The Crystal and Molecular Structures (at −40 °C) of the Tetrabenzyls of Titanium, Hafnium, and Tin

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Summary Tetrabenzylhafnium has a molecular structure identical to that of tetrabenzylzirconium with a distorted tetrahedral arrangement of ligands around the metal and angles at the methylene carbons of around 90°; tetrabenzyltitanium shows a similar distortion from a tetrahedral arrangement but the angle M–CH_2–C now averages 103°; an interaction between the aromatic ring and the transition-metal atoms is suggested to account for the distortion; in contrast, tetrabenzyltin has a perfectly regular structure.

WE have recently reported[1] the crystal and molecular structure of tetrabenzylzirconium. Because of the unusual structural feature of an approximately 90° angle at the ligand methylene carbon atoms in this zirconium compound, we have now studied† the structures of three related tetrabenzyls. Table 1 lists the crystal data and refinement details for tetrabenzyltitanium,‡ tetrabenzylhafnium, and tetrabenzyltin. The observed molecular geometries are compared in Table 2.

The hafnium complex crystallises in the same space group as the zirconium compound and the molecular structure is essentially identical, with a distorted tetrahedral arrangement of ligands around the metal atom and a range of angles (all below 109°) at the methylene carbons. (See Figure in ref. 1 for a drawing of the molecular shape.) Titanium tetrabenzyl, although taking up a different space group, has a molecular structure very similar with a distorted tetrahedral co-ordination around the metal. There is also a range of values for the M–CH_2–C angles, this time both above and below 109°, but the mean is closer to a perfect tetrahedral value than in the zirconium and hafnium analogues.

In complete contrast to the transition-metal benzyls tetrabenzyltin has a nearly ideally regular structure with non-crystallographic but almost perfect tetrahedral co-ordination of the ligands to the metal. In addition the Sn–CH_2–C angles are all nearly equal to 112°, the value expected from analogy with organic structures.

Comparison of the transition-metal complexes with the

TABLE 1

Crystal data and refinement details

$C_{28}H_{28}M$	$Ti(CH_2Ph)_4$	$Zr(CH_2Ph)_4$[a]	$Hf(CH_2Ph)_4$	$Sn(CH_2Ph)_4$
Crystal colour	deep red	orange	orange	colourless
M	412·2	455·5	542·8	483·0
Crystal class	orthorhombic	orthorhombic	orthorhombic	monoclinic
a (Å)	9·204(12)	19·945(6)	20·146(13)	10·185(5)
b	13·026(14)	13·716(7)	13·656(7)	12·326(9)
c	19·120(17)	16·306(5)	16·386(14)	19·257(12)
U (Å^3)	2292	4461	4508	2416
Space group	$P2_12_12_1$	*Pbca*	*Pbca*	$P2_1/n$
Z	4	8	8	4
F(000)	872	1888	2144	984
μ(cm^{-1})	4·0	5·0	49·1	10·4
Number of reflections in refinement[a]	667	2216	2821	3130
Final *R*	0·122	0·102	0 057	0·056

[a] The data for each compound were collected from a crystal cooled (G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc.* (*A*), 1970, 1725) to −40 °C on a Picker single-crystal diffractometer using Mo-K_α radiation. Reflections with $|F_0| > 3\sigma$ and $> 5e$ were used in the least-squares refinement with isotropic parameters for the carbon atoms and anisotropic for the metal atoms. [b] Ref. 1.

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† Preliminary details have been reported by D. G. H. Ballard of this Laboratory at the 23rd IUPAC Congress, Boston, Mass., July, 1971.

‡ A note has recently appeared (I. W. Bassi, G. Allegra, R. Scordamaglia, and G. Chioccola, *J. Amer. Chem. Soc.*, 1971, **93**, 3787) describing the structure of tetrabenzyltitanium at room temperature. The results are in close agreement with those described here.

TABLE 2

Selected molecular geometry details

	$Ti(CH_2Ph)_4$	$Zr(CH_2Ph)_4$[a]	$Hf(CH_2Ph)_4$	$Sn(CH_2Ph)_4$
M–C (Å)	2·04, 2·11 2·15, 2·21	2·23, 2·26 2·28, 2·29	2·23, 2·24 2·26, 2·27	2·17, 2·17 2·18, 2·19
M–C (mean)	2·13(4)	2·27(1)	2·25(1)	2·18(1)
C–M–C (°) . ..	104, 105, 105, 109, 115, 119	94, 96, 113, 116, 118, 122	99, 100, 110, 115, 116, 118	108, 108, 109, 110, 111, 111
M–C–C (°) . ..	92, 98, 109, 115	85, 90, 92, 101	88, 92, 93, 101	110, 110, 112, 114
M–C–C (mean) ..	103(3)	92(1)	94(1)	111(1)
Dihedral angle (°) M–C–C/aromatic ..	80, 84, 85, 86	81, 82, 83, 85	79, 80, 83, 83	78, 82, 84, 85
Torsion angle τ(C–M–CH_2–C) ..	−2, 40, −52, −52	−12, −22, 23, 28	−18, −22, 22, 26	−39, 46, 49, 56
$\|\tau\|$ (°) (mean) ..	—	21	22	48

[a] Ref. 1.

tin compound indicates that there must be an extra structural influence causing the novel distortion in the transition-metal structures. Simple interatomic repulsions (non-bonded) and the normal bonding forces should produce structures analogous to that of the tin compound.

The two essential features that need to be explained are the variation in angle around the transition-metal atoms and the low angle at the methylene carbon atoms. The values, τ(C–M–CH_2–C), for the torsion angles about the bond M–CH_2, given in Table 2, suggest a basic difference between the transition metal and the tin compounds. There is a tendency in the transition-metal complexes of zirconium and hafnium for a conformation to be adopted in which the bond CH_2–C eclipses (*i.e.* τ *ca.* 0°), when viewed down the relevant M–C bond, one of the other M–C bonds. In tetrabenzyltin the predominating conformation is that expected to minimise non-bonded repulsions, *i.e.* with the CH_2–C bond staggered (τ *ca.* 60°) with respect to the other Sn–C bonds. The titanium complex is intermediate in behaviour: one benzyl ligand resembles those in the zirconium and hafnium complexes whereas the other three adopt a conformation similar to the benzyl ligands in $Sn(benzyl)_4$.

We suggest that the presence of vacant *d* orbitals on the transition-metal atoms readily provides alternative hybrid bonding orbitals[2] and results in a low barrier to distortion of the C–M–C angle from a tetrahedral value of 109·5°. We also suggest that a weak interaction§ exists between the aromatic ring and the transition-metal atom causing distortion. This interaction is most prominent (as measured by the angle M–CH_2–C and the consequent close approach of the carbon of the aromatic ring to the metal atom) in the zirconium and hafnium complexes and is less pronounced in the titanium compound. It has no structural influence in tin tetrabenzyl although there is n.m.r. evidence[3] of some interaction within the tin molecule.

The variation, from the mean, of individual values for both the C–M–C and the M–CH_2–C angles is well outside experimental error and consequently the specific values observed are to some extent an influence of the crystal packing. (It should be noted, however, that the only compound with internally self-consistent angles has normal angles and the lowest *R* value.) In other environments different values might be found.

The suggested weak intramolecular interaction could account for the enhanced stability of these transition-metal benzyls relative to their alkyl (*e.g.* $TiMe_4$) and simple aryl (*e.g.* $TiPh_4$) counterparts. Other complexes of transition metals early in the transition series might be stabilised by interactions similar to that suggested here.

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§ Preliminary orbital overlap integral calculations (R. M. Canadine, personal communication) indicate this is feasible.

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[2] G. Pilcher and H. A. Skinner, *J. Inorg. Nuclear Chem.*, 1958, **7**, 8.
[3] L. Verdonck and G. P. van der Kelen, *J. Organometallic Chem.*, 1966, **5**, 532.