6.71 (1H, t, C_9H_7), 6.10 (2H, d, C_9H_7), 5.41 (5H, s, C_5H_5). ^{13}C-NMR: δ 192.57 (C_q of Ph), 137.48 (Ph), 126.65 (Ph), 125.39 (Ph), 125.20 (C_9H_7), 123.77 (C_9H_7) 122.06 (C_a of C_9H_7), (C_q of C_9H_7) not observed, 113.04 (C_5H_5), 100.73 (C_b of C_9H_7). MS (m/z): 514 [M^+], 435 [$M^+ - Ph$].

4.15. [Hf (η^5-C_5H_5)(η^5-C_9H_7)($SPh)_2$] (11f)

To a vigorously stirred suspension of **6a** (2 g, 4.66 mmol) in diethyl ether (40 cm^3) at −78°C was added LiSPh (10.3 cm^3 of a 1 M thf solution) dropwise over a period of 30 min. The mixture became cream–white in colour. The mixture was stirred for 15 h and allowed to warm to ambient temperature over this period. Work-up as in **10f** yielded **11f** 1.15 g (43%) as a cream coloured powder. M.p. 123–125°C. Found (calculated for $C_{26}H_{22}S_2Hf$): C, 54.77 (54.12) H, 4.24 (3.84)%. ^{1}H-NMR ($CDCl_3$): δ 7.96 (4H, m, Ph), 7.26 (2H, m, C_9H_7), 7.14 (4H, m, Ph), 6.98 (2H, m, Ph), 6.75 (2H, m, C_9H_7), 6.41 (1H, t, C_9H_7), 6.08 (2H, d, C_9H_7), 5.38 (5H, s, C_5H_5). ^{13}C-NMR: δ 143.59 (C_q of Ph), 132.84 (Ph), 128.22 (Ph), 125.25 (Ph), 125.08 (C_9H_7), 125.01 (C_9H_7) 122.20 (C_a of C_9H_7), 121.38 (C_q of C_9H_7), 111.91 (C_5H_5), 98.71 (C_b of C_9H_7). MS (m/z): 467/469 [M − SPh].

4.16. [Ti(η^5-C_5H_5)(η^5-$C_5H'_4Bu$)(CH_2Ph)Cl] (2c)

To a solution of **2a** (0.54 g, 1.8 mmol) in toluene (20 cm^3) was added dropwise with stirring to a solution of **7c** (0.75 g, 1.8 mmol) in toluene (20 cm^3). The mixture was stirred overnight at r.t. After concentrating the solution (20 cm^3) and cooling to −30°C, ca. 0.41 g (71%) of brown solid of **2c** was isolated. M.p. 38°C (dec.). ^{1}H-NMR (C_6D_6): δ 7.32 (2H, m, C_6H_5), 7.15 (2H, m, C_6H_5), 7.00 (1H, m, C_6H_5), 6.63 (1H, m, H_a), 6.30 (1H, m, H_b), 5.75 (5H, s, C_5H_5), 5.05 (1H, m, H_c), 4.82 (1H, m, H_d), 2.85 (1H, d, $J = 9.8$ Hz, CH_2), 2.20 (1H, d, $J = 9.8$ Hz, CH_2), 1.16 (9H, s, ^{t}Bu). ^{13}C-NMR: δ 153.20 (C_q of C_6H_5), 145.97 (C_q of C_5H_4), 128.89 (C_6H_5), 126.14 (C_6H_5), 124.99 (C_6H_5), 122.55 (C_5H_4), 119.11 (C_5H_4), 116.65 (C_5H_5), 109.60 (C_5H_4), 105.66 (C_5H_4), 72.10 (CH_2), 33.12 (CMe_3), 30.80 ($C(CH_3)_3$).

4.17. [Ti(η^5-C_5H_5)(η^5-$C_5H'_4Bu$)(SPh)Cl] (2f)

To a solution of **2a** (0.33 g, 1.1 mmol) in toluene (20 cm^3) was added dropwise with stirring a solution of **2f** (0.5 g, 1.1 mmol) in toluene (20 cm^3). The mixture was stirred overnight at r.t. After concentrating the solution (20 cm^3) and cooling to −30°C, 0.611 g (73%) of pink solid **2f**. M.p. 93°C (dec.) was isolated. Found (calculated for $C_{20}H_{23}SClTi$): C, 62.43 (62.22); H, 5.99 (6.32)%. ^{1}H-NMR (C_6D_6): δ 7.64 (2H, m, C_6H_5), 7.18 (1H, m, C_6H_5), 7.00 (2H, m, C_6H_5), 6.40 (1H, m, H_a), 6.34 (1H, m, H_b), 5.90 (5H, s, C_5H_5), 5.59 (1H, m, H_c), 5.16 (1H, m, H_d), 1.23 (9H, s, ^{t}Bu). ^{13}C-NMR: δ 149.96 (C_q of C_6H_5), 145.75 (C_q of C_5H_4), 133.75 (C_6H_5), 132.56 (C_6H_5), 127.73 (C_6H_5), 120.11 (C_5H_4), 117.12 (C_5H_4), 115.77 (C_5H_5), 110.69 (C_5H_4), 109.49 (C_5H_4), 30.80 ($C(Me)_3$), 31.33 ($C(CH_3)_3$).

4.18. [Zr(η^5-C_5H_5)(η^5-C_9H_7)(CH_2SiMe_3)Cl] (5d)

To a Schlenk tube charged with **5a** (0.5 g, 1.46 mmol), **10d** (0.65 g, 1.46 mmol), and LiCl (0.010 g, 0.23 mmol) was added thf (15 cm^3) at ambient temperature. A pale yellow suspension resulted and this mixture was heated to 40°C and stirred for 15 h. A pale yellow solution was obtained. The solvent was removed under reduced pressure and to the resulting residue was added pentane (30 cm^3). The resulting pale yellow suspension was stirred at 40°C for 1 h and filtered. The solvent was reduced in volume to one third volume (10 cm^3) and the solution cooled to −18°C for 64 h to yield **5d** (0.47 g, 42%) as a pale yellow powder. M.p. 97–99°C (dec.). Found (calculated for $C_{18}H_{23}ClSiZr$): C, 53.56 (54.85); H, 5.36 (5.88)%. ^{1}H-NMR ($CDCl_3$): 7.59 (2H, m, C_9H_7), 7.21 (2H, m, C_9H_7), 6.73 (1H, t, C_9H_7), 6.55 (1H, m, C_9H_7), 6.18 (1H, m, C_9H_7), 5.99 (5H, s, C_5H_5), 0.74 (1H, d, J 10.4 Hz, CH_2SiMe_3), 0.35 (1H, d, J 10.4 Hz, CH_2SiMe_3, 0.05 (9H, s, CH_2SiMe_3).

4.19. [Zr(η^5-C_5H_5)(η^5-C_9H_7)PhCl] (5e)

The procedure described for the preparation of **5d** above was followed with the following exceptions. To a Schlenk tube charged with **5a** (0.5 g, 1.46 mmol), **10e** (0.62 g, 1.46 mmol) and LiCl (0.010 g, 0.23 mmol) was added thf (15 cm^3) at ambient temperature. A pale yellow suspension resulted and this mixture was heated to 40°C and stirred in the absence of light for 15 h. Work-up as in **5d** yielded **5e** (0.29 g, 52%) as a pale yellow light sensitive powder. M.p. 143–145°C (dec.). ^{1}H-NMR (C_6D_6): δ 7.36 (2H, m, Ph), 7.25 (2H, m, Ph), 7.27 (1H, m, C_9H_7), 7.17 (1H, m, C_9H_7), 7.20 (1H, m, Ph), 6.87 (2H, m, C_9H_7), 6.35 (1H, t, C_9H_7), 6.30 (1H, m, C_9H_7), 5.82 (1H, m, C_9H_7), 5.65 (5H, s, C_5H_5).

4.20. [Zr(η^5-C_5H_5)(η^5-C_9H_7)(SPh)(Cl)] (5f)

The procedure described for the preparation of **5d** above was followed here with the following exceptions. To a Schlenk tube charged with **5a** (0.5 g, 1.46 mmol), **10f** (0.71 g, 1.46 mmol), and LiCl (0.010 g, 0.23 mmol) was added thf (15 cm^3) at ambient temperature. A pale yellow suspension resulted and this mixture was heated

to 40°C and stirred for 6 h. Work-up as in **5d** yielded **5f** (0.48 g, 67%) as a yellow solid. M.p. 137–139°C (dec.). ^{1}H-NMR (C_6D_6): δ 7.75 (2H, m, SPh), 7.50–7.20 (over lapping multiplets from C_9H_7 and SPh), 6.88 (2H, m, C_9H_7), 6.39 (1H, t, C_9H_7), 6.23 (1H, m, C_9H_7), 5.86 (1H, m, C_9H_7), 5.64 (5H, s, C_5H_5).

4.21. [Hf(η^5-C_5H_5)(η^5-C_9H_7)(CH_2SiMe_3)Cl] (6d)

To a solution of **6a** (1.0 g, 2.33 mmol) in thf (30 cm^3) at −78°C was added a solution of $LiCH_2SiMe_3$ (4.8 cm^3 of a 1 M solution in pentane). A pale yellow solution resulted and this mixture was stirred and allowed to warm to ambient temperature over 15 h. After 15 h a pale yellow solution was obtained. The solvent was removed under reduced pressure and to the resulting residue was added pentane (30 cm^3). The resulting suspension was stirred at 40°C for 1 h and filtered. The solvent was reduced to one third volume (10 cm^3) and the solution was cooled to −18°C for 48 h to yield **6d** (0.47 g, 42%) as a pale yellow powder. M.p. 108–110°C. ^{1}H-NMR (C_6D_6): δ 7.45 (1H, m, C_9H_7), 7.28 (1H, m, C_9H_7), 6.93 (2H, m, C_9H_7), 6.33 (1H, t, C_9H_7), 6.13 (1H, m, C_9H_7), 5.72 (1H, m, C_9H_7), 5.64 (5H, s, C_5H_5), 0.25 (1H, d, J = 11.2 Hz, CH_2SiMe_3), 0.22 (9H, s, CH_2SiMe_3), 0.01 (1H, d, J = 11.2 Hz, CH_2SiMe_3). ^{13}C-NMR: δ 125.27 (C_9H_7), 124.93 (C_9H_7), 124.74 (C_9H_7), 124.67 (C_9H_7), 123.34 (C_9H_7), 119.22 (C_9H_7), 111.67 (C_5H_5), 106.75 (C_9H_7), 101.13 (C_9H_7), 97.06 (C_9H_7), 49.06 (CH_2SiMe_3), 3.21 (CH_2SiMe_3).

4.22. General procedure for transmetalation with chloroboranes

To a solution of **7**–**11** (1 mmol) in toluene (40 cm^3) at r.t. was added chlorocatecholborane or DIP–Cl (1 mmol) in toluene (10 cm^3). The solution was stirred overnight and the solvent was removed in vacuo. It was not possible to isolate the chiral-at-metal products **2**–**6** from the by-product. The product mixtures were characterised by ^{1}H-NMR spectroscopy.

4.23. [Ti(η^5-C_5H_5)(η^5-$C_5H'_4Bu$)($SPh)_2$] (7f)

A pink crystal (0.15 × 0.10 × 0.10mm) of **7f** ($C_{26}H_{28}S_2Ti$) was selected, coated in dry Nujol and mounted at 180 K on a quartz fibre on a Siemens SMART area detector system equipped with a dry N_2 stream low-temperature device. Lattice parameters were obtained by least squares refinement of 3880 reflections. Graphite monochromated radiation, λ = 0.71073 Å, Mo–K_α. Monoclinic system, space group $P2_1/n$, a = 12.5217(9), b = 12.2106(9), c = 29.649(2) Å, β = 90.515(2)°, V = 4533.0(6) Å^3, D_{calc} = 1.326 Mg m^{-3}, Z = 4, μ = 0.572 mm^{-1}, $F(000)$ = 1904.

An empirical absorption correction was carried out using $T_{max,min}$ = 1.000, 0.676. Structure solution was carried out using SHELXTL version 5.0 software [17] on a Silicon Graphics Indy workstation. Refinements were by least squares, carried out using SHELXL-96 software, [17] minimising on the weighted R factor wR_2. A total of 21 786 reflections were collected, with 7933 independent reflections. 3516 reflections with $I > 2\sigma(I)$ were used for refinement. Anisotropic thermal parameters were used for all non-hydrogen atoms, hydrogen atoms were inserted in calculated positions and fixed with isotropic thermal parameters U = 0.08 Å^3 where R = 0.0789 and wR_2 = 0.1731.

4.24. [Zr(η^5-C_5H_5)(η^5-$C_5H'_4Bu$)($SPh)_2$] (9f)

A pale yellow crystal (0.54 × 0.30 × 0.16mm) of **9f** ($C_{26}H_{28}S_2Zr$) was selected, coated in a perfluorinated oil and mounted at 180 K on a quartz fibre on a Siemens SMART area detector system equipped with a dry N_2 stream low-temperature device. Lattice parameters were obtained by least-squares refinement of 25 reflections. Graphite monochromated radiation, λ = 0.71073 Å, Mo–K_α. Monoclinic system, space group $P2_1/n$, a = 12.2071(5), b = 13.2027(5), c = 14.5879(6) Å, β = 95.9670(10)°, V = 2338.3(2) Å^3, D_{calc} = 1.408 Mg m^{-3}, Z = 4, μ = 0.659 mm^{-1}, $F(000)$ = 1024.

An empirical absorption correction was carried out using $T_{max,min}$ = 0.92, 0.78. Structure solution was carried out using SHELXTL version 5.0 software [17] on a Silicon Graphics Indy workstation. Refinements were by least squares, carried out using SHELXL-96 software, [17] minimising on the weighted R factor wR_2. A total of 13 555 reflections were collected, with 5460 independent reflections (R_{int} = 0.0271), 4202 reflections with $I > 2\sigma(I)$ were used for refinement. Anisotropic thermal parameters were used for all non-hydrogen atoms, hydrogen atoms were inserted in calculated positions and fixed with isotropic thermal parameters U = 0.08 Å^3. A total of 265 parameters were refined, residual electron density = 0.371 and −0.483 e Å^{-3}, GOF on F^2 = 0.959, R = 0.0278, wR_2 = 0.0657.

4.25. [Zr(η^5-C_5H_5)(η^5-C_9H_7)(Ph)2] (10e)

A pale yellow crystal of **10e** ($C_{26}H_{22}Zr$) was selected, coated in a perfluorinated oil and mounted at 180(2) K on a quartz fibre on a Siemens SMART area detector system equipped with a dry N_2 stream low temperature device. Lattice parameters were obtained by least squares refinement of 25 reflections. Graphite monochromated radiation, λ = 0.71073 Å, Mo–K_α. Orthorhombic crystal system, space group *Pbca*, a = 14.6088(4), b = 15.1651(4), c = 17.5486(4) Å, V = 3887.79(17) Å^3, D_{calc} = 1.454 Mg m^{-3}, Z = 8, μ = 0.573 mm^{-1}, $F(000)$ = 1744.

A semi-empirical absorption correction was carried out using $T_{max,min} = 0.93$, 0.73. Structure solution was carried out using SHELXTL version 5.0 software [17] on a Silicon Graphics Indy workstation. Refinements were by least squares, carried out using SHELXL-96 software [17], minimising on the weighted R factor wR_2. A total of 21 889 reflections were collected, with 4659 independent reflections ($R_{int} = 0.0924$). Anisotropic thermal parameters were used for all non-hydrogen atoms, hydrogen atoms were inserted in calculated positions and fixed with isotropic thermal parameters $U = 0.08$ Å^3. 244 parameters were refined, residual electron density = 0.645 and −0.758 e Å^{-3}, GOF on $F^2 = 1.016$, $R = 0.0582$, $wR_2 = 0.1160$ (for all data).

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 137689–137691. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the EPSRC for studentships to SLH and PJM, the EPSRC and the University of Warwick for financial support and Dr Peter Scott for helpful discussions. HJC thanks Memorial University of Newfoundland for granting study leave.

References

[1] (a) R.O. Duthaler, A. Hafner, Chem. Rev. 92 (1992) 807. (b) R.L. Halterman, Chem. Rev. 92 (1992) 965. (c) H.H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143.
[2] A.H. Hoveyda, J.P. Morken, Angew. Chem. Int. Ed. Engl. 35 (1996) 1263.
[3] A. Dormond, J. Tirouflet, F. LeMoigne, J. Organomet. Chem. 69 (1974) C7.
[4] E.W. Abel, S. Moorhouse, J. Chem. Soc. Dalton Trans. (1973) 1706.
[5] K.C. Ott, E.J.M. deBoer, R.H. Grubbs, Organometallics 3 (1984) 223.
[6] A very useful summary of these methods can be found in: D.J. Cardin, M.F. Lappert, C.L. Raston, Chemistry of Organo-Zirconium and -Hafnium Compounds, Ellis Horwood, Chichester, 1986.
[7] S.L. Hart, D.J. Duncalf, J.J. Hastings, A. McCamley, P.C. Taylor, J. Chem. Soc. Dalton Trans. (1996) 2843.
[8] (a) P. Renaut, G. Tainturier, B.J. Gautheron, J. Organomet. Chem. 148 (1978) 43. (b) S. Couturier, B.J. Gautheron, J. Organomet. Chem. 157 (1978) C61. (c) S. Couturier, G. Tainturier, B.J. Gautheron, J. Organomet. Chem. 195 (1980) 291.
[9] S.L. Hart, A. McCamley, P.C. Taylor, Synlett (1999) 90.
[10] (a) J. Jeffery, M.F. Lappert, N.T. Luong-Thi, J.L. Atwood, W.E. Hunter, J. Chem. Soc. Chem. Commun. (1978) 1081. (b) G.S. Bristow, M.F. Lappert, T.R. Martin, J.L. Atwood, W.E. Hunter, J. Chem. Soc. Dalton Trans. (1984) 399.
[11] R.J. Puddephatt, M.A. Stalteri, Organometallics 2 (1983) 1400.
[12] R.F. Jordan, J. Organomet. Chem. 294 (1985) 321.
[13] P.M. Druce, B.M. Kingston, M.F, Lappert, T.R. Spalding, R.C. Scrivastava, J. Chem. Soc. A (1969) 2106.
[14] S.L. Hart, A. McCamley, P.J. McCormack, P.C. Taylor, J. Organomet. Chem. 584 (1999) 382.
[15] R. Quintanilla, T.E. Cole, Tetrahedron 51 (1995) 4297.
[16] P.J. McCormack, PhD Thesis, University of Warwick.
[17] (a) G.M. Sheldrick, SHELXTL PLUS, Siemens Analytical Instruments, Madison, WI, 1990. (b) G.M. Sheldrick, SHELXTL-93, University of Göttingen, 1993.