

Structures of Homoleptic Benzyl Derivatives of Zirconium

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Abstract

Crystals of $\text{Zr}(p\text{-CH}_2\text{C}_6\text{H}_4\text{CMe}_3)_4$, tetra(4-*tert*-butylbenzyl)zirconium (1), have been studied by X-ray diffraction. The crystals belong to the tetragonal system, space group $I\bar{4}$, with $a = 16.481$ (2), $c = 7.131$ (4) Å, so that chemically equivalent ligands are also structurally equivalent, unlike other known homoleptic $M(\text{CH}_2\text{-C}_6\text{H}_5)_4$ compounds. $\text{Zr}-\text{CH}_2-\text{C}_{\text{ipso}}$ bond angles of 90.0 (2)° suggest that ligands are η^2 -bonded. The structure is discussed along with that of $\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_4$, tetrabenzylzirconium (2) (redetermined), which is crystallographically unsymmetrical but also of approximate S_4 symmetry. The distortion of (2) from tetragonal symmetry (the four $\text{Zr}-\text{CH}_2-\text{C}_{\text{ipso}}$ bond angles being rather different) is discussed along with crystal packing.

1. Introduction

The structure and reactivity of transition metal compounds containing benzyl ligands are often much different from similar compounds containing alkyl ligands owing to the ability of benzyl to involve more than one electron in metal bonding, giving rise to η^n compounds with $n > 1$ (Scholz *et al.*, 1993; Legzdins *et al.*, 1991; Pellecchia, Immirzi, Pappalardo & Peluso, 1994). In particular, coordinatively unsaturated benzyl derivatives of group 4 elements are widely studied for their catalytic behaviour in stereospecific polymerization (Pellecchia *et al.*, 1993; Pellecchia, Immirzi & Zambelli, 1994).

The exact geometrical structures of benzyl compounds are of course of much interest, just because there is no clear-cut separation among η^n cases. Recently a systematic study has been undertaken (Tedesco, 1996; Immirzi & Tedesco, 1996) with the aim of establishing, by considering all known structures on statistical grounds, correlations between bonding modes and structural details, including small aromatic ring distortions.

Of special interest are the homoleptic benzyl compounds of group 4 metals whose catalytic behaviour in polymerization reactions is well known (Giannini *et al.*, 1970). In already known cases (Davies, Jarvis, Kilbourn & Pioli, 1971; Davies, Jarvis & Kilbourn, 1971; Bassi *et al.*, 1971) the four chemically equivalent ligands

are crystallographically non-equivalent and the $M-\text{CH}_2-\text{C}_{\text{ipso}}$ bond angles are somewhat different, thus providing uncertainty on the hapticity of the ligands. Many of these compounds have been studied by diffraction methods, but the structures were not accurate enough and were reported as short communications without atomic coordinates and devoid of most structural information.

In our department several zirconium compounds have been studied which were derived from $\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_4$ (2) (Pellecchia, Grassi & Immirzi, 1993), $\text{Zr}(p\text{-CH}_2\text{C}_6\text{H}_4\text{CMe}_3)_4$ (1) and $\text{Zr}[m,m'\text{-CH}_2\text{C}_6\text{H}_3(\text{CMe}_3)_2]_4$ (3) (Longo *et al.*, 1996). Lacking complete structural information on group 4 metal homoleptic benzyl compounds, we considered it to be worthwhile to perform X-ray diffraction studies on both novel and known compounds.

While crystallization of (3) failed, single crystals were obtained for (1) and (2). Therefore, we have investigated the crystal structures of (1) (unknown) and (2) (already known without details).

2. Experimental

Compounds $\text{Zr}(p\text{-CH}_2\text{C}_6\text{H}_4\text{CMe}_3)_4$ (1) and $\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_4$ (2) were prepared according to Zucchini *et al.* (1971) and crystallized from *n*-heptane by slow cooling to 253 K. Single crystals for X-ray diffraction measurements were sealed in glass capillaries under nitrogen. Diffraction experiments were performed, at room temperature, by means of a Rigaku AFC-7S diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation ($\lambda = 0.71069$ Å). Lattice constants and the crystal orientation were obtained from the setting angles of 25 centred reflections in the range $36 < 2\theta < 44^\circ$. Details are given in Table 1.

Intensity data were corrected for Lorentz and polarization, and absorption (North *et al.*, 1968); no decay correction was applied. The unit-cell volume resulting for (2) is ~4% higher than the value published by Davies, Jarvis, Kilbourn & Pioli (1971), who operated at 233 K.

Both structures [lacking coordinate information (2) was also treated as unknown] were solved by means of SIR92 (Altomare *et al.*, 1994) and DIRDIF92

Table 1. *Experimental details*

	(1)	(2)
Crystal data		
Chemical formula	C ₄₄ H ₆₀ Zr	C ₂₈ H ₂₈ Zr
Chemical formula weight	680.14	455.72
Cell setting	Tetragonal	Orthorhombic
Space group	$\bar{I}4$	<i>Pbca</i>
<i>a</i> (Å)	16.481 (2)	16.387 (1)
<i>b</i> (Å)	16.481 (2)	20.022 (1)
<i>c</i> (Å)	7.131 (4)	13.758 (6)
<i>V</i> (Å ³)	1937 (1)	4514 (2)
<i>Z</i>	2	8
<i>D</i> _x (Mg m ⁻³)	1.166	1.341
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71069	0.71069
No. of reflections for cell parameters	25	25
θ range (°)	18–22	18–22
μ (mm ⁻¹)	0.311	0.498
Temperature (K)	293 (2)	293 (2)
Crystal form	Prism	Prism
Crystal size (mm)	0.5 × 0.4 × 0.3	0.8 × 0.7 × 0.6
Crystal colour	Orange	Orange
Data collection		
Diffractometer	Rigaku AFC-7S	Rigaku AFC-7S
Data collection method	ω -2 θ scans	ω -2 θ scans
Absorption correction	Empirical	Empirical
<i>T</i> _{min}	0.86	0.88
<i>T</i> _{max}	1	1
No. of measured reflections	1512	6593
No. of independent reflections	1512	6593
No. of observed reflections	1160	2347
Criterion for observed reflections	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)
θ _{max} (°)	30	30
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 23 0 → <i>k</i> → 23 0 → <i>l</i> → 10	0 → <i>h</i> → 23 0 → <i>k</i> → 28 0 → <i>l</i> → 19
No. of standard reflections	3	3
Frequency of standard reflections (min)	Every 150 reflections	Every 150 reflections
Intensity decay (%)	1.5	—
Refinement		
Refinement on	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0330	0.0362
<i>wR</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0822	0.0969
<i>S</i>	1.053	1.084
No. of reflections used in refinement	1511	6567
No. of parameters used	102	263
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.6589P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 4.6197P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ / σ) _{max}	0.001	-1.804
$\Delta\rho$ _{max} (e Å ⁻³)	0.368	0.463
$\Delta\rho$ _{min} (e Å ⁻³)	-0.545	-0.454
Extinction method	None	<i>SHELXL93</i> (Sheldrick, 1993)
Extinction coefficient	—	0.0028 (2)
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs		
Data reduction	<i>TEXSAN</i> (Molecular Structure Corporation, 1992)	<i>TEXSAN</i> (Molecular Structure Corporation, 1992)
Structure solution	<i>SIR92</i> (Altomare <i>et al.</i> , 1994)	<i>SIR92</i> (Altomare <i>et al.</i> , 1992)
Structure refinement	<i>SHELXL93</i> (Sheldrick, 1993)	<i>SHELXL93</i> (Sheldrick, 1993)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (1)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^j a_j$$

	x	y	z	U_{eq}
Zr1	1/2	0	1/4	0.0467 (2)
C1	0.5057 (2)	0.1007 (2)	0.0322 (5)	0.0582 (8)
C2	0.5917 (2)	0.1143 (2)	0.0777 (5)	0.0492 (7)
C3	0.6533 (2)	0.0647 (2)	0.0070 (5)	0.0533 (8)
C4	0.7331 (2)	0.0725 (2)	0.0645 (5)	0.0513 (7)
C5	0.7561 (2)	0.1287 (2)	0.2001 (5)	0.0514 (8)
C6	0.6952 (2)	0.1793 (2)	0.2664 (9)	0.0555 (9)
C7	0.6162 (2)	0.1721 (2)	0.2111 (5)	0.0550 (11)
C8	0.8424 (2)	0.1353 (2)	0.2753 (9)	0.0612 (12)
C9	0.9011 (3)	0.0758 (3)	0.1826 (9)	0.102 (2)
C10	0.8415 (3)	0.1161 (3)	0.4885 (8)	0.0832 (13)
C11	0.8751 (2)	0.2215 (2)	0.2498 (12)	0.0775 (10)

(Beurskens *et al.*, 1992) program systems, both included in the *TEXSAN* structure solution package (Molecular Structure Corporation, 1992). Least-squares refinement was achieved with *SHELXL93* (Sheldrick, 1993), using anisotropic displacement parameters for non-H atoms. H atoms were placed in idealized positions [$r(\text{C}-\text{H}) = 1.08 \text{ \AA}$] and included in structure-factor calculations, but not refined. Further details are given in Table 1. Final disagreement R indices ($R = \sum |F_o - F_c| / \sum F_o$) based on reflections with $F_o > 4\sigma$ are 0.033 and 0.036 for (1) and (2), respectively [*cf.* $R = 0.122$ given by Davies, Jarvis, Kilbourn & Pioli, 1971, for (2) at 233 K]. wR_2 indices by Sheldrick (1993) ($wR_2^2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]$) are 0.092 for (1) and 0.227 for (2). Least-squares weight factors were evaluated as $w = 1/\sigma^2(F_o^2) + (AP)^2 + BP$, where $P = (F_o^2 + 2F_c^2)/3$, and A and B are empirical constants, given in Table 1. Atomic fractional coordinates and equivalent isotropic displacement parameters for (1) and (2) are listed in Tables 2 and 3, respectively.†

3. Results and discussion

Molecular models (*ORTEP* drawings; Johnson, 1965) for (1) and (2) are shown in Figs. 1 and 2, respectively. The most relevant bond lengths and angles within each benzyl ligand are listed in Tables 4 and 5. New geometrical data for (2) do not contradict Davies data (where comparison is possible); standard errors are $\sim 30\%$ of the previous ones and this allows a deeper discussion.

Owing to the S_4 molecular symmetry the four benzyl groups of (1) are structurally equivalent to the $\text{Zr}-\text{CH}_2$ distance 2.276 (4) \AA , $\text{Zr}-\text{CH}_2-\text{C}_{\text{ipso}}$ bond angle $90.0 (2)^\circ$ and $\text{Zr}-\text{C}_{\text{ipso}}$ distance 2.710 (3) \AA . These features indicate that (1) is a fourfold η^2 -bonded struc-

 Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^j a_j$$

	x	y	z	U_{eq}
Zr1	0.26510 (2)	0.15741 (2)	1.50281 (3)	0.0642 (2)
C1a	0.1422 (3)	0.1858 (3)	1.5647 (3)	0.092 (2)
C2a	0.1364 (3)	0.1184 (3)	1.5997 (3)	0.0719 (13)
C3a	0.1799 (3)	0.0977 (3)	1.6817 (3)	0.0766 (14)
C4a	0.1834 (3)	0.0322 (3)	1.7111 (4)	0.089 (2)
C5a	0.1459 (4)	-0.0160 (3)	1.6582 (6)	0.111 (2)
C6a	0.1038 (4)	0.0005 (4)	1.5759 (7)	0.115 (2)
C7a	0.0986 (3)	0.0654 (4)	1.5467 (4)	0.099 (2)
C1b	0.3030 (3)	0.0496 (3)	1.4884 (3)	0.0779 (13)
C2b	0.3855 (2)	0.0614 (2)	1.5259 (3)	0.0617 (11)
C7b	0.4057 (3)	0.0523 (2)	1.6235 (3)	0.0726 (12)
C6b	0.4801 (4)	0.0693 (3)	1.6592 (4)	0.085 (2)
C5b	0.5382 (3)	0.0964 (3)	1.5994 (5)	0.085 (2)
C4b	0.5215 (3)	0.1058 (3)	1.5031 (4)	0.0838 (14)
C3b	0.4457 (3)	0.0890 (2)	1.4669 (3)	0.0692 (12)
C1c	0.3390 (3)	0.2176 (2)	1.6090 (4)	0.0817 (14)
C2c	0.3454 (3)	0.2717 (2)	1.5383 (3)	0.0652 (11)
C7c	0.4096 (3)	0.2747 (3)	1.4722 (4)	0.0774 (13)
C6c	0.4115 (3)	0.3205 (3)	1.3991 (4)	0.089 (2)
C5c	0.3493 (4)	0.3650 (3)	1.3871 (4)	0.106 (2)
C4c	0.2850 (4)	0.3643 (3)	1.4513 (5)	0.096 (2)
C3c	0.2833 (3)	0.3182 (2)	1.5263 (4)	0.0759 (13)
C1d	0.2746 (3)	0.1814 (3)	1.3429 (3)	0.091 (2)
C2d	0.1880 (3)	0.1766 (3)	1.3169 (3)	0.0668 (12)
C7d	0.1364 (4)	0.2315 (3)	1.3214 (4)	0.086 (2)
C6d	0.0558 (4)	0.2274 (3)	1.3044 (4)	0.096 (2)
C5d	0.0204 (3)	0.1680 (4)	1.2839 (5)	0.099 (2)
C4d	0.0680 (4)	0.1131 (3)	1.2775 (4)	0.099 (2)
C3d	0.1509 (3)	0.1176 (2)	1.2941 (4)	0.0773 (14)

ture. The aromatic ring is planar (root mean-square deviation, r.m.s.d., 0.011 \AA), but the six bond lengths deviate from the mean value (1.389 \AA) up to 5σ , far beyond the effects of thermal motion (Domenicano, 1992). If C_{2v} symmetry is considered rather than D_{6h} for the bare ring, deviations from the means are $1 - 2\sigma$. So

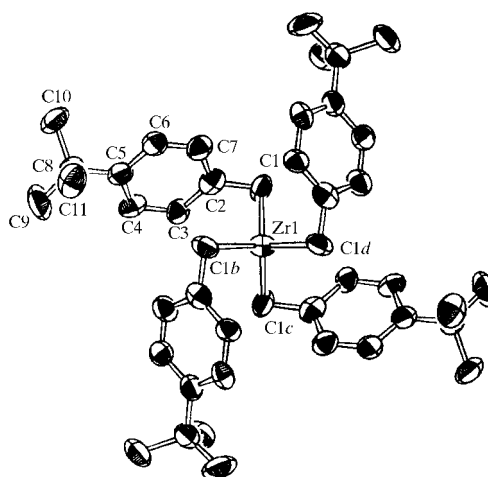


Fig. 1. *ORTEP* (Johnson, 1965) drawing of $\text{Zr}(p\text{-CH}_2\text{C}_6\text{H}_4\text{CMe}_3)_4$ (1) projected along the crystallographic c edge (ellipsoids at the 50% probability level).

† Lists of atomic coordinates, anisotropic displacement parameters, structure factors and least-squares planes data have been deposited with the IUCr (Reference: NA0084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Relevant distances (Å) and bond angles (°) for (1) and (2)

(a)–(d) denote the four benzyl groups for (2); (2av) is the average value among the four benzyls. C1(arom) is the distance from the C1 atom to the aromatic ring; r.m.s.d. is the root mean-square deviation for the six aromatic C atoms.

	(1)	(2a)	(2b)	(2c)	(2d)	(2av)
Zr–C1	2.276 (4)	2.259 (5)	2.255 (5)	2.248 (5)	2.258 (4)	2.255 (3)
Zr–C2	2.710 (3)	2.614 (4)	2.773 (3)	2.684 (4)	2.879 (4)	2.743 (57)
Zr–C3	3.244 (3)	3.072 (5)	3.298 (5)	3.249 (4)	3.519 (5)	3.282 (92)
Zr–C7	3.434 (3)	3.347 (6)	3.535 (4)	3.361 (5)	3.589 (6)	3.467 (61)
Zr–C1–C2	90.0 (2)	87.0 (3)	93.9 (3)	90.2 (3)	99.1 (3)	92.5 (26)
C1–C2	1.471 (5)	1.437 (7)	1.467 (6)	1.459 (6)	1.465 (6)	1.458 (7)
C2–C3	1.397 (5)	1.397 (6)	1.391 (6)	1.390 (6)	1.365 (6)	1.386 (7)
C2–C7	1.405 (5)	1.428 (8)	1.395 (6)	1.391 (6)	1.389 (7)	1.398 (9)
C3–C4	1.385 (5)	1.374 (7)	1.380 (7)	1.383 (8)	1.382 (7)	1.379 (2)
C4–C5	1.392 (4)	1.355 (8)	1.366 (7)	1.375 (8)	1.352 (8)	1.362 (5)
C5–C6	1.387 (5)	1.366 (10)	1.370 (7)	1.364 (8)	1.353 (8)	1.363 (4)
C6–C7	1.367 (5)	1.363 (9)	1.358 (7)	1.360 (7)	1.344 (7)	1.355 (4)
C7–C2–C3	115.6 (3)	114.4 (5)	116.5 (4)	116.5 (5)	115.1 (4)	115.7 (5)
C1–C2–C3	122.1 (3)	121.0 (5)	120.8 (4)	121.6 (5)	123.0 (5)	121.5 (5)
C1–C2–C7	121.9 (3)	123.7 (5)	122.4 (4)	121.5 (5)	121.7 (5)	122.3 (5)
C2–C3–C4	122.0 (3)	122.8 (5)	121.6 (5)	121.4 (5)	122.2 (5)	122.0 (3)
C3–C4–C5	121.7 (3)	120.1 (6)	119.9 (5)	120.1 (5)	120.2 (5)	120.1 (1)
C4–C5–C6	116.1 (3)	120.2 (6)	119.8 (5)	119.2 (5)	118.8 (5)	119.4 (3)
C5–C6–C7	122.6 (4)	120.4 (6)	120.4 (5)	120.8 (5)	120.8 (6)	120.6 (1)
C6–C7–C2	121.8 (3)	122.0 (6)	121.9 (5)	122.0 (5)	122.9 (5)	122.2 (2)
C1(arom)	0.161 (6)	0.173 (8)	0.134 (8)	0.176 (8)	0.120 (8)	0.151 (14)
r.m.s.d.	0.011	0.007	0.003	0.006	0.007	0.006 (1)

Table 5. Other relevant distances (Å) and bond and torsion angles (°) for (1) and (2)

C8(arom) is the distance from the C8 atom to the plane of the aromatic ring.

(1)	(2)
C1–Zr–C1b	117.8 (1)
C1–Zr–C1c	93.9 (2)
C4–C5–C8–C9	1.7 (6)
C8(arom)	0.093 (7)
C1a–Zr–C1b	121.3 (2)
C1a–Zr–C1c	95.8 (2)
C1a–Zr–C1d	112.0 (2)
C1b–Zr–C1c	115.0 (2)
C1b–Zr–C1d	95.7 (2)
C1c–Zr–C1d	118.8 (3)

C3–C4 and C6–C7 bonds (mean 1.376 Å) would be really shorter than C2–C7 and C2–C3 (mean 1.401 Å), and C5–C4 and C5–C6 bonds (mean 1.390 Å). This could strengthen the hypothesis that an anionic resonance form might have a role (see below).

Deviations from the plane of C1 [0.161 (6) Å] and C8 atoms [0.093 (7) Å], and deviations from 120° of C7–C2–C3 and C4–C5–C6 bond angles [115.6 (3) and 116.1 (3)°, respectively] are more remarkable and also less affected by the effects of solid-state thermal motion (Domenicano, 1992).

From the decrease of the C7–C2–C3 angle one could infer the sp^2 hybridization of the C2 atom to be unsymmetrical; also many η^1 -compounds display the same feature, but to a lesser extent [average angle from 108 η^1 -benzyls is 117.2°, see Tedesco (1996)]; the present value of 115.6° suggests, however, that the M –CH₂–C_{ipso} interaction also contributes to the decreasing of the angle. One cannot exclude the possibility that the p -*tert*-

butyl group could have an effect; indeed, in gaseous *tert*-butylbenzene the C–C–C angle opposite the *tert*-butyl is 118.1 (3)° (Campanelli *et al.*, 1994).

C4–C5–C6 angles different from 120° have been observed in other cases: in the gaseous *tert*-butylbenzene the angle is 117.1 (3)° (Campanelli *et al.*, 1994). From the structures considered by Tedesco (1996) it appears that in η^2 -unsubstituted metal–benzyl compounds the mean value is 119.6° and in η^1 -compounds the mean value is 119.5°.

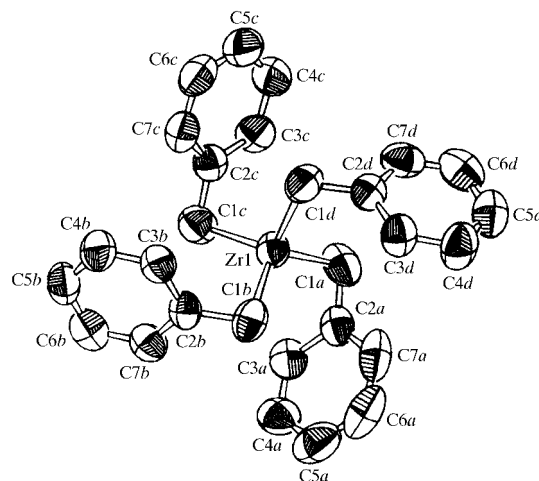


Fig. 2. ORTEP (Johnson, 1965) drawing of $Zr(CH_2C_6H_5)_4$ (2) projected along the approximate S_4 molecular axis (ellipsoids at the 50% probability level).

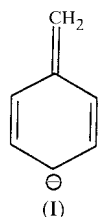
Table 6. A comparison between η^2 - and η^4 -benzyl compounds

The following differences $\delta_{ih} = (M-C_{\text{ipso}}) - (M-CH_2)$, $\delta_{oh} = (M-C_{\text{ortho}}) - (M-CH_2)$, $\delta_{o'h} = (M-C_{\text{ortho}}) - (M-CH_2)$, $\delta_{o'o} = (M-C'_{\text{ortho}}) - (M-C_{\text{ortho}})$ are useful to compare different benzyl compounds. Only benzyl ligands with the smallest $M-CH_2-C_{\text{ipso}} = MCC$ angle are shown.

	$M-CH_2$	δ_{ih}	δ_{oh}	$\delta_{o'h}$	$\delta_{o'o}$	MCC	References
Cp*Th(CH ₂ C ₆ H ₅) ₃	2.58	0.29	0.77	0.99	0.22	86	Mintz <i>et al.</i> (1982)
UMe(CH ₂ C ₆ H ₅) ₃ (dmpe)	2.54	0.22	0.55	0.91	0.36	83	Edwards <i>et al.</i> (1984)
Th(CH ₂ C ₆ H ₅) ₄ (dmpe)	2.53	0.34	0.78	0.96	0.18	88	Edwards <i>et al.</i> (1984)
Zr(CH ₂ C ₆ H ₅) ₄ (dmpe)	2.26	0.53	1.08	1.29	0.20	94	Girolami <i>et al.</i> (1984)
Zr(CH ₂ C ₆ H ₅) ₄	2.26	0.35	0.81	1.09	0.27	87	This work
Zr(<i>p</i> -CH ₂ C ₆ H ₄ CMe ₃) ₄	2.28	0.43	0.97	1.16	0.19	90	This work

Comparison with other η^2 -*p*-alkyl-substituted benzyl derivatives is not possible (the present case seems to be the first). If η^1 - and η^3 -compounds are considered (Cotton & LaPrade, 1968; Wadepohl & Pritzkow, 1992; Chesnut *et al.*, 1991; Sieber *et al.*, 1984; Barratt *et al.*, 1987; Hermes & Girolami, 1987; Jiabi *et al.*, 1988; Wadepohl *et al.*, 1994) one observes a mean value of 117.8° [also including (1)]. In halogen *para*-substituted cases the mean value is 121.6° (Latesky *et al.*, 1985; Byers *et al.*, 1990; Cascrall *et al.*, 1990; Shu *et al.*, 1990).

Thus, while the nature of the substituent plays a remarkable role, the hapticity seems to have only a modest influence. Anyway, our value is particularly small and this suggests that the following anionic resonance form could have a role.



Concerning the deviations of C1 and C8 atoms from the aromatic plane, it is worth noting that the former is usually present in transition-metal-benzyl compounds, not only in η^2 cases, but also in η^1 cases (Tedesco, 1996); the latter is frequently observed in aromatics with *tert*-butyl groups.

The conformation of the *p-tert*-butyl group is such that the C4 and C9 atoms are eclipsed [C4–C5–C8–C9 = 1.7 (6)°]. Gas-phase electron diffraction and theoretical calculations (Campanelli *et al.*, 1994) have shown that also in *tert*-butylbenzene such a conformation is preferred.

The S_4 symmetrical compound (1) exhibits a feature also observed in unsymmetrical cases (Davies, Jarvis & Kilbourn, 1971): the four Zr–CH₂ bonds are not directed as in a regular tetrahedron, since four C–Zr–C angles are 117.8 (1)° and two are 93.9 (2)°. Therefore, the distortion is toward a ‘prolate’ rather than an ‘oblate’ figure. Note that Zr(CH₂C₆H₅)₄ and Hf(CH₂C₆H₅)₄ are also prolate, while Ti(CH₂C₆H₅)₄ is oblate. In Sn(CH₂C₆H₅)₄, a group 14 homoleptic

compound, the tetrahedral symmetry is almost exact (Davies, Jarvis & Kilbourn, 1971).

Compound (2), as well as other known homoleptic MR_4 compounds, displays approximate S_4 molecular symmetry (also considering the benzyl conformations). Comparing (1) and (2) one indeed observes a small difference between the Zr–CH₂ distance in (1) [2.276 (4) Å] and in (2) [mean distance 2.255 (3) Å] with four values not significantly different. The four Zr–CH₂–C_{ipso} bond angles instead, as well as Zr–C2, Zr–C3 and Zr–C7 distances, are rather scattered with mean values close to those observed in (1). These differences might either be ascribed to a particularly high flexibility of the Zr–CH₂–C_{ipso} angle (so that unsymmetrical intermolecular interactions are sufficient to distort the S_4 molecular symmetry, see Fig. 3) or indicate that the four ligands are differently bound, possibly having different hapticity.

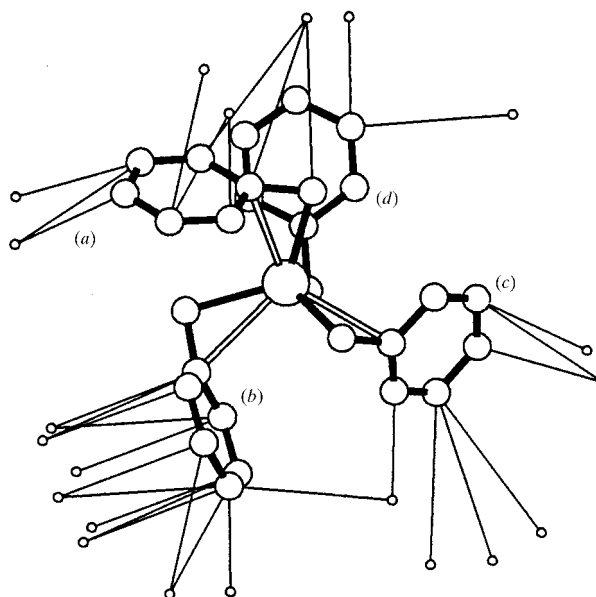


Fig. 3. Ball-and-stick drawing of Zr(CH₂C₆H₅)₄ (2) projected along the crystallographic *c* edge, indicating intermolecular C...C distances shorter than 3.90 Å. Only atoms in contact among neighbouring molecules have been drawn as small circles. Labels (a)–(d) specify the benzyl ligands.

Indeed, $M-\text{CH}_2-\text{C}_{\text{ipso}}$ angles observed in actinide-benzyl compounds, depicted as η^4 (Mintz *et al.*, 1982; Edwards *et al.*, 1984), have values comparable to the present ones (see Table 6) and this indicates an η^4 interaction in the present case, *e.g.* for benzyl (*2a*). Nevertheless, the Zr–C3 and Zr–C7 distances, 3.07 and 3.34 Å for benzyl (*2a*), remain so large that a chemical bond is barely credible.

We have thus looked at intermolecular interactions (see Fig. 3) to check if low Zr–CH₂–C_{ipso} angles correspond to tightly packed benzyls. Indeed, the H···H distances are all well beyond the van der Waals distance, while the C atoms are close to neighbouring C atoms with C···C distances never shorter than 3.70 Å. The four benzyls are quite differently packed with 9, 14, 3 and 2 contacts below 3.90 Å for benzyls (*a*), (*b*), (*c*) and (*d*), respectively. Thus, the loosest benzyl is that forming the higher Zr–CH₂–C_{ipso} angle, but that forming the smallest angle is *not* the tightest; it is also true, however, that the tightest *b* is the only one displaying a clear graphitic interaction (see Fig. 3) and this explains the high number of contacts.

In conclusion, our opinion is that the variable $M-\text{CH}_2-\text{C}_{\text{ipso}}$ angles in (*2*) could hardly be ascribed to a variable hapticity, considering the Zr–C3 and Zr–C7 observed distances. The most convincing conclusion is simply that Zr(CH₂C₆H₅)₄ has, in the free state, exact S_4 molecular symmetry, but also a high flexibility (with particular reference to $M-\text{CH}_2-\text{C}_{\text{ipso}}$ angle bending), so that even weak non-bonding interactions can modify the molecular geometry. Only if the crystal packing is also symmetric [as occurs in (*1*)] is the S_4 symmetry observed in the solid state. The same conclusion is applicable to other homoleptic group 4 metal complexes, $M(\text{CH}_2\text{C}_6\text{H}_5)_4$. Such flexibility should be peculiar to the transition metal complexes, so that the Sn(CH₂C₆H₅)₄ molecule (Davies, Jarvis & Kilbourn, 1971) displays in the solid state equal bond angles and conformations for the four benzyl groups, in spite of the unsymmetric crystal packing.

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