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STRUCTURE AND REACTIVITY OF SUBSTITUTED Di-η^5-CYCLOPENTADIENYL METAL DIHALIDES. CRYSTAL STRUCTURE OF DICHLOROBIS(η^5-t-BUTYLCYCLOPENTADIENYL)ZIRCONIUM(IV)

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Summary

A new approach to the synthesis of t-butylcyclopentadienyl and related anions, via the addition of methyl- or other alkyl-lithium compounds to dimethylfulvene, is reported and details are given for the preparation of (η^5-t-BuCp)$_2$ZrCl$_2$ and (η^5-t-BuCp)$_2$TiCl$_2$. The zirconium compound is orthorhombic, $P2_12_12$, *a* 13.003(17), *b* 10.761(10), *c* 6.703(8) Å. A crystal structure determination ($R = 0.037$, 980 reflections) shows that the t-butyl groups are directed away from each other on opposite sides of the molecule: this structure appears to be adopted only in molecules in which the substituent groups are too bulky to be accommodated directly above and below the MCl$_2$ group.

Introduction

As part of a general study of structure–reactivity relationships in substituted di-η^5-cyclopentadienylmetal–organoaluminium reagent systems [1,2], we describe a general method for the synthesis of di-η^5-alkylcyclopentadienyl-titanium and -zirconium dihalides and report the crystal and molecular structure of dichlorobis(η^5-t-butylcyclopentadienyl)zirconium(IV). The results help to identify overall structural trends in substituted di-η^5-cyclopentadienyl-titanium and -zirconium compounds and lead to some preliminary observations on the nature of feasible intermediates in Group IVA metal–aluminium promoted hydroalkylations of unsaturated molecules.

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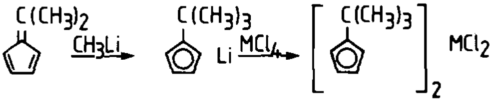
Experimental

Preparative

Published methods for the synthesis of (η^5-t-BuCp)$_2$MCl$_2$ compounds (M = Ti, Zr) [3,4] although effective, are rather tedious, involving the preparation of t-butylcyclopentadiene by nucleophilic displacement of a t-butyl halide with a Group I metal cyclopentadienide, followed by metallation with n-BuLi to form t-BuCpLi and then by reaction with the titanium or zirconium tetrahalide to form the desired product. We have found that an alternative route from dimethylfulvene, based on the original Sullivan and Little [5] synthesis of dichlorobis(η^5-isopropylcyclopentadienyl)titanium(IV), is convenient and general. For (η^5-t-BuCp)$_2$MCl$_2$, the addition of methyllithium to dimethylfulvene yields t-BuCpLi which in turn reacts with the metal tetrahalide:



(η^5-t-BuCp)$_2$ZrCl$_2$. Dimethylfulvene was prepared in near-quantitative yield from cyclopentadiene and acetone using the method of Freiesleben [6]. Methyllithium (1.5 *M* in diethyl ether) and ZrCl$_4$ (reactor grade) were obtained from Aldrich and Alfa-Ventron, respectively. Anhydrous diethyl ether and n-hexane were distilled under nitrogen from LiAlH$_4$. All reactions were performed in a dry nitrogen atmosphere; liquids were transferred using syringe techniques and solids were weighed in a dry box.

A 500 ml three-necked flask fitted with a rubber septum cap, 125-ml dropping funnel, gas inlet and magnetic follower was purged with dry N$_2$, charged with dimethylfulvene (0.20 mol, 24 ml) and diethyl ether (175 ml) and cooled to 0°C. Methyllithium (0.19 mol) was added dropwise over a period of 30 min, and the resulting yellow suspension of t-BuCpLi stirred for 2 h at 0°C.

A 1 l two-necked flask fitted with a rubber septum, reflux condenser with nitrogen inlet and a magnetic follower was purged with dry N$_2$, charged with hexane (200 ml) and ZrCl$_4$ (0.095 mol, 22 g), and cooled to 0°C. The t-BuCpLi was added over a period of 20 min using N$_2$ pressure to force the slurry through a 17-gauge stainless steel tube from the original reaction flask. The resulting off-white suspension was stirred at 0°C for 1 h and then heated at reflux for 16 h. After cooling again to 0°C, the reaction mixture was quenched by addition of 200 ml 1 *M* HCl containing 16 g NaCl. Filtration of the resulting mixture yielded 8 g of (η^5-t-BuCp)$_2$ZrCl$_2$ and a further 2 g of product were obtained by extraction of the aqueous filtrate layer with dichloromethane. Pure crystalline material was obtained by slow evaporation of dichloromethane/hexane solutions. The ^{1}H and ^{13}C NMR shifts were in agreement with literature values [4].

(η^5-t-BuCp)$_2$TiCl$_2$. This compound was prepared in a similar way to the zirconium compound using a solution of TiCl$_4$ in diethyl ether instead of hexane. Initial yield, with no optimisation of reaction conditions is typically 50–60%. ^{13}C NMR (CDCl$_3$): δ 31.5 [C(CH$_3$)$_3$]; 34.9 [C(CH$_3$)$_3$]; 118.0 (Cp,C(3,4)); 120.4 (Cp,C(2,5)); 149.9 (Cp,C(1)) ppm. The ^{13}C NMR spectrum has not been reported previously. The carbon atom resonances of the t-butyl groups in the titanium and zirconium compounds are at essentially the same positions; the ring carbon atom

TABLE 1

ATOMIC POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS

Atom	x	y	z	$B_{\mathrm{iso(eq)}}$(Å^3) ^{a}
Zr	0.5000	0.5000	0.8503(1)	3.09
Cl	0.4007(2)	0.6167(2)	1.0996(2)	4.56
C(1)	0.3517(5)	0.3455(5)	0.8624(11)	3.98
C(2)	0.4401(5)	0.2829(5)	0.7886(13)	4.32
C(3)	0.4680(4)	0.3324(5)	0.6060(10)	3.34
C(4)	0.3943(4)	0.4263(5)	0.5620(9)	3.08
C(5)	0.3224(4)	0.4325(4)	0.7157(9)	2.87
C(6)	0.2209(4)	0.5058(7)	0.7056(9)	4.09
C(7)	0.2409(5)	0.6419(5)	0.6450(13)	5.00
C(8)	0.1632(4)	0.4989(9)	0.9070(14)	6.54
C(9)	0.1562(5)	0.4460(8)	0.5388(14)	7.18

^{a} $B_{\mathrm{iso(eq)}} = 4/3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2)$.

resonances in the titanium compound are ca. 5 ppm downfield relative to those in the zirconium compound.

Structure determination

Crystal data. (η^5-t-BuCp)$_2$ZrCl$_2$, $C_{18}H_{26}Cl_2Zr$, $M = 404.5$; orthorhombic, $P2_12_12$ (No 18); a 13.003(17), b 10.761(10), c 6.703(8) Å; V 937.9 Å^3; d_c 1.43 g cm^{-3}, $Z = 2$; $F_{000} = 416$ electrons, μ 8.50 cm^{-1}, λ 0.71069 Å (Mo-K_α).

Single crystal fragment 1.0 × 0.5 × 0.25 mm, Nicolet P3 automatic four-circle diffractometer, graphite-monochromated Mo-K_α radiation (λ 0.71069 Å). Cell dimensions from setting angles for 16 reflections ($20° < 2\theta < 30^0$). 1186 intensities measured in $h\ k\ l$ octant, θ–2θ scan technique, variable scan speed, room temperature, $0 < 2\theta < 50°$, yielded 980 independent observed reflections [$I > 2\sigma(I)$] h $0 \rightarrow 15$, k $0 \rightarrow 12$, l $0 \rightarrow 7$. Lorentz and polarisation corrections, no absorption correction. No evidence of crystal decomposition.

Solution from Patterson and Fourier synthesis, block-diagonal least-squares refinement [7] to $R = 0.045$, all atoms anisotropic. Approximate H atom positions from difference map, included as fixed contributions in least-squares calculations with B_{iso} 8.0 Å^3, gave $R = 0.037$. Concluding difference map showed no significant area of electron density. Weight scheme $w = \{1 + [(|F_0| - 19)/11]^2\}^{-\frac{1}{2}}$, function minimised $\Sigma w\ (|F_0| - |F_c|)^2$, neutral-atom scattering factors from International Tables [8]. Final atomic parameters are listed in Table 1.

Results and discussion

The structure of (η^5-t-BuCp)$_2$ZrCl$_2$ is illustrated in Fig. 1 and details of bond lengths and angles are given in Table 2. The compound is isostructural with (η^5-t-BuCp)$_2$TiCl$_2$ [2] with the expected pseudo-tetrahedral coordination of the metal atom. The cyclopentadienyl rings are slightly staggered in projection on the ZrCl$_2$ plane and the t-butyl groups are directed away from each other on opposite sides of the molecule.

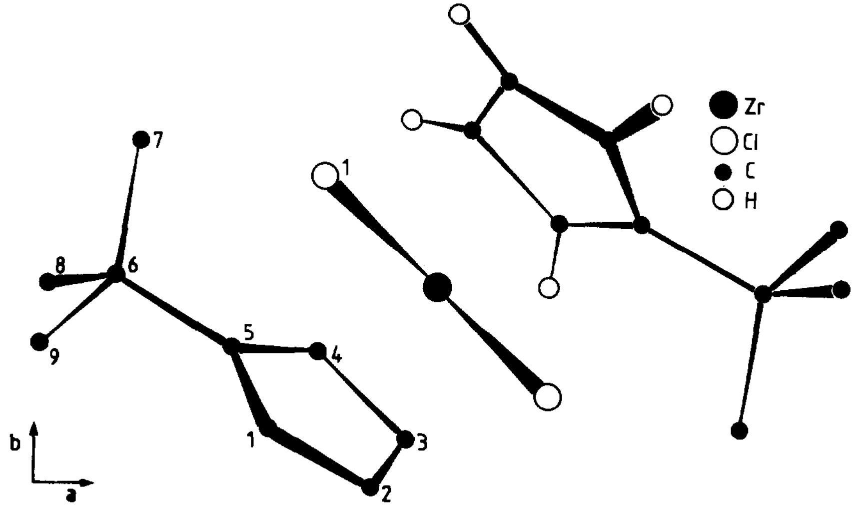


Fig. 1. $(\eta^5\text{-t-BuCp})_2ZrCl_2$. Methyl hydrogen atoms omitted, approximate positions of ring hydrogen atoms from difference map.

In Table 3 we list some of the more important structural parameters for a number of substituted $(\eta^5\text{-RCp})_2MCl_2$ compounds, together with similar data for some related molecules. The structures of the substituted compounds divide into two distinct groups, illustrated schematically in I and II. Structure I is adopted by compounds with bulky substituent groups [e.g. $(\eta^5\text{-t-BuCp})_2MCl_2$] but in other cases the more compact structure II is preferred, with the substituents exactly or approximately eclipsed above and below the MCl_2 group. The increase in atomic

TABLE 2

BOND LENGTHS (Å) AND ANGLES (°) [a]

Zr–Cl	2.457(1)	Cl–Zr–Cl	94.2(6)
Zr–C(1)	2.547(6)	C(5)–C(1)–C(2)	107.8(5)
Zr–C(2)	2.497(6)	C(1)–C(2)–C(3)	109.5(5)
Zr–C(3)	2.471(6)	C(2)–C(3)–C(4)	106.3(5)
Zr–C(4)	2.500(6)	C(3)–C(4)–C(5)	109.4(5)
Zr–C(5)	2.583(6)	C(4)–C(5)–C(1)	106.5(5)
Zr–Cp(c)	2.217	C(4)–C(5)–C(6)	124.6(5)
C(1)–C(2)	1.421(9)	C(1)–C(5)–C(6)	127.7(5)
C(2)–C(3)	1.383(10)	C(5)–C(6)–C(7)	110.7(5)
C(3)–C(4)	1.424(8)	C(5)–C(6)–C(8)	110.7(6)
C(4)–C(5)	1.393(8)	C(5)–C(6)–C(9)	106.6(6)
C(5)–C(1)	1.410(9)	C(7)–C(6)–C(8)	110.9(6)
C(5)–C(6)	1.540(8)	C(7)–C(6)–C(9)	107.3(6)
C(6)–C(7)	1.542(10)	C(8)–C(6)–C(9)	110.4(6)
C(6)–C(8)	1.546(11)	Cp(c)–Zr–Cp(c)	128.6(8)
C(6)–C(9)	1.540(12)		

[a] Cp(c) = centroid of C(1)–C(5) ring. Cp–Zr–Cp angle measured between perpendiculars to mean planes of cyclopentadienyl rings is 125.8°. C(5)–C(6) is displaced outwards by 9.9° from mean plane through ring.

TABLE 3

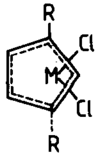
STRUCTURAL PARAMETERS FOR SOME η^5-Cp_2MCl_2 COMPOUNDS

	Structure type	Cp(c)–M–Cp(c) (°)	M–Cp(c) (Å)	M–C range (Å)	Cl–M–Cl (°)	M–Cl (Å)	Reference
η^5-Cp_2TiCl_2	Staggered	131.0(av)	2.058(av)	-	94.5(av)	2.364(av)	8
$(\eta^5$-$Me_5Cp)_2TiCl_2$	Staggered	137.4	2.127	-	92.94(4)	2.349(av)	9
$(\eta^5$-$MeCp)_2TiCl_2$	II	130.2	2.067	2.286–2.354(7)	93.15(8)	2.361(av)	10
$(\eta^5$-i-$PrCp)_2TiCl_2$	II	132.9	2.068	2.351–2.443(4)	92.5(1)	2.372(1)	11
$(\eta^5$-t-$BuCp)_2TiCl_2$	I	131.5	2.093	2.330–2.475(5)	92.5(5)	2.370(2)	2
$(\eta^5$-$MCp)(\eta^5$-$Cp)TiCl_2$ [a]	I	132.9	2.064 [b]	2.332–2.450(7) [b]	94.8(1)	2.368(av)	12
η^5-Cp_2ZrCl_2	Staggered	126.0–128.3	2.19(av)	-	97.1(av)	2.44(av)	13
$(\eta^5$-t-$BuCp)_2ZrCl_2$	I	128.6	2.217	2.471–2.583(6)	94.2(6)	2.457(1)	
$(\eta^5$-$BzCp)_2ZrCl_2$ [c]	II	116.4 [d]	2.350 [d]				
		126 [e]	2.16 [f]	2.42–2.55(2)	94.4(1)	2.461(6)	14
$(\eta^5$-$MeCp)_2VCl_2$	II	133.4	1.991	2.336–2.416(6)	87.1(1)	2.398(2)	10

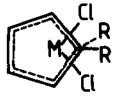
[a] M = (−) Menthyl. [b] Substituted ring. [c] Bz = benzyl. [d] Measured to centre of gravity of ring. [e] Angle between perpendiculars to mean planes. [f] Along perpendicular to mean plane.

radius from Ti to Zr is not sufficient to allow (η^5-t-BuCp)$_2$ZrCl$_2$ to adopt a "type

I



II



II" structure: the non-bonded H--Cl contacts with the t-butyl groups above and below the ZrCl$_2$ group would still be unacceptably close at ~ 2.5 Å.

The Cp–Ti–Cp tilt angles in the six titanium compounds listed in Table 3 appear to be constrained primarily by the developing contacts between the approaching edges of the cyclopentadienyl rings. The closest inter-ring distances in (η^5-t-BuCp)$_2$TiCl$_2$ [2], using the same numbering system as for the zirconium compound, are C(4)–C(3)′ 2.96, C(4)–H(3)′ ~ 2.7 and H(4)–H(3)′ ~ 2.2 Å, all of which represent firm non-bonded contacts. The corresponding closest distances in (η^5-i-PrCp)$_2$TiCl$_2$[11] are C–C′ 2.91, C–H′ ~ 2.6 and H–H′ ~ 2.1 Å. The larger size of the zirconium atom should enable the corresponding zirconium compounds to adopt more nearly tetrahedral conformations before equivalent contacts occur. In fact, the Cp–Zr–Cp angles in (η^5-t-BuCp)$_2$ZrCl$_2$ and η^5-Cp$_2$ZrCl$_2$ [13] are only 0.3–4.3° less than those in (η^5-t-BuCp)$_2$TiCl$_2$ and η^5-Cp$_2$TiCl$_2$ [8]. The closest inter-ring contact distances in (η^5-t-BuCp)$_2$ZrCl$_2$ are C(4)–C(3)′ 3.17, C(4)–H(3)′ ~ 2.8 and H(4)–H(3) ~ 2.4 Å, all of which are about 0.2 Å greater than the corresponding distances in (η^5-t-BuCp)$_2$TiCl$_2$. The experimental data do not suggest any excessive or unusual thermal motion in the zirconium compound: it appears that the molecular geometry is not determined solely by steric effects but must represent a genuine minimum energy conformation.

In the two pairs of titanium and zirconium compounds for which directly comparable data are available [η^5-Cp$_2$MCl$_2$ and (η^5-t-BuCp)$_2$MCl$_2$] the M–Cp distances increase by 0.13–0.14 Å from Ti or Zr, exactly in line with the increase in the covalent radius of the metal atom. The metal–chlorine distances, in contrast, increase by only 0.08 Å. These differences are significant relative to the accuracies of the structure determinations and must imply an appreciable increase in M–Cl bond strength from Ti to Zr. This appears to be another example of the general tendency for M–X σ-bond strengths to increase rather sharply down the early subgroups of the *d*-block elements [15a–d].

A final point emerging from Table 3 concerns the asymmetry of the metal–ring interaction induced by the introduction of a substituent group into the cyclopentadienyl ring. In all the cases for which reliable structural data are available, the individual metal–ring carbon atom distances reveal a small but consistent shift of the ring in such a direction as to increase the separation of the metal atom from the carbon atom carrying the substituent group. The effect is only just detectable in the methyl compounds but is noticeably greater in the isopropyl compound and greater still in the t-butyl compounds, suggesting a relationship between the extent of the ring displacement and the inductive effect of the alkyl group. The differences in the metal–carbon distances in (η^5-t-BuCp)$_2$ZrCl$_2$ are roughly comparable with those in (η^5-t-BuCp)$_2$TiCl$_2$. The substituent effects should also presumably lead to small differences in the ring C–C bond lengths, but these are not detectable above the residual uncertainties in the atomic positions.

Preliminary studies of alkyne hydroalkylation reactions [1] using di-η^5-cyclopentadienyltitanium–organoaluminium reagent systems show little effect resulting from monoalkylation of the cyclopentadienyl ligands. In a typical series of reactions, the hydroalkylation (carbometallation followed by hydrolysis) of 3-butyn-l-ol with η^5-Cp_2TiCl_2–Al_2Me_6, (η^5-MeCp)$_2$TiCl$_2$–Al$_2$Me$_6$ or (η^5-t-BuCp)$_2$TiCl$_2$–Al$_2$Me$_6$ proceeded in consistently good yield and with no significant variation in regioselectivity, a mixture of *trans*-3-penten-l-ol and 3-methyl-3-buten-l-ol being obtained in each case.

It is clear from the structural data that internal rotation of the cyclopentadienyl rings around the M–Cp(c) axis will be effectively prevented in compounds with t-butyl ring substituents. The structures of (η^5-t-BuCp)$_2$TiCl$_2$ and (η^5-t-BuCp)$_2$ZrCl$_2$ in solution should therefore correspond, at least approximately, to those in the crystal. In molecules with less bulky substituent groups, internal rotation may be hindered to some extent but will still be possible, with some synchronisation of the motion of the two rings in certain cases [9]. Thus, if the active Ti–Al (or Zr–Al) species is formed initially by approach of an alkyl group along the general direction of the axis bisecting the MCl_2 bond, the t-butyl groups will be in no position to interfere and the smaller substituent groups will be able to move away to "type I" positions as the reaction develops. The alkyl groups therefore exert no control over this stage of the reaction: detectable substituent effects will probably only appear in systems with multiply substituted cyclopentadienyl ligands. Further studies of these effects are in progress.

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