Journal of Organometallic Chemistry, 293 (1985) 51–60
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE FORMATION AND CRYSTAL AND MOLECULAR STRUCTURES OF (η^5-PENTAMETHYLCYCLOPENTADIENYL)(η^5-CYCLOPENTADIENYL)-DICHLORO-TITANIUM, -ZIRCONIUM AND -HAFNIUM

ROBIN D. ROGERS*, MATTHEW M. BENNING, LYNN K. KURIHARA,
Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115 (U.S.A.)

KEVIN J. MORIARTY and MARVIN D. RAUSCH*
Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003 (U.S.A.)

(Received February 4th, 1985)

Summary

A reaction between (η^5-C_5Me_5)$TiCl_3$ and C_5H_5Tl in benzene solution has afforded (η^5-C_5Me_5)(η^5-C_5H_5)$TiCl_2$ (I) in quantitative yield. (η^5-C_5Me_5)(η^5-C_5H_5)$HfCl_2$ (III) has been prepared in 83% yield from a reaction between (η^5-C_5Me_5)$HfCl_3$ and $C_5H_5Na \cdot DME$ in refluxing toluene solution. The crystal and molecular structures of (η^5-C_5Me_5)(η^5-C_5H_5)$TiCl_2$ (I), (η^5-C_5Me_5)(η^5-C_5H_5)$ZrCl_2$ (II) and (η^5-C_5Me_5)(η^5-C_5H_5)$HfCl_2$ (III) have been determined from X-ray data measured by counter methods. The three compounds are isostructural, crystallizing in the orthorhombic space group *Pnma*. The cell constants are: (I): *a* 9.873(1), *b* 12.989(3), *c* 11.376(4) Å and D_{calc} 1.45 g cm^{-3} for $Z = 4$; (II): *a* 9.930(3), *b* 13.231(9), *c* 11.628(3) Å and D_{calc} 1.58 g cm^{-3} for $Z = 4$; (III): *a* 9.938(1), *b* 13.156(2), *c* 11.582(2) Å and D_{calc} 1.97 g cm^{-3} for $Z = 4$. In each case the metal atom resides on a crystallographic mirror plane which bisects both cyclopentadienyl rings and the Cl–M–Cl bond angle. The M–Cl bond lengths are 2.3518(9) for I, 2.4421(9) for II and 2.415(1) Å for III. The metal–cyclopentadienyl and metal–pentamethylcyclopentadienyl bond distances average 2.38(5) and 2.42(2) Å for I, 2.50(4) and 2.53(2) Å for II, and 2.48(4) and 2.50(1) Å for III respectively.

Introduction

Recent joint studies between our laboratories have been directed toward the syntheses and structural comparisons of Group IVB metallocene derivatives. As part of this program, we have recently reported new syntheses and the molecular structures of the decamethylmetallocene dicarbonyls, (η^5-C_5Me_5)$_2$M(CO)$_2$ (M = Ti, Zr, Hf) [1]. Another interesting series of half- and permethylated Group IVB

0022-328X/85/$03.30

metallocene derivatives are the dichlorides, $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)MCl_2$ and $(\eta^5\text{-}C_5Me_5)_2MCl_2$ (M = Ti, Zr, Hf). It is well established that replacement of an η^5-cyclopentadienyl ligand by an η^5-pentamethylcyclopentadienyl ligand in transition metal complexes results in significant changes in reactivity, stability, and other properties, owing to both steric as well as electronic changes that accompany replacement of the hydrogen atoms by methyl substituents.

In Group IVB metallocene chemistry, half-methylated metallocene derivatives of the type $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)ML_2$ (L = ligand) might be anticipated to exhibit intermediate structural, reactivity and spectral features compared to their $(\eta^5\text{-}C_5H_5)_2ML_2$ and $(\eta^5\text{-}C_5Me_5)_2ML_2$ couterparts. In particular, the dichloride complexes $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)MCl_2$ are noteworthy, since they serve as the most useful precursors to the half-methylated complexes $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)ML_2$. Moreover, the complexes $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)MCl_2$ (M = Ti, Zr, Hf) have recently been the subject of detailed ESCA, electrochemical, and ^{49}Ti NMR studies which have demonstrated dramatic electronic effects by substitution of methyl groups for hydrogens on the cyclopentadienyl ligand [2,3].

In order to investigate structural effects in an additional series of Group IVB metallocene derivatives in which only the central metal atom is changed, we decided to undertake X-ray structural determinations of $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TiCl_2$ (I), $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)ZrCl_2$ (II), and $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)HfCl_2$ (III). The crystal and molecular structure of I has previously been reported [4], however, it has been reinvestigated since it was refined in the wrong space group. In addition, an improved synthetic route to I and a detailed synthesis of III are also described.

Results and discussion

The titanium complex $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TiCl_2$ (I) was originally prepared in 54% yield by interaction of $(\eta^5\text{-}C_5Me_5)TiCl_3$ and C_5H_5Na in tetrahydrofuran (THF) solution [5]. More recently, I has been synthesized in 46% yield from a similar reaction between $(\eta^5\text{-}C_5Me_5)TiCl_3$ and C_5H_5Li in THF solution [6]. In the latter synthesis of I, appreciable amounts of $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ were also reported to be frequently formed, necessitating fractional crystallization procedures in order to obtain pure I.

We have developed an alternative route to I involving a reaction between $(\eta^5\text{-}C_5Me_5)TiCl_3$ and C_5H_5Tl in benzene solution. Filtration and removal of the solvent afforded I in quantitative yield. The product obtained in this manner is sufficiently pure for further reactions, e.g., the synthesis of $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)Ti(CO)_2$ [7].

By adaptation of the procedure of Wolcyanski and Bercaw [8] for the synthesis of $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)ZrCl_2$ (II), we have synthesized $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)HfCl_2$ (III). Thus, a reaction between $(\eta^5\text{-}C_5Me_5)HfCl_3$ [9] and $C_5H_5Na \cdot DME$ [10] in refluxing toluene produced, after work-up and recrystallization, III in 83% yield. Complex III was obtained as fine white crystals and was characterized by elemental analysis and its ^{1}H NMR spectrum.

An ORTEP illustration of the molecular structure and atom labelling scheme for all three compounds is given in Fig. 1. Bond distances and angles can be found in Table 1. All three molecules are isostructural. The metal atom resides on a crystallographic mirror plane bisecting the cyclopentadienyl rings. (An earlier report of the

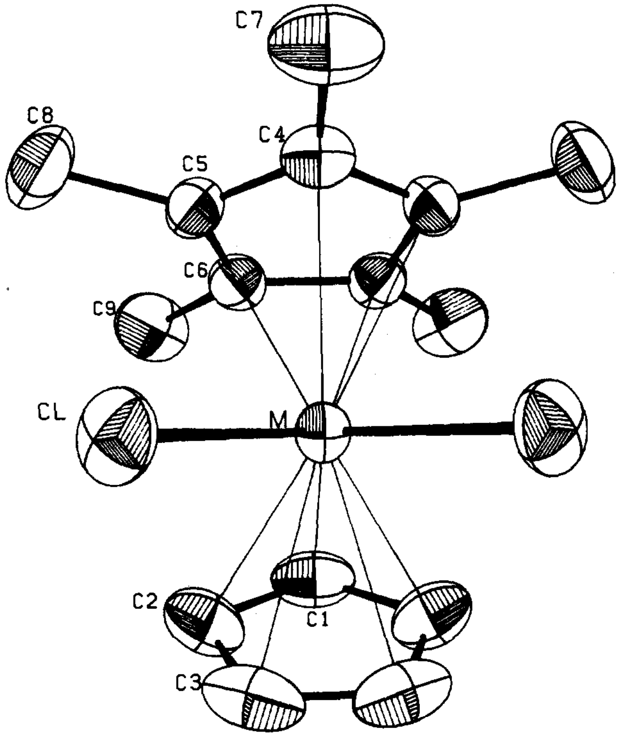

Fig. 1. Molecular structure and atom labelling scheme for $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)MCl_2$. The atoms are represented by their 50% probability ellipsoids for thermal motion. Hydrogen atoms are omitted for clarity. M = Zr.

titanium compound indicated no crystallographic symmetry [4]). These compounds contain none of the disorder in the aromatic rings as found recently by Atwood for $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)Zr(CO)_2$ [11].

The major structural features of these compounds are normal. The geometry at each metal center is that of a distorted tetrahedron. The centroids of the two staggered π-bonded rings and the two chlorine atoms make up the four vertices. All of the five-membered rings are planar to within 0.02 Å. The C–C bond distances and C–C–C bond angles average 1.40(2), 1.41(2), 1.40(2) Å and 108.2(8), 108.0(6), 108.2(7)° for the Ti, Zr, and Hf compounds, respectively.

The most detailed study can be made of $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TiCl_2$ (I). Both of the bracketing structures $(\eta^5\text{-}C_5H_5)_2TiCl_2$ [12,13] and $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ [14] as well as $(\eta^5\text{-}C_5H_4Me)_2TiCl_2$ [15] have been reported. Upon changing from unsubstituted cyclopentadienyl ligands in $(\eta^5\text{-}C_5H_5)_2TiCl_2$ to the electron-rich pentamethylcyclopentadienyl ligands in $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ the Ti–Cl bond length decreased from 2.364(3) to 2.349(4) Å. The title compound, I, shows its intermediate status with a Ti–Cl distance of 2.3518(9) Å, between the two earlier reports. It is interesting to note that the Ti–Cl value in I is closer to the bispentamethylcyclopentadienyl compound while a value of 2.360(2) Å, closer to the biscyclopentadienyl analogue, was observed for $(\eta^5\text{-}C_5H_4Me)_2TiCl_2$ [15].

Steric factors seem to influence the geometry about titanium the most. In

TABLE 1

BOND DISTANCES (Å) AND ANGLES (°) FOR COMPOUNDS I–III

Atoms	M = Ti (I)	M = Zr (II)	M = Hf (III)
M–Cl	2.3518(9)	2.4421(9)	2.415(1)
M–C(1)	2.344(4)	2.475(5)	2.453(8)
M–C(2)	2.356(3)	2.486(3)	2.462(7)
M–C(3)	2.428(3)	2.544(4)	2.530(6)
M–C(4)	2.429(4)	2.540(5)	2.514(9)
M–C(5)	2.440(3)	2.534(3)	2.512(5)
M–C(6)	2.398(3)	2.507(3)	2.489(4)
C(1)–C(2)	1.374(5)	1.391(5)	1.41(1)
C(2)–C(3)	1.412(6)	1.405(5)	1.41(1)
C(3)–C(3) [a]	1.384(8)	1.387(9)	1.36(2)
C(4)–C(5)	1.410(4)	1.416(4)	1.401(7)
C(4)–C(7)	1.499(7)	1.490(7)	1.50(1)
C(5)–C(6)	1.415(4)	1.401(4)	1.430(7)
C(5)–C(8)	1.488(5)	1.508(5)	1.500(8)
C(6)–C(9)	1.493(5)	1.503(5)	1.524(7)
C(6)–C(6) [a]	1.431(6)	1.435(6)	1.417(9)
Cent(1)–M	2.07	2.21	2.18
Cent(2)–M	2.10	2.22	2.19
Cl–M–Cl [a]	94.44(5)	97.78(5)	96.04(8)
C(1)–C(2)–C(3)	107.5(4)	107.7(4)	107.3(8)
C(2)–C(1)–C(2) [a]	109.5(5)	108.5(5)	108(1)
C(2)–C(3)–C(3) [a]	107.7(2)	108.0(2)	108.9(5)
C(5)–C(4)–C(7)	125.4(2)	126.2(2)	125.3(3)
C(4)–C(5)–C(6)	107.8(3)	108.8(3)	107.8(5)
C(4)–C(5)–C(8)	127.4(3)	125.9(3)	127.0(6)
C(6)–C(5)–C(8)	124.4(3)	124.9(3)	124.8(6)
C(5)–C(4)–C(5) [a]	108.9(4)	107.3(4)	109.2(7)
C(5)–C(6)–C(6) [a]	107.8(2)	107.6(2)	107.7(3)
C(6) [a]–C(6)–C(9)	126.9(2)	126.7(2)	127.8(3)
C(5)–C(6)–C(9)	124.4(3)	125.0(3)	123.9(5)
Cent(1)–M–Cent(2)	132.0	130.0	130.6
Cent(1)–M–Cl	105.4	105.4	105.4
Cent(2)–M–Cl	106.7	106.9	107.0

[a] Atom related to that in Table 3 by a crystallographic mirror plane.

(η^5-C_5Me_5)$_2$TiCl$_2$ [14] the two bulky rings open up to give a Centroid–Ti–Centroid angle of 137.4 and a Cl–Ti–Cl angle of 92.94(4)°. In I with one less bulky aromatic ring these same angles are 132.0 and 94.44(5)°, while values of 130.97 and 94.53(6)° were observed for (η^5-C_5H_5)$_2$TiCl$_2$ [13]. It is also worth mentioning that the most sterically demanding position for a methyl group in (η^5-C_5Me_5)$_2$TiCl$_2$ corresponds to the unsubstituted C(1) position in I. It is perhaps for this reason that the title compounds show no disorder of substituted and unsubstituted rings as observed for (η^5-C_5Me_5)(η^5-C_5H_5)Zr(CO)$_2$ [11]. The largest deviations of the methyl carbons from the plane of the five-membered ring can be found for C(9) (0.204 Å away from Ti). C(7) appears to be the least sterically hindered deviating only 0.072 Å from this plane.

The ring carbon atoms also seem to have undergone slight adjustments to the new steric requirements, an environment less sterically hindered than in the totally substituted case, more sterically demanding than the totally unsubstituted molecule. In I the Ti–C (unsubstituted ring) distances range from 2.344(4) to 2.428(3) Å and average 2.38(5) Å. The Ti–Cent(1) distance is 2.07 Å. These values are just slightly longer than observed for $(\eta^5\text{-}C_5H_5)_2TiCl_2$ (Ti–C average 2.366, Ti–Cent average 2.06 Å) [13]. The pentamethylcyclopentadienyl ring in I has an average Ti–C separation of 2.42(2) Å (range 2,398(3) to 2.440(3) Å) and Ti–Cent(2) distance of 2.10 Å. These are only slightly shorter than the 2.44 and 2.13 Å found for the similar distances in $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ [14].

When comparing the four similar structures, $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ [14], $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TiCl_2$ (I), $(\eta^5\text{-}C_5H_4Me)_2TiCl_2$ [15], and $(\eta^5\text{-}C_5H_5)_2TiCl_2$ [13], it is important to note that a single methyl substituent on each ring has an essentially negligible effect on the basic molecular geometry. The bond distances and angles differ by less than 0.01 Å and 1.3° from the unsubstituted derivative. Use of one or two more bulky pentamethylcyclopentadienyl rings, on the other hand, causes a much greater change directly corresponding to greater steric demands. It would be interesting to determine a number of other structures of this type in order to more fully sort out the steric effects from the accompanying changes in electronic environment.

The three title compounds clearly show the effect of metal atom size. As expected the Zr–Cl (2.4421(9) Å), Zr–C (2.50(4), 2.53(2) Å) and Zr–Cent (2.21, 2.22 Å) distances are longer and the Cl–Zr–Cl (97.78(5)°) angle larger than the smaller titanium analogue. The hafnium values, Hf–Cl 2.415(1), Hf–C 2.48(2) (C_5H_5), 2.50(1) (C_5Me_5), Hf–Cent 2.18 (C_5H_5), 2.19 Å (C_5Me_5), and Cl–Hf–Cl 96.04(8)°, are slightly smaller than found for the corresponding zirconium compound reflecting the lanthanide contraction. The larger metals, Zr and Hf, also decrease the steric strain on the molecules. The Cent(1)–M–Cent(2) angles are seen to decrease to 130.0 for Zr and 130.6° for Hf. The deviations of the most sterically demanding methyl groups from the plane of the five-membered ring decreases from 0.204 for Ti to 0.183 and 0.182 Å for Zr and Hf, respectively.

In the compounds available for direct comparison of the Zr and Hf bond distances and angles, the same trends as observed for Ti are repeated but the larger metals cause the steric effects to be much less pronounced. In $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ [16] the average Zr–Cl length is 2.446 Å and the Cl–Zr–Cl angle is 97.1° compared to 2.4421(9) Å and 97.78(5)° in II. The average Zr–C(π) and Zr–Cent distances of 2.49 and 2.20 Å are also similar to the values found for the Zr–C(cyclopentadienyl) and Zr–Cent(1) separation in II (2.50(2), 2.21 Å). As expected the Zr–C(pentamethylcyclopentadienyl) and Zr–Cent(2) distances in II are larger at 2.53(2) and 2.22 Å than the unsubstituted ligand in $(\eta^5\text{-}C_5H_5)_2ZrCl_2$.

The structure of $(\eta^5\text{-}C_5H_4)(CH_2)_3(\eta^5\text{-}C_5H_4)HfCl_2$ has also been determined [17]. In this structure the cyclopentadienyl rings are bridged together resulting in a Cent–Hf–Cent angle of 129.5°, very close to the 130.6° angle found for III. The Hf–C(π) and Hf–Cent distances (2.482(4), 2.18 Å) are identical to the 2.48(2) and 2.18 Å found for the Hf–C(C_5H_5) and Hf–Cent(1) separation in III. Slight differences can be found for the Hf–Cl bond length and Cl–Hf–Cl bond angle observed in $(\eta^5\text{-}C_5H_4)(CH_2)_3(\eta^5\text{-}C_5H_4)HfCl_2$ (2.423(6) Å, 95.87(8)°) and in III (2.415(1) Å, 96.04(8)°). It would appear that restricting the cyclopentadienyls by bridging them together produced an effect similar to the addition of a more bulky ligand as in III.

Experimental

All reactions and synthetic manipulations were conducted under a purified argon atmosphere using Schlenk techniques. Gases and solvents were purified as described previously [18]. (η^5-C_5Me_5)$TiCl_3$ [9], (η^5-C_5Me_5)$HfCl_3$ [9], C_5Me_5Li [19], $C_5H_5Na \cdot$ DME (DME = 1,2-dimethoxyethane) [10], C_5H_5Tl [20] and (η^5-C_5Me_5)(η^5-C_5H_5)$ZrCl_2$ [8] were prepared by literature methods. $HfCl_4$ was purified by double sublimation at 270–290°C/10^{-4} Torr and was stored under argon until used.

Preparation of (η^5-C_5Me_5)(η^5-C_5H_5)$TiCl_2$ (I)

Into a 250-ml single-neck round-bottom flask with sidearm stopcock and magnetic stirring bar were added C_5H_5Tl (2.00 g, 7.5 mmol), (η^5-C_5Me_5)$TiCl_3$ (2.16 g, 7.5 mmol) and 100 ml of dry benzene. A condenser was attached and the mixture was heated to reflux with stirring for 24 h. The reaction mixture was cooled to room temperature and then filtered through a fritted funnel that contained a plug of Celite covered by 1.5 cm of sea sand. The plug was eluted with methylene chloride until the solution emerging was colorless. The solvent was removed under reduced pressure, yielding 2.39 g (100%) of I as a red crystalline solid. An analytical and X-ray sample was obtained by recrystallization of the product from methylene chloride/hexane. ^1H NMR ($CDCl_3$) δ 1.97 (s, C_5Me_5), 6.00 (s, C_5H_5). (Found: C, 56.35; H, 6.27. $C_{15}H_{20}Cl_2Ti$ calcd.: C, 56.45; H, 6.32%).

Preparation of (η^5-C_5Me_5)(η^5-C_5H_5)$HfCl_2$ (III)

Into a 250-ml single-neck round-bottom flask with sidearm stopcock and magnetic stirring bar were added (η^5-C_5Me_5)$HfCl_3$ (7.85 g, 19 mmol), $C_5H_5Na \cdot$ DME (3.74 g, 21 mmol) and 150 ml of dry toluene. A condenser was attached and the mixture was heated to reflux with stirring for 48 h. The toluene was then removed under reduced pressure, the residue was dissolved in methylene chloride and 4 *N* hydrochloric acid was added with stirring at room temperature. The use of an argon atmosphere was discontinued at this point. The organic layer was separated and the aqueous layer was extracted four times with 25-ml portions of methylene chloride. The combined organic layers were dried over anhydrous magnesium sulfate. The solution was filtered and the methylene chloride was removed under reduced pressure. The resulting yellow solid was recrystallized from methylene chloride/hexane to yield 7.0 g (83%) of III as small white crystals which were suitable for X-ray diffraction studies. ^1H NMR ($CDCl_3$) δ 2.00 (s, C_5Me_5), 5.95 (s, C_5H_5). (Found: C, 40.35; H, 4.63. $C_{15}H_{20}Cl_2Hf$ calcd.: C, 40.06; H, 4.48%).

X-ray data collection, structure determination and refinement

Single crystals of compounds I, II and III were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for (23 reflections ($\theta > 15°$) accurately centered on the diffractometer are given in Table 2. The space group was determined to be either the centric *Pnma* or the acentric $Pn2_1a$ (non standard setting) from the systematic absences. (η^5-C_5Me_5)(η^5-C_5H_5)$TiCl_2$ (I) had been previously determined to be in the acentric space group $Pn2_1a$ [4], however, statistical methods indicated that the correct space group was the centric *Pnma*. Solution and refinement of all three structures in the space group *Pnma* proved that to be the correct choice.

TABLE 2

CRYSTAL DATA AND SUMMARY OF INTENSITY DATA COLLECTION AND STRUCTURE REFINEMENT

Compound	M = Ti (I)	M = Zr (II)	M = Hf (III)
Mol. weight	319.1	362.5	449.7
Space group	*Pnma*	*Pnma*	*Pnma*
Cell constants a (Å)	9.873(1)	9.930(3)	9.938(1)
b (Å)	12.989(3)	13.231(9)	13.156(2)
c (Å)	11.376(4)	11.628(3)	11.582(2)
Cell Volume (Å^3)	1459	1528	1514
Molecules/unit cell	4	4	4
ρ_{calc} (g cm^{-3})	1.45	1.58	1.97
μ_{calc} (cm^{-1})	9.48	10.37	75.77
Radiation	Mo-K_α(λ 0.71073 Å)		
Maximum crystal dims. (mm)	0.40×0.55×0.60	0.43×0.55×0.58	0.35×0.50×0.65
Scan width	0.80+0.35 tan θ	0.90+0.20 tan θ	1.20+0.35 tan θ
Standard reflections	400, 060, 006	400, 006, 0$\bar{8}$0	080, 006, 400
Decay of standards	0.3%	2%	0.3%
Reflections measured	1201	1475	1559
2θ range	$2° \leq 2\theta \leq 46°$	$1° \leq 2\theta \leq 48°$	$0° \leq 2\theta \leq 50°$
Reflections collected	842	928	1232
Number of parameters varied	119	88	88
GOF	0.59	1.03	0.22
R	0.035	0.020	0.025
Rw	0.050	0.023	0.043

Data were collected on an Enraf–Nonius CAD-4 diffractometer by the θ–2θ scan technique. A summary of data collection parameters is given in Table 2. The intensities for all three compounds were corrected for Lorentz and polarization effects and those for $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TiCl_2$ (I) and $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)HfCl_2$ (III) were corrected for absorption.

Calculations were carried out with the SHELX system of computer programs. Neutral atom scattering factors for Ti, Zr, Hf, Cl, C and H were taken from ref. 21. The scattering was corrected for the real and imaginary components of anomalous dispersion [21].

In the solution of $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TiCl_2$ (I), the position of the titanium atom on a mirror plane was revealed by the inspection of a Patterson map. A difference Fourier map phased on the titanium atom revealed the positions of the nonhydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.099$. The hydrogen atoms were located with the aid of a difference Fourier map and their positional parameters were refined for several least-squares cycles prior to being fixed. Final refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.035$ and $Rw = 0.050$. A final difference Fourier showed no feature greater than $0.3e^-/Å^3$. The weighting scheme was based on $[(1/\sigma_{F_o}) + (1/pF_o^2)]$ where the "ignorance factor", p, was 0.004. No systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table 3 [22].

The fractional coordinates for all nonhydrogen atoms of I were used as a starting point in the refinement of $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)ZrCl_2$ (II) and $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}$

TABLE 3

FINAL FRACTIONAL COORDINATES FOR $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TiCl_2$ (I)

Atom	x/a	y/b	z/c
Ti	0.39651(7)	0.2500	0.47608(6)
Cl	0.3506(1)	0.38289(7)	0.34145(8)
C(1)	0.5876(4)	0.2500	0.5984(4)
C(2)	0.5973(3)	0.3364(3)	0.5292(3)
C(3)	0.6207(3)	0.3033(3)	0.4128(3)
C(4)	0.1559(4)	0.2500	0.5209(4)
C(5)	0.2106(3)	0.3383(2)	0.5752(3)
C(6)	0.3048(3)	0.3051(2)	0.6609(2)
C(7)	0.0463(5)	0.2500	0.4298(5)
C(8)	0.1679(4)	0.4471(3)	0.5583(4)
C(9)	0.3706(3)	0.3740(3)	0.7490(3)
H(1)	0.582	0.250	0.680
H(2)	0.593	0.405	0.548
H(3)	0.641	0.338	0.339
H(4)	−0.036	0.250	0.458
H(5)	0.043	0.190	0.386
H(6)	0.235	0.495	0.557
H(7)	0.137	0.457	0.479
H(8)	0.106	0.462	0.613
H(9)	0.430	0.420	0.717
H(10)	0.310	0.399	0.795
H(11)	0.426	0.337	0.799

TABLE 4

FINAL FRACTIONAL COORDINATES FOR $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)ZrCl_2$ (II)

Atom	x/a	y/b	z/c
Zr	0.39772(4)	0.2500	0.47028(4)
Cl	0.3516(1)	0.38907(7)	0.33793(8)
C(1)	0.5999(5)	0.2500	0.5948(4)
C(2)	0.6112(4)	0.3353(3)	0.5256(4)
C(3)	0.6348(4)	0.3024(3)	0.4124(3)
C(4)	0.1500(5)	0.2500	0.5247(5)
C(5)	0.2077(3)	0.3362(2)	0.5775(3)
C(6)	0.3015(3)	0.3042(2)	0.6598(3)
C(7)	0.0391(6)	0.2500	0.4385(5)
C(8)	0.1642(4)	0.4442(3)	0.5593(4)
C(9)	0.3713(4)	0.3721(3)	0.7446(3)
H(1)	0.586	0.250	0.682
H(2)	0.603	0.418	0.556
H(3)	0.642	0.341	0.337
H(4)	−0.046	0.250	0.457
H(5)	0.050	0.303	0.387
H(6)	0.084	0.462	0.602
H(7)	0.131	0.453	0.477
H(8)	0.257	0.493	0.585
H(9)	0.431	0.419	0.710
H(10)	0.312	0.399	0.801
H(11)	0.441	0.334	0.794

TABLE 5

FINAL FRACTIONAL COORDINATES FOR (η^5-C_5Me_5)(η^5-C_5H_5)$HfCl_2$ (III)

Atom	x/a	y/b	z/c
Hf	0.39588(3)	0.2500	0.47199(2)
Cl	0.3493(2)	0.3864(1)	0.3384(1)
C(1)	0.5954(7)	0.2500	0.5967(8)
C(2)	0.6066(6)	0.3364(8)	0.5255(6)
C(3)	0.6309(6)	0.3016(6)	0.4119(6)
C(4)	0.1507(9)	0.2500	0.5254(6)
C(5)	0.2066(5)	0.3368(4)	0.5766(5)
C(6)	0.3015(4)	0.3038(4)	0.6614(4)
C(7)	0.041(1)	0.2500	0.437(1)
C(8)	0.1645(8)	0.4450(5)	0.5579(7)
C(9)	0.3708(6)	0.3749(5)	0.7467(6)
H(1)	0.582	0.250	0.680
H(2)	0.596	0.408	0.549
H(3)	0.626	0.357	0.344
H(4)	−0.058	0.250	0.443
H(5)	0.041	0.185	0.390
H(6)	0.218	0.498	0.515
H(7)	0.154	0.475	0.637
H(8)	0.077	0.444	0.525
H(9)	0.403	0.421	0.707
H(10)	0.318	0.392	0.820
H(11)	0.408	0.325	0.824

C_5H_5)$HfCl_2$ (III). Least-squares refinement with isotropic thermal parameters led to $R = 0.070$ for II and $R = 0.051$ for III. The hydrogen atoms for II were located with the aid of a difference Fourier map and were not refined. The hydrogen atoms of the cyclopentadienyl ring of III were placed at calculated positions 0.95 Å from the bonded carbon atom and were not refined. The methyl hydrogen atoms of III were located on a difference Fourier map and were also not refined. Refinement of II and III with anisotropic temperature factors led to final agreement indices of $R = 0.020$, $Rw = 0.033$ (II) and $R = 0.025$, $Rw = 0.043$ for III. The final difference Fourier for both compounds showed no feature greater than $0.3e^-/Å^3$. Unit weights were used in the refinement of compound II. The weighting scheme used for III was the same as for compound I with $p = 0.004$. No systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters for (η^5-C_5Me_5)(η^5-C_5H_5)$ZrCl_2$ (II) and (η^5-C_5Me_5)(η^5-C_5H_5)$HfCl_2$ (III) are given in Tables 4 and 5, respectively [22].

Aknowledgement

We are indebted to the National Science Foundation (M.D.R.) and to Research Corporation (R.D.R.) for grants in support of this research. Special thanks are due Professor Jerry L. Atwood, and Dr. William E. Hunter, for collection of the X-ray data on the Zr compound and Enraf–Nonius, Bohemia, NY, for the use of a CAD-4 diffractometer.

Supplementary material available

Tables of thermal parameters, least-squares planes, and observed and calculated structure factors for all three compounds are available. See NAPS document No. 04311 for 20 pages of supplementary material. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance in U.S. funds only $7.75 for photocopies or $4.00 for microfiche. Outside the U.S. and Canada, add postage of $4.50 for the first 20 pages and $1.00 for each 10 pages of material thereafter. $1.50 for microfiche postage.

References

1 D.J. Sikora, M.D. Rausch, R.D. Rogers and J.L. Atwood, J. Am. Chem. Soc., 103 (1981) 1265.
2 P.G. Gassman, D.W. Macomber and J.W. Hershberger, Organometallics, 2 (1983) 1470.
3 P.G. Gassman, W.H. Campbell and D.W. Macomber, Organometallics, 3 (1984) 385.
4 T.L. Khotsyanova and S.I. Kuznetsov, J. Organomet. Chem., 57 (1973) 155.
5 A.N. Nesmeyanov, O.V. Nogina and V.A. Dubovitsky, Izv. Akad. Nauk SSSR, Ser. Khim., 3 (1968) 527.
6 K.C. Ott, E.J.M. de Boer and R.H. Grubbs, Organometallics, 3 (1984) 223.
7 K.J. Moriarty, Ph.D. Dissertation, University of Massachusetts, Amherst, 1984.
8 P.T. Wolczanski and J.E. Bercaw, Organometallics, 1 (1982) 793.
9 J. Blenkers, H.J. de Liefde Meijer and J.H. Teuben, J. Organomet. Chem., 218 (1981) 383.
10 J.C. Smart and C.J. Curtis, Inorg. Chem., 16 (1977) 1788.
11 J.L. Atwood and W.E. Hunter, private communication (1985).
12 V.V. Tkachev and L.O. Atovmyan, Zh. Struk. Khim., 13 (1972) 287.
13 A. Clearfield, D.K. Warner, C.H. Saldarriaga-Molina, R. Ropal, and I. Bernal, Can. J. Chem., 53 (1975) 1622.
14 T.C. McKenzie, R.D. Sanner, and J.E. Bercaw, J. Organomet. Chem., 102 (1975) 457.
15 J.L. Petersen and L.F. Dahl, J. Am. Chem. Soc., 97 (1975) 6422.
16 K. Prout, T.S. Cameron, R.A. Forder, S.R. Critchley, B. Denton, and G.V. Rees, Acta Cryst., B30 (1974) 2290.
17 C.H. Saldarriaga-Molina, A. Clearfield, and I. Bernal, Inorg. Chem., 13 (1974) 2880.
18 M.D. Rausch, W.H. Boon and H.G. Alt, J. Organomet. Chem., 141 (1977) 299.
19 D.W. Macomber and M.D. Rausch, J. Am. Chem. Soc., 105 (1983) 5325.
20 C.C. Hunt and J.R. Doyle, Inorg. Nucl. Chem. Lett., 2 (1966) 283.
21 International Tables for X-ray Crystallography, Kynoch Press, Birmingham, England, Vol IV (1974) pp. 72, 99, 149.
22 See paragraph at the end of paper regarding supplementary material.