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Silylmethyl and Related Complexes. 5.[1] Metallocene Bis(trimethylsilyl)methyls and Benzhydryls of Early Transition Metals $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{R}]$ (M = Ti or V) and $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{X})\mathrm{R}]$ (M = Zr or Hf and X = Cl or R), and the Crystal and Molecular Structures of $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{CHPh_2})_2]$ (M = Zr or Hf)

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Abstract: The reactions of some $\mathrm{d^0}$ or $\mathrm{d^1}$ metallocene dichlorides or $[\{\mathrm{V}(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Br}\}_2]$ with the sterically hindered β-hydrogen-free lithium alkyls $\mathrm{LiCHPh_2}$ or $\mathrm{LiCH(SiMe_3)_2}$ have been investigated. The following new compounds were isolated as analytically pure, thermally stable crystals: $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{R}]$ [M = Ti and R = $\mathrm{Ph_2CH}$ or $(\mathrm{Me_3Si})_2\mathrm{CH}$; or M = V and R = $(\mathrm{Me_3Si})_2\mathrm{CH}$], $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{Cl})\{\mathrm{CH(SiMe_3)_2}\}]$ (M = Zr or Hf), $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{CHPh_2})_2]$ (M = Zr or Hf), and $[\mathrm{Zr}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{Bu}\text{-}n)\{\mathrm{CH(SiMe_3)_2}\}]$. It is interesting that the titanocene(IV) or vanadocene(IV) dichlorides (unlike the $\mathrm{Zr^{IV}}$ or $\mathrm{Hf^{IV}}$ analogues) are reduced; for Ti, the $\mathrm{Ti^{III}}$ chloride was an isolable intermediate; in the $\mathrm{V^{IV}}$ or $\mathrm{V^{III}}/\mathrm{LiCHPh_2}$ system, reduction gave $[\mathrm{V}(\eta^5\text{-}\mathrm{C_5H_5})_2]$ and $\mathrm{Ph_2CHCHPh_2}$. The benzhydryl ligand is evidently less sterically demanding than $(\mathrm{Me_3Si})_2\overline{\mathrm{C}}\mathrm{H}$; thus, $\mathrm{LiCH(SiMe_3)_2}$ failed to react with $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{Cl})\{\mathrm{CH(SiMe_3)_2}\}]$ (M = Zr or Hf), although LiBu-*n* gave the stable mixed alkyl which at 150 °C gave $\mathrm{H_2}$ and $\mathrm{C_4H_{10}}$ but no $\mathrm{C_4H_8}$. By contrast the bis(benzhydryls) of $\mathrm{Zr^{IV}}$ or $\mathrm{Hf^{IV}}$ were readily accessible. The $\mathrm{Ti^{III}}$ and $\mathrm{V^{III}}$ compounds show magnetic moments consistent with spin-only values and $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_5})_2\{\mathrm{CH(SiMe_3)_2}\}]$ is a monomer in benzene by cryoscopy. IR, ESR, and NMR data are reported. A single crystal x-ray analysis has been carried out for the isostructural $\mathrm{Zr^{IV}}$ and $\mathrm{Hf^{IV}}$ compounds $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{CHPh_2})_2]$ (M = Zr or Hf). For the former, the metal-carbon σ-bond length {2.388 (12) Å compared with 2.251 (6) Å in $[\mathrm{Zr}(\eta^5\text{-}\mathrm{C_9H_7})_2\mathrm{Me_2}]$} is markedly influenced by the bulk of the benzhydryl ligand, whereas this is not the case for the latter {2.36 (4) Å compared with 2.332 (12) Å in $[\mathrm{Hf}(\eta^5\text{-}\mathrm{C_9H_7})_2\mathrm{Me_2}]$}. A comparison of the M–C (indenyl) lengths shows that the approach is closer for Hf [2.46 (5) Å] than Zr [2.513 (15) Å].

This paper results from complementary and overlapping interests of two laboratories. At Sussex attention has focused on ligands such as $\mathrm{Me_3SiCH_2^-}$ and $(\mathrm{Me_3Si})_2\mathrm{CH^-}$, to provide unusually stable homoleptic transition metal alkyls and subvalent main group element alkyls[3-15] (see also ref 16 and 17). At Alabama extensive structural investigations have been carried out on a large number of organotransition metal complexes.[18-25]

Although there has been considerable interest in the benzyls of transition metals,[15] little work has been done (but see ref 26) using the bulkier benzhydryl ligand, $\mathrm{Ph_2CH^-}$.

A large number of $\mathrm{d^0}$ and $\mathrm{d^1}$ metallocene dialkyls $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{R_2}]$ (M = Ti, Zr, Hf, Nb, or Ta) are now known,[17] but attempts to make vanadium analogues were unsuccessful unless $\mathrm{R_2}$ is a chelate or R = $\mathrm{PhC{\equiv}C}$. It is interesting that $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Cl_2}]$ and the allyl-Grignard reagent yielded a $\mathrm{Ti^{III}}$ product $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_5})_2(\eta^3\text{-}\mathrm{C_3H_5})]$ and biallyl,[27a] whereas the corresponding experiment with $[\mathrm{Zr}(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Cl_2}]$ gave $[\mathrm{Zr}(\eta^5\text{-}\mathrm{C_5H_5})_2(\eta^1\text{-}\mathrm{C_3H_5})_2]$.[27b] Various monoalkyls $[\mathrm{V}(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{R}]$ are known, but for corresponding Ti alkyls only a few (R = $\mathrm{Me_3SiCH_2}$) derivatives are well characterized.[28,41]

The chemistry of zirconium and hafnium is well known to be quite similar[29] because of the closeness of atomic radii (1.45 and 1,44 Å, respectively). However, x-ray crystallographic studies of organometallic analogues have produced several interesting structural differences. The most dramatic of these is found with the tetracyclopentadienyl derivatives: tetracyclopentadienylzirconium(IV) is reported[30] to exist as $[\mathrm{Zr}(\eta^5\text{-}\mathrm{C_5H_5})_3(\eta^1\text{-}\mathrm{C_5H_5})]$, while tetracyclopentadienylhafnium(IV) is thought[31] to be $[\mathrm{Hf}(\eta^5\text{-}\mathrm{C_5H_5})_2(\eta^1\text{-}\mathrm{C_5H_5})_2]$ {but not isostructural with $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_5})_2(\eta^1\text{-}\mathrm{C_5H_5})_2]$}.[32] Unfortunately, the crystallographic quality of the structural studies has generated doubts.[33] More subtle differences can be found in bond length comparisons. The Hf–C(η^5-cyclopentadienyl) bond lengths are invariably slightly shorter than the Zr–C(η^5-cyclopentadienyl) distances. For the particularly well-determined structures $[\mathrm{MCl_2}\{(\mathrm{CH_2})_3(\mathrm{C_5H_4})_2\}]$,[34] the values are Hf–C (average) = 2.482 (4) Å and Zr–C (average) = 2.494 (4) Å. However, the opposite trend has been found for the metal-carbon σ bond lengths in $[\mathrm{M}(\eta^5\text{-}\mathrm{C_9H_7})_2\mathrm{Me_2}]$.[21] Here, the Hf–C ($\sigma$) length of 2.332 (12) Å is significantly longer than the Zr–C (σ) distance of 2.251 (6) Å. In order to clarify the factors responsible for the σ- and π-bond length trends, further data are required. This is one reason why the present comparative structural study of $[M(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$ (M = Zr or Hf) is of interest.

Results and Discussion

Synthesis of the Metallocene Alkyls. The deep-red lithiodiphenylmethane[36] and the colorless lithiobis(trimethylsilyl)methane[37] were prepared by lithiation of the appropriate organic chloride. As described previously,[36,37] the form of the lithium metal and choice of solvent are important [Li wire containing ca. 1% Na in THF for $LiCHPh_2$ and Li powder in refluxing Et_2O for $LiCH(SiMe_3)_2$]. By contrast, it proved impossible to convert the more bulky $(Me_3C)_2CHCl$[38] into either the lithium or the Grignard reagent.

Reaction of the metallocene(IV) dichloride with 2 mol of organolithium reagent gave the metallocene(III) monoalkyl:

$$[M(\eta^5\text{-}C_5H_5)_2Cl_2] + 2LiR \rightarrow [M(\eta^5\text{-}C_5H_5)_2R] \quad (1)$$

$$[M = Ti \text{ and } R = Ph_2CH \text{ or } (Me_3Si)_2CH; \text{ or } M = V \text{ and } R = (Me_3Si)_2CH]$$

It is possible that the bulk of these ligands prevents two alkyl groups being placed around the Ti^{4+} or V^{4+} ion. However, the initial isolable product is the metallocene(III) chloride, which may well be formed via an unstable $[M(\eta^5\text{-}C_5H_5)_2(Cl)R]$ precursor and M–R homolysis:

$$[M(\eta^5\text{-}C_5H_5)_2Cl_2] + LiR \rightarrow [M(\eta^5\text{-}C_5H_5)_2Cl]_{1 or 2} \quad (2)$$

which is subsequently alkylated:

$$[M(\eta^5\text{-}C_5H_5)_2Cl]_{1 or 2} + LiR \rightarrow [M(\eta^5\text{-}C_5H_5)_2R] \quad (3)$$

Thus, the reaction of $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ with 1 mol of $LiCH(SiMe_3)_2$ gave $[Ti(\eta^5\text{-}C_5H_5)_2Cl]_2$.

For titanium, the above reaction path (eq 1 is unusual [see, however,[27a] experiments with $Mg(Cl)C_3H_5$]. Thus, titanocene dichloride readily reacts with numerous alkyllithium reagents LiR including the somewhat less bulky $LiCH_2SiMe_3$,[7] to give $[Ti(\eta^5\text{-}C_5H_5)_2R_2]$. There is thermochemical evidence that for Ti^{IV} homoleptic alkyls $[TiR_4]$, the mean metal–carbon bond strength can be influenced significantly by steric effects [e.g., $\bar{D}(Ti\text{–}CH_2SiMe_3) > \bar{D}(Ti\text{–}CH_2CMe_3)$];[39] hence the proposal that an intermediate bulky $[Ti(\eta^5\text{-}C_5H_5)_2(Cl)R]$ is unstable toward homolysis appears to be reasonable. It is interesting that the reduction of Ti^{4+} to Ti^{3+} is more facile with $LiCH(SiMe_3)_2$ than with $LiCHPh_2$. Further evidence to indicate that the $(Me_3Si)_2CH^-$ ligand is sterically more demanding than Ph_2CH^- derives from the possibility of preparing the heavier group 4b metallocene dialkyls for the benzhydryl case only. The homolysis argument is also supported by the isolation of $(Ph_2CH)_2$ in the vanadium experiment.

Whereas reductive alkylation is unusual for titanium, for vanadium it is a standard reaction. It is likely that an intermediate d^1-vanadocene (chloro)alkyl or dialkyl would be more susceptible to M–C homolysis than its d^0-titanium analogue. (Nevertheless, in the literature the instability of V^{IV} alkyls is usually ascribed to steric factors.[17]) To observe the reductive alkylation reaction for vanadium was therefore not surprising. However, only $[V(\eta^5\text{-}C_5H_5)_2CH(SiMe_3)_2]$ was isolated (42%). Attempts to prepare $[V(\eta^5\text{-}C_5H_5)_2CHPh_2]$ from $[V(\eta^5\text{-}C_5H_5)_2Cl_2]$ and 2 mol of $LiCHPh_2$ resulted in almost quantitative yields of $[V(\eta\text{-}C_5H_5)_2]$ and $Ph_2CHCHPh_2$. The isolation of the dimer, tetraphenylethane, suggests that the benzhydryl radical is an intermediate. The latter has considerable thermodynamic stability and hence the free energy change for homolysis of the V^{III} alkyl is greater for R = Ph_2CH than R = $(Me_3Si)_2CH$.

By omitting the reduction step, using $[V(\eta^5\text{-}C_5H_5)_2Br]$ as a starting material, a higher yield (80%) of $[V(\eta^5\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}]$ was obtained, but reaction of vanadocene(III) monobromide and lithiodiphenylmethane once again afforded vanadocene and tetraphenylethane.

As shown above, the reaction of $LiCHPh_2$ or $LiCH(SiMe_3)_2$ with titanocene dichloride is similar, but with Zr or Hf analogous qualitative differences were noted.

Reaction of 2 mol of lithiodiphenylmethane with zirconocene or hafnocene dichloride gave the dialkyl product in high yield:

$$[M(\eta^5\text{-}C_5H_5)_2Cl_2] + 2LiCHPh_2 \rightarrow [M(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2] \quad (4)$$

$$[M = Zr \text{ or } Hf]$$

These highly colored complexes (orange/red for zirconium and orange for hafnium) were crystallized from benzene or toluene in ca. 70% yield.

Using the same stoichiometry and reaction conditions with $LiCH(SiMe_3)_2$ a different reaction was observed:

$$[M(\eta^5\text{-}C_5H_5)_2Cl_2] + 2LiCH(SiMe_3)_2 \rightarrow [M(\eta^5\text{-}C_5H_5)_2(Cl)\{CH(SiMe_3)_2\}] \quad (5)$$

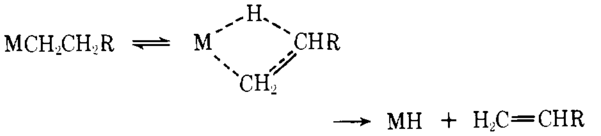
$$[M = Zr \text{ or } Hf]$$

Even after prolonged stirring and heating under reflux, only one chloride could be replaced, giving ca. 50% yield of the metallocene (chloro)alkyl. There was no evidence of any dialkyl product being formed.

The difference between the two ligands must be due to steric rather than electronic factors, because the remaining chloride ligand in the metallocene (chloro)alkyl may be displaced by a less bulky carbanion such as Bu-*n*⁻, but not by the more bulky Bu-*t*⁻ or $(Me_3Si)_2N^-$.

$$[Zr(\eta^5C_5H_5)_2(Cl)\{CH(SiMe_3)_2\}] + LiBu\text{-}n \rightarrow [Zr(\eta^5\text{-}C_5H_5)_2(Bu\text{-}n)\{CH(SiMe_3)_2\}] \quad (6)$$

The reluctance of $[Zr(\eta\text{-}C_5H_5)_2(Bu\text{-}n)\{CH(SiMe_3)_2\}]$ to undergo β-elimination may be a result of steric crowding. For a transition metal alkyl to decompose by β-elimination a vacant coordination site is required:



(7)

(A similar interpretation has been suggested for $[U(\eta\text{-}C_5H_5)_3R]$ [R = Me, Pr-*i*, Bu-*n*, Bu-*t*, Ph, C_3H_5, or Me_3CH_2] to explain the thermal behavior of the complexes.[40]) Further support for this rationalization comes from examination of the volatile thermolysis products at 150 °C; these are C_4H_{10} and H_2, but no butenes.

It is interesting that the zirconocene and hafnocene dialkyls or (chloro)alkyls are readily obtained, as in eq 4, whereas $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ yields the Ti^{III} alkyl, rather than the Ti^{IV}, analogues (with these bulky ligands). There are probably three contributory factors. Firstly, Ti–C bonds are much weaker than Zr–C which in turn are only marginally weaker than Hf–C.[39] Thus M–C homolysis is energetically preferred for Ti. Secondly, the oxidation state +3 is much better known for Ti than its heavier congeners, as reflected in the relative M^{4+} reduction potentials. Finally, the ionic radius of Ti^{4+} is significantly smaller than that of Zr^{4+} or Hf^{4+}, and hence more sensitive to steric effects in the ligand.

Attempts to prepare homoleptic alkyls from the reaction of LiR [R = Ph_2CH or $(Me_3Si)_2CH$] with $[MCl_4]$ (M = Ti, Zr, or Hf), $[VCl_3(NMe_3)_2]$, $[CrCl_3(THF)_3]$, $[MoBr_3(py)_3]$, $[MnCl_2]$, $[FeCl_3]$, or $[YCl_3]$ invariably gave an oil; from these

Table I. Physical Data on $[M(\eta^5\text{-}C_5H_5)_2R]$

Compd	Color	Yield, (%)	ESR g value[a]	Magnetic moment,[b] μ_B
$[Ti(\eta^5\text{-}C_5H_5)_2(CHPh_2)]$	Dark green	44	1.98	
$[Ti(\eta^5\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}]$	Khaki	63	1.96	1.4
$[V(\eta^5\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}]$	Dark green	42,[c] 80[d]	[e]	2.71

[a] C_6H_6 solution. [b] By ^1H NMR. [c] From $[V(\eta^5\text{-}C_5H_5)_2Cl_2]$. [d] From $[V(\eta^5\text{-}C_5H_5)_2Br]$. [e] Weak, broad lines, characteristic of many d^2 systems.[41]

crystals were obtained only for $[TiR_3]$, $[M(Cl)R_3]$ (M = Zr or Hf), $[VR_3]$, or $[CrR_3]$ $[R = CH(SiMe_3)_2]$.[5] Previous attempts to prepare $[Cr(CHPh_2)_3]$ were unsuccessful, but $[Cr(Cl)_2CHPh_2(THF)_2]$ was isolated.[26] Reaction of this with LiPh gave the trialkyl $[Cr(CHPh_2)Ph_2]$. Interestingly, the addition of 2,2′-bipyridine or 2 mol of LiPh to the latter resulted in cleavage of the benzhydryl ligand, with reduction of Cr^{III} to Cr^{II}, to give $[Cr(Ph)_2(bipy)_2]$ or $Li_2[Cr(Ph)_4(THF)_4]$, respectively. The facile cleavage of the M–C bond may account for the instability of the benzhydryl homoleptic alkyls.

Properties of the Metallocene Alkyls. The metallocene monoalkyls are dark-green crystalline solids. They are very air sensitive, decomposing to orange-yellow residues on exposure to air. Some data are shown in Table I.

The ESR spectra of these d^1 or d^2 paramagnetic compounds were run as benzene solutions. For the titanium complexes, a singlet was observed in both cases, with no splitting from the α hydrogen. The g values of 1.96 and 1.98 for the Ti^{III} complexes may be compared with 2.0 and 1.97 for $[Ti(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}C_3H_5)]$[27a] and $[Ti(\eta^5\text{-}C_5H_5)_2(CH_2Ph)]$,[41] respectively (both being unresolved singlets).

The magnetic moments were obtained using Evans' NMR method[42] and are close to the spin only values (Table I). They may be compared with 1.58 μ_B recorded for $[Ti(\eta^5\text{-}C_5H_5)_2Ph]$,[41] 2.63 μ_B for $[V(\eta^5\text{-}C_5H_5)_2(CH_2SiMe_3)]$, and 2.94 μ_B for $[V(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_3H_5)]$.[43]

The molecular weight of $[Ti(\eta^5\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}]$ was measured by cryoscopy in benzene. The complex was found to be monomeric in benzene, as is the case for related compounds.[17]

At −80 °C neither $[Ti(\eta^5\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}]$ nor $[Ti(\eta^5\text{-}C_5H_5)_2(CHPh_2)]$ reacted with dinitrogen. This is not surprising because such a reaction has previously only been observed for $[Ti(\eta^5\text{-}C_5H_5)_2Ar]$ (Ar = C_6H_5, C_6F_5, or Me_3CCH_2), but not the Me_3SiCH_2 analogue.[28,44]

The physical data for the zirconocene(IV) and hafnocene(IV) dialkyls and (chloro)alkyls are summarized in Table II. The compounds are slightly air sensitive in the solid state, but decompose rapidly when in solution. The benzhydryl complexes are highly colored, in contrast to the bis(trimethylsilyl)methyls. The intense color of the benzhydryl complexes is probably mainly due to electronic transitions involving the ligand, because the lithium starting material is deep red.

The ^1H NMR spectra of the benzhydryl complexes were run in deuteriobenzene. The observed spectrum was first order, showed sharp singlets for $\eta^5\text{-}C_5H_5$ and appropriate integration for these and the secondary alkyl proton. The phenyl groups were observed as multiplets due to coupling of the ortho, meta, and para hydrogens and integrated correctly for 20 protons. The ^1H NMR spectra of the metallocene (chloro)alkyls were run in methylene chloride and showed sharp singlets for $\eta^5\text{-}C_5H_5$, and appropriate integration. For these complexes the cyclopentadienyl peak was at lower field than for the dialkyl complexes. The large difference (ca. 1.3 τ) could be due to the chloro complexes having substantial ionic character, in the limit being $[Zr(\eta^5\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}]^+Cl^-$. In related compounds of Ti^{IV}, there is evidence for MCl ionicity.[45] However, contrary to this view the zirconocene (chloro)alkyl proved to be unreactive toward LiBu-*t*.

The infrared spectra were run as Nujol mulls. All complexes showed bands attributed to the cyclopentadienyl ring at 3100, 1020, and 830 cm^{-1}. The remainder of the spectrum consisted of bands due to the alkyl ligands: (a) for benzhydryl at 3020, 1590, 1240, 1170, 1090, 1030, 755, and 710 cm^{-1}; and (b) for bis(trimethylsilyl)methyl at 1257, 1250, 1247, 865, 772, 753, and 670 cm^{-1}. The following assignments are proposed: ν(Ti–C) [R = $(Me_3Si)_2CH$], 463 cm^{-1}; ν(Zr–C) (R = Ph_2CH), 458 and 442 cm^{-1}; ν(Hf–C) (R = Ph_2CH), 465 and 450 cm^{-1}; ν(Zr–C) [R = $(Me_3Si)_2CH$], 452 cm^{-1}; and ν(Zr–Cl) [R = $(Me_3Si)_2CH$], 348 cm^{-1}.

Solid-State Structures of $[M(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$ (M = Zr or Hf). An examination of the crystal data given in Table III allows the observation that $[Zr(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$ and its hafnium analogue are isostructural. This has also proved to be the case with $[M(\eta^5\text{-}C_5H_5)_2Cl_2]$,[49] $[M\{(\eta^5\text{-}C_5H_4)_2(CH_2)_3\}Cl_2]$,[34,35] and $[M(\eta^5\text{-}C_9H_7)Me_2]$[21] (M = Zr or Hf). The only appparently nonisostructural organometallic compounds are $[Zr(\eta^5\text{-}C_5H_5)_3(\eta^1\text{-}C_5H_5)]$[30] and $[Hf(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)_2]$.[31]

The molecular structures of $[M(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$ and the atom numbering schemes are shown in Figure 1, while the important bond distances and angles are listed in Table IV. One of the primary reasons for the structural study was the determination of the effect of the bulky benzhydryl ligands on the metal–carbon σ bond lengths. This is shown most dramatically for $[Zr(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$: the average[46] σ bond length of 2.388 (12) Å is much greater than the 2.251 (6) Å reported for the bond to the methyl carbon atom in $[Zr(\eta^5\text{-}C_9H_7)_2Me_2]$.[21] For the hafnium analogue the σ bond length, 2.36 (4) Å, does not differ significantly from the 2.332 (12) Å found in $[Hf(\eta^5\text{-}C_9H_7)_2Me_2]$.[21]

A comparison of the metal–carbon cyclopentadienyl lengths shows that the approach is closer for the hafnium [2.46 (5) Å] than for the zirconium case [2.513 (12) Å]. Although the large standard deviations associated with the hafnium structure render the difference[48] mathematically insignificant (Δ =

Table II. Physical Data on $[M(\eta^5\text{-}C_5H_5)_2R_2]$ and $[M(\eta^5\text{-}C_5H_5)_2(Cl)R]$

Compd	Color	Yield, %	Mp,[a] °C	^1H NMR chemical shifts, τ[b]			
				C_6H_5	C_5H_5	MCH	Me_3Si
$[Zr(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$	Orange-red	66	>130 dec	3.47 m	5.2 s	7.3 s	
$[Hf(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$	Orange	71	192–194	3.42 m	5.25 s	7.4 s	
$[Zr(\eta^5\text{-}C_5H_5)_2(Bu\text{-}n)\{CH(SiMe_3)_2\}]$[e]	Pale yellow	78	84–86		3.85 s	8.47 s	9.98 s
$[Zr(\eta^5\text{-}C_5H_5)_2(Cl)\{CH(SiMe_3)_2\}]$	Yellow	43	221–223		3.94 s[c]	7.53 s	9.65 s
					3.65 s[d]	7.48 s	9.85 s
$[Hf(\eta^5\text{-}C_5H_5)_2(Cl)\{CH(SiMe_3)_2\}]$	Pale yellow	37				8.3 s	9.6 s

[a] In sealed capillaries. [b] In C_6D_6 for benzhydryl or CH_2Cl_2 for $(Me_3Si)_2CH$ complexes. [c] In C_6D_6. [d] In CH_2Cl_2. [e] Bu-*n* occurs as a series of multiplets at τ 8.4–9.6.

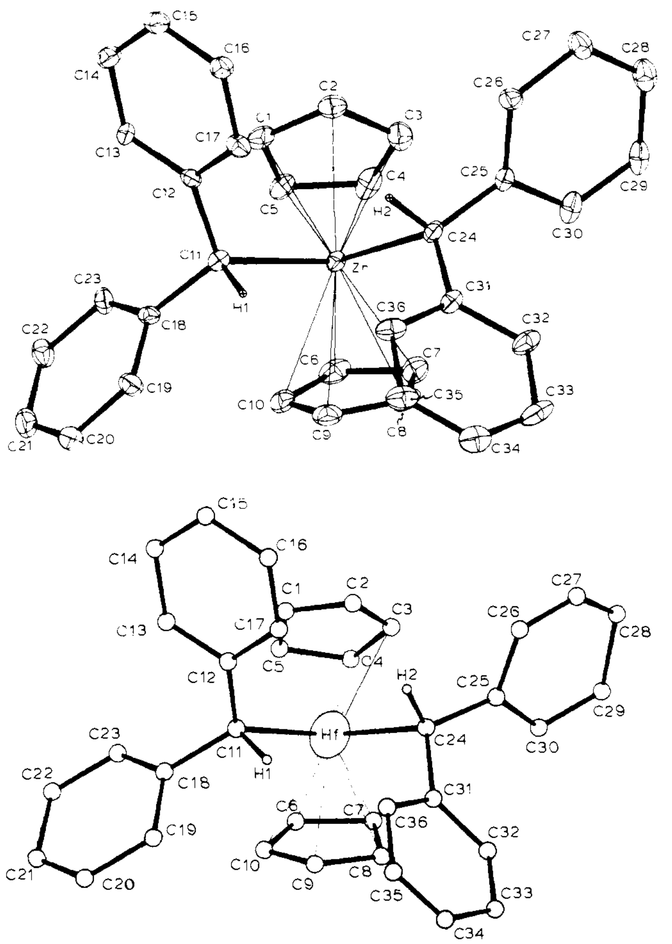


Figure 1. (top) Molecular structure of bis(η^5-cyclopentadienyl)bis(benzhydryl)zirconium(IV) with the atoms displayed as their 40% probability ellipsoids for thermal motion. (bottom) Molecular structure of bis(η^5-cyclopentadienyl)bis(benzhydryl)hafnium(IV) with the atoms displayed as spheres.

Table III. Crystal Data

Compd		[Zr(η^5-C_5H_5)$_2$-($CHPh_2$)$_2$]	[Hf(η^5-C_5H_5)$_2$-($CHPh_2$)$_2$]
Mol wt		555.9	643.2
Linear abs coeff μ		4.15 cm^{-1}	39.61 cm^{-1}
Calcd density		1.33 g cm^{-3}	1.53 g cm^{-3}
Max crystal dimensions		0.08 × 0.12 × 0.24 mm	0.18 × 0.25 × 0.32 mm
Space group		$P2_1/n$	$P2_1/n$
Molecules/unit cell		4	4
Cell constants,[a]	a	12.658 (7) Å	12.660 (9) Å
	b	17.202 (7) Å	17.130 (9) Å
	c	12.807 (7) Å	12.910 (9) Å
	β	92.45 (5)°	92.39 (5)°
Cell vol		2786.0 Å^3	2797.2 Å^3

[a] Mo Kα radiation, λ 0.71069 Å. Ambient temperature of 23 °C.

Table IV. Comparison of Structural Parameters for Bis(η^5-cyclopentadienyl)bis(benzhydryl)zirconium(IV) and Its Hafnium Analogue

Bond	Zirconium	Hafnium
	Bond Length, Å	
M-C11	2.379 (6)	2.33 (3)
M-C24	2.396 (6)	2.38 (3)
M-C1	2.523 (7)	2.40 (3)
M-C2	2.498 (7)	2.45 (3)
M-C3	2.494 (7)	2.44 (4)
M-C4	2.503 (7)	2.43 (3)
M-C5	2.511 (8)	2.50 (4)
M-C6	2.539 (8)	2.43 (4)
M-C7	2.537 (8)	2.48 (4)
M-C8	2.503 (8)	2.54 (4)
M-C9	2.492 (8)	2.44 (4)
M-C10	2.528 (7)	2.44 (3)
M-C (cyclopentadienyl average)	2.513 (15)	2.46 (5)
	Bond Angle, deg	
C11-M-C24	95.5 (4)	95.4 (9)
Cent1[a]-M-C11	106.3	106.4
Cent1-M-C24	107.2	108.9
Cent2-M-C11	107.8	107.4
Cent2-M-C24	106.2	105.6
Cent1-M-Cent2	128.2	128.2

[a] Cent1 is defined as the centroid of the cyclopentadienyl ring with C1 → C5; Cent2 is the centroid of the ring with C6 → C10.

1.0σ), it does fit the general pattern established for other such structures (Table V).[34,35] It thus appears that, in the absence of large steric effects, the metal-carbon σ bond length is shorter for zirconium, while the π bond distance is shorter for hafnium. For the title compounds, the size of the benzhydryl ligand greatly affects the Zr-C (σ) length, but has little or no effect on the structural parameters of the hafnium-containing molecule.

As is shown in Tables IV and V, all angles involving the centroids of the cyclopentadienyl rings are close to the values given for related compounds.[25,34,45,49,50]

The least-squares plane calculations show that the cyclopentadienyl rings are planar to within 0.02 Å in the zirconium structure,[51] and the phenyl rings exhibit a maximum deviation of 0.03 Å. The C-C(cyclopentadienyl) bond lengths range from 1.357 (13) to 1.423 (14) Å, and average 1.386 (19) Å. Even though a value of 1.43 Å[52,53] is to be expected for a thermally rigid system, 1.39 Å is common for compounds[54,55] in which a large degree of librational motion is found. The 1.504 (10) Å C(sp^3)-C(sp^2) length in the benzhydryl ligands is normal,[56] as is the 1.383 (16) Å average for the C-C (phenyl) lengths.[25]

The unit cell packing, shown in Figure 2, is typical of a molecular compound of this type.

Experimental Section

Materials. [M(η^5-C_5H_5)$_2$$Cl_2$](M = Ti, Zr, Hf, or V) were purchased from Aldrich. [V(η^5-C_5H_5)$_2$Br], prepared by the equimolar reaction of [V(η^5-C_5H_5)$_2$] and [V(η^5-C_5H_5)$_2$$Br_2$],[57] was purified by sublimation and stored in glass ampules prior to use. $LiCHPh_2$ was prepared, as a standard solution, by reaction of Ph_2CHCl (Emanuel) with lithium wire (1% Na) (Fisons)[36] and $LiCH(SiMe_3)_2$ by reaction of $(Me_3Si)_2CHCl$[37] with lithium powder (99%). LiBu-n and LiBu-t were obtained as standard solutions (ca. 2.0 M in hexane) from Cortourch Chemicals and Alfa, respectively.

Physical and Analytical Measurements. Elemental analyses were performed by the microanalytical laboratory at the University of Sussex and by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany.

Infrared spectra were obtained from Nujol mulls between CsI plates using a Perkin-Elmer 457 spectrometer.

^1H NMR spectra were obtained from a Varian T60 or A60 spectrometer. Benzene-d_6 and methylene chloride were used as the NMR solvents with Me_4Si as the reference.

ESR spectra were recorded on a Varian E-3 spectrometer as benzene solutions.

Molecular weight determinations were made under an argon atmosphere in an all-glass cryoscopic apparatus.

General Procedures. Owing to the air sensitivity of the complexes all preparations and other operations were carried out under a dry and oxygen-free argon atmosphere or in vacuo, using standard Schlenk techniques. Solvents were dried and distilled over K (for benzene and

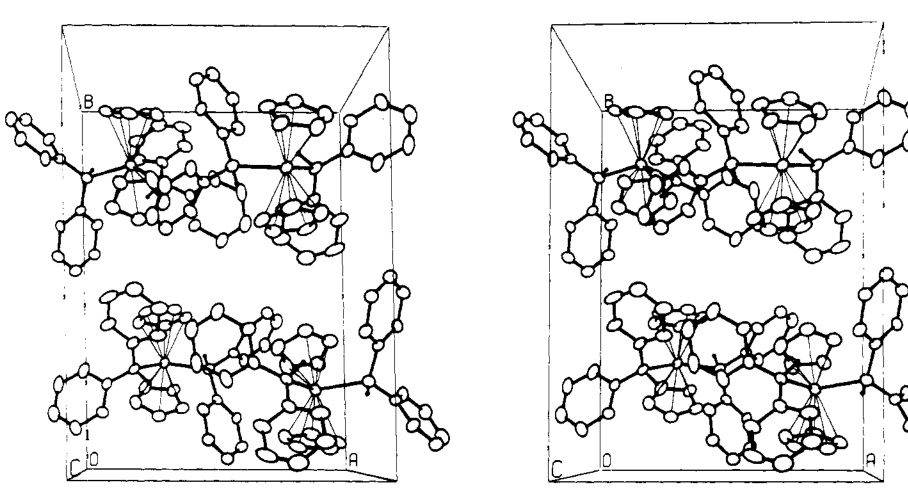


Figure 2. Stereoscopic view of the crystal packing of four molecules of $[Zr(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$.

Table V. Summary of Structural Parameters Related to the Metal-Cyclopentadienyl Ring Interaction for $[M(\eta^5\text{-}C_5H_5)_2X_2]$

Compd	M-C av, Å	M-centroid, Å	Centroid-M-centroid, deg	X-M-X, deg	Ref
$[Zr\{(\eta^5\text{-}C_5H_4)_2(CH_2)_3\}Cl_2]$	2.494 (4)	2.193	129.5	96.92 (7)	34
$[Hf\{(\eta^5\text{-}C_5H_4)_2(CH_2)_3\}Cl_2]$	2.482 (4)	2.176	129.5	95.87 (8)	35
$[Zr(\eta^5\text{-}C_9H_7)_2Me_2]$	2.548	2.23	120.8	96.9 (3)	21
$[Hf(\eta^5\text{-}C_9H_7)_2Me_2]$	2.527	2.22	121.0	96.0 (6)	21
$[Zr(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$	2.513 (15)	2.22	128.4	95.5 (4)	
$[Hf(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$	2.46 (5)	2.16	128.2	95.4 (9)	
$[Zr(\eta^5\text{-}C_5H_5)_2F_2]$	2.50 (1)		127.8	96.2 (3)	50
$[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$	2.522 (5)	2.20	134	104. (2)	49
$[Zr(\eta^5\text{-}C_5H_5)_2I_2]$	2.48 (2)		126.3	96.2 (1)	50
$[Hf(\eta^5\text{-}C_5H_5)_2(C_4Ph_4)]$	2.49 (3)	2.20	134	78.7 (8)	25

toluene), sodium/benzophenone (for ether and THF), P_2O_5 (for CH_2Cl_2), sodium (for hexane), and CaH_2 (for pentane) under a nitrogen atmosphere prior to use.

Attempted Preparation of LiCHBu-t_2 and Mg(CHBu-t_2)$_2$. Bu-t_2CHCl was prepared in 22% yield from Bu-t_2CHOH.[58] Reaction of Bu-t_2CHOH with phosgene gave Bu-t_2CHOCOCl which was thermally decomposed at ca. 120 °C to give a mixture of Bu-t(Me)-C=CMe$_2$ and Bu-t_2CHCl. The chloride was isolated by fractional distillation, 37-39 °C (5 mmHg).

(a) Bu-t_2CHCl + Li. To a solution of Bu-t_2CHCl (1.2 g, 7.2 mmol) in ether (50 mL) was added Li powder (0.4 g excess) and the mixture was refluxed for 3 days. At 1 day intervals a sample of the reaction mixture was hydrolyzed and a GLC run. The GLC trace showed that no reaction had taken place (only a peak corresponding to Bu-t_2CHCl was observed). Prolonged refluxing, over a period of weeks, resulted in slow decomposition of the chloride to Bu-t(Me)C=CMe$_2$.

(b) Bu-t_2CHCl + Mg. To a solution of Bu-t_2CHCl (1.5 g, 9.1 mmol) in ether (50 mL) was added Mg turnings (0.36 g excess) and the mixture was refluxed for 2 days. A GLC trace of a hydrolyzed sample of the reaction mixture showed that no appreciable reaction had taken place. The ether was distilled off and THF (50 mL) added. After refluxing for a further 2 days a GLC trace showed that no reaction had occurred except partial decomposition to Bu-t(Me)C=CMe$_2$.

Preparation of Bis(η^5-cyclopentadienyl)benzhydryltitanium(III) [Ti(η^5-C$_5$H$_5$)$_2$(CHPh$_2$)]. Lithiodiphenylmethane (8.6 mmol) in THF (10 mL) was added over 1 h to a suspension of titanocene dichloride (1.03 g, 4.1 mmol) in benzene (20 mL) at room temperature. The mixture was stirred for 3 days during which time the solution turned from red to dark green. Volatiles were removed and the green residue extracted with toluene (50 mL) and filtered. The filtrate was concentrated and hexane floated on the surface. Cooling to −30 °C afforded dark-green crystals of bis(η^5-cyclopentadienyl)benzhydryltitanium(III) (0.62 g, 44%). Anal. Calcd for $C_{23}H_{21}Ti$: C, 80.0; H, 6.1. Found: C, 79.4; H, 5.9.

Preparation of Bis(η^5-cyclopentadienyl)bis(trimethylsilyl)methyltitanium(III) [Ti(η^5-C$_5$H$_5$)$_2$\{CH(SiMe$_3$)$_2$\}]. Lithiobis(trimethylsilyl)methane (4.9 mmol) in ether (5 mL) was added dropwise to a suspension of titanocene dichloride (0.61 g, 2.45 mmol) in ether (60 mL) at −30 °C. The mixture was allowed to warm up to room temperature over 3 h and then volatiles were removed in vacuo. The green-brown residue was extracted with hexane (50 mL) and filtered. The filtrate was concentrated and cooled to −30 °C affording dark-green crystals of bis(η^5-cyclopentadienyl)bis(trimethylsilyl)methyltitanium(III) (0.52 g, 63%). Anal. Calcd for $C_{17}H_{29}Si_2Ti$: C, 60.5; H, 8.4; Si, 14.1; Ti, 16.9. Found: C, 60.2; H, 8.7; Si, 14.2; Ti, 16.7.

Preparation of Bis(η^5-cyclopentadienyl)bis(trimethylsilyl)methylvanadium(III) [V(η^5-C$_5$H$_5$)$_2$\{CH(SiMe$_3$)$_2$\}]. (a) From Vanadocene Dichloride. Lithiobis(trimethylsilyl)methane (4.0 mmol) in ether (10 mL) was added dropwise to a suspension of vanadocene dichloride (0.51 g, 2.0 mmol) in ether (30 mL) at −50 °C. The solution changed from green to black and was allowed to warm slowly to room temperature. After stirring for 1 h volatiles were removed in vacuo and the residue extracted with hexane (30 mL) and filtered. Concentration of the filtrate and cooling to −30 °C gave very dark-green crystals of bis(η^5-cyclopentadienyl)bis(trimethylsilyl)methylvanadium(III) (0.29 g, 42%). Anal. Calcd for $C_{17}H_{29}Si_2V$: C, 60.0; H, 8.0; Si, 16.5; V, 15.0. Found: C, 59.7; H, 8.4; Si, 16.4; V, 15.3.

(b) From Vanadocene Monobromide. Lithiobis(trimethylsilyl)methane (2.1 mmol) in ether (10 mL) was added slowly to a suspension of vanadocene monobromide (0.53 g, 2.03 mmol) in ether (20 mL) at −30 °C. The mixture was stirred for 4 h and was allowed to warm up slowly to room temperature. Volatiles were removed, the dark-green residue was extracted with pentane (30 mL), and the solution, was filtered. Concentration of the filtrate and cooling to −30 °C gave dark-green crystals of bis(η^5-cyclopentadienyl)bis(trimethylsilyl)methylvanadium(III) (0.54 g, 80%). Characterization of the complex was performed on the basis of its IR spectrum, which was found to be identical with that for the fully analyzed complex prepared by method (a).

Attempted Preparation of Bis(η^5-cyclopentadienyl)benzhydrylvanadium(III) [V(η^5-C$_5$H$_5$)$_2$(CHPh$_2$)]. (a) From Vanadocene Dichloride. To a slurry of vanadocene dichloride (0.49 g, 1.9 mmol) in ether (20 mL) was added dropwise lithiodiphenylmethane (3.8 mmol) in THF (4 mL) at −40 °C. The mixture was stirred at the low temperature for 1 h and was then allowed to warm up slowly, stirring overnight. The purple solution was filtered, concentrated, and cooled to −30 °C, depositing dark-purple crystals. These crystals were shown to be vanadocene from the IR spectrum. The solid residue and remaining

Table VI. Other Bond Lengths and Angles for $[M(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$

Bond	Zirconium	Hafnium
	Bond Lengths, Å	
C1-C2	1.394 (12)	1.39 (4)
C2-C3	1.374 (11)	1.49 (4)
C3-C4	1.384 (12)	1.43 (4)
C4-C5	1.394 (13)	1.37 (4)
C5-C1	1.404 (12)	1.31 (4)
C6-C7	1.371 (13)	1.23 (5)
C7-C8	1.357 (13)	/42 (5)
C8-C9	1.423 (14)	1.40 (4)
C9-C10	1.394 (11)	1.33 (4)
C10-C6	1.360 (14)	1.29 (4)
C11-C12	1.492 (9)	1.55 (4)
C11-C18	1.500 (9)	1.46 (4)
C24-C25	1.507 (8)	1.59 (4)
C24-C31	1.519 (9)	1.49(4)
C12-C13	1.393 (10)	1.39 (4)
C13-C14	1.398 (12)	1.39 (5)
C14-C15	1.384 (12)	1.44 (6)
C15-C16	1.367 (12)	1.33 (5)
C16-C17	1.414 (12)	1.46 (4)
C17-C12	1.391 (10)	1.38 (5)
C18-C19	1.388 (10)	1.42 (5)
C19-C20	1.380 (11)	1.41 (5)
C20-C21	1.346 (13)	1.42 (6)
C21-C22	1.352 (15)	1.37 (6)
C22-C23	1.397 (12)	1.42 (6)
C23-C18	1.387 (10)	1.36 (4)
C25-C26	1.408 (9)	1.38 (4)
C26-C27	1.392 (10)	1.41 (4)
C27-C28	1.371 (11)	1.32 (5)
C28-C29	1.382 (11)	1.41 (5)
C29-C30	1.377 (10)	1.34 (4)
C30-C25	1.388 (9)	1.41 (4)
C31-C32	1.388 (9)	1.47 (4)
C32-C33	1.368 (12)	1.38 (5)
C33-C34	1.373 (14)	1.55 (6)
C34-C35	1.358 (10)	1.31 (6)
C35-C36	1.388 (10)	1.26 (5)
C36-C31	1.395 (10)	1.39 (4)
	Bond Angle, deg	
C1-C2-C3	110.2 (8)	111 (3)
C2-C3-C4	107.3 (8)	98 (3)
C3-C4-C5	108.3 (7)	113 (3)
C4-C5-C1	108.4 (8)	110 (3)
C5-C1-C2	105.8 (7)	107 (3)
C6-C7-C8	111.1 (9)	113 (4)
C7-C8-C9	106.6 (8)	100 (3)
C8-C9-C10	105.7 (8)	107 (3)
C9-C10-C6	110.1 (8)	112 (4)
C10-C6-C7	106.4 (8)	108 (4)
M-C11-C12	119.0 (4)	121 (2)
M-C11-C18	115.8 (5)	119 (2)
C12-C11-C18	114.6 (6)	113 (3)
M-C24-C25	117.4 (4)	114 (2)
M-C24-C31	115.7 (4)	117 (2)
C25-C24-C31	114.3 (5)	114 (2)
C12-C13-C14	122.0 (8)	118 (3)
C13-C14-C15	120.1 (8)	123 (4)
C14-C15-C16	120.1 (8)	118 (4)
C15-C16-C17	118.9 (8)	120 (4)
C16-C17-C12	123.0 (8)	121 (3)
C17-C12-C13	115.9 (7)	119 (3)
C18-C19-C20	122.9 (8)	122 (4)
C19-C20-C21	120.8 (9)	121 (4)
C20-C21-C22	118.6 (8)	118 (4)
C21-C22-C23	121.3 (9)	119 (4)
C22-C23-C18	121.3 (9)	125 (4)
C23-C18-C19	114.9 (7)	115 (3)
C25-C26-C27	121.5 (7)	118 (3)
C26-C27-C28	120.5 (7)	123 (3)
C27-C28-C29	118.2 (7)	119 (4)
C28-C29-C30	122.0 (7)	118 (4)
C29-C30-C25	121.1 (7)	124 (3)
C30-C25-C26	116.6 (6)	117 (2)
C31-C32-C33	121.3 (8)	118 (3)
C32-C33-C34	120.1 (8)	118 (3)
C33-C34-C35	119.3 (8)	115 (3)
C34-C35-C36	121.3 (8)	125 (5)
C35-C36-C31	120.0 (8)	125 (4)
C36-C31-C32	117.2 (7)	116 (3)
C11-C12-C13	123.1 (6)	120 (4)
C11-C12-C17	121.0 (6)	120 (3)
C11-C18-C19	121.1 (6)	128 (3)
C11-C18-C23	124.1 (7)	118 (4)
C24-C25-C26	118.6 (6)	118 (3)
C24-C25-C30	124.8 (6)	124 (3)
C24-C31-C32	123.8 (6)	124 (3)
C24-C31-C36	118.9 (6)	119 (3)

solution were slurried in benzene (50 mL) and boiled with charcoal. The mixture was filtered, concentrated, and cooled to ca. 0 °C. White needles were deposited and were shown to be tetraphenylethane from the IR spectrum and melting point determination (mp 210 °C).

(b) **From Vanadocene Monobromide.** The same procedures were adopted as in method (a) using vanadocene monobromide (0.95 g, 3.64 mmol) and lithiodiphenylmethane (3.7 mmol).

Only vanadocene and tetraphenylethane were isolated from the reaction mixture.

Preparation of Bis(η^5-cyclopentadienyl)bis(benzhydryl)zirconium(IV) $[Zr(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$. Lithiodiphenylmethane (8.8 mmol) in THF (10 mL) was added, over 1 h, to a suspension of zirconocene dichloride (1.27 g, 4.36 mmol) in benzene (20 mL) at room temperature. The mixture was stirred for 20 h and then volatiles were removed under vacuum. The orange-red residue was extracted with benzene and filtered. The benzene was removed and the oily solid recrystallized from ether/CH_2Cl_2 at −30 °C, affording orange-red crystals of bis(η^5-cyclopentadienyl)bis(benzhydryl)zirconium(IV) (1.6 g, 66%). Anal. Calcd for $C_{36}H_{32}Zr$: C, 77.8; H, 5.8. Found: C, 77.5; H, 5.7.

Preparation of Bis(η^5-cyclopentadienyl)bis(benzhydryl)hafnium(IV) $[Hf(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$. The preparation of $[Hf(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$ was identical with that of the zirconium analogue, using hafnocene dichloride (1.02 g, 2.7 mmol) and lithiodiphenylmethane (5.6 mmol). Recrystallization from ether/CH_2Cl_2 gave bis(η^5-cyclopentadienyl)bis(benzhydryl)hafnium(IV) (1.23 g, 71%). Anal. Calcd for $C_{36}H_{32}Hf$: C, 67.2; H, 5.0. Found: C, 66.7; H, 5.1.

Preparation of Chlorobis(η^5-cyclopentadienyl)bis(trimethylsilyl)methylzirconium(IV) $[Zr(\eta^5\text{-}C_5H_5)_2(Cl)\{CH(SiMe_3)_2\}]$. Lithiobis(trimethylsilyl)methane (5.3 mmol) in ether)20 mL) was added slowly over 1 h to zirconocene dichloride (1.55 g, 5.3 mmol) in ether (30 mL) at room temperature. The mixture was stirred for a further 1 h and then the volatiles were removed in vacuo. The yellow residue was extracted with toluene and filtered. Concentration of the filtrate and cooling to −30 °C gave yellow, air-stable crystals of chlorobis(η^5-cyclopentadienyl)bis(trimethylsilyl)methylzirconium(IV) (0.95 g, 43%). Anal. Calcd for $C_{17}H_{29}ClZr$: C, 49.0; H, 7.0; Cl, 8.5. Found: C, 49.1; H, 6.9; Cl, 8.7.

Preparation of Chlorobis(η^5-cyclopentadienyl)bis(trimethylsilyl)methylhafnium(IV) $[Hf(\eta^5\text{-}C_5H_5)_2(Cl)\{CH(SiMe_3)_2\}]$. The preparation of $[Hf(\eta^5\text{-}C_5H_5)_2(Cl)\{CH(SiMe_3)_2\}]$ was identical with that of $[Zr(\eta^5\text{-}C_5H_5)_2(Cl)\{CH(SiMe_3)_2\}]$ using hafnocene dichloride (0.77 g, 2.0 mmol) and lithiobis(trimethylsilyl)methane (2.04 mmol). Recrystallization from toluene gave pale-yellow crystals of chlorobis(η^5-cyclopentadienyl)bis(trimethylsilyl)methylhafnium(IV) (0.4 g, 37%). Anal. Calcd for $C_{17}H_{29}ClHf$: C, 40.5; H, 5.8. Found: C, 39.9; H, 5.7.

Attempted Reaction of LiBu-*t* or $LiN(SiMe_3)_2$ with $[Zr(\eta^5\text{-}C_5H_5)_2(Cl)\{CH(SiMe_3)_2\}]$. To a solution of $[Zr(\eta^5\text{-}C_5H_5)_2(Cl)\{CH(SiMe_3)_2\}]$ (1.13 g, 2.72 mmol) in pentane (30 mL) at −20 °C was added LiBu-*t* (3 mmol) or $LiN(SiMe_3)_2$ (3 mmol) in ether (10 mL). The mixture was stirred at the low temperature for 0.5 h and was then allowed to warm up slowly. Stirring was continued for 3 days with no visible signs of change. Volatiles were removed in vacuo and the residue was extracted with toluene (30 mL). Filtration, concentration, and cooling to −30 °C gave the unchanged starting material $[Zr(\eta^5\text{-}C_5H_5)_2(Cl)\{CH(SiMe_3)_2\}]$ in ca. 80% yield.

Preparation of *n*-Butylbis(η^5-cyclopentadienyl)bis(trimethylsilyl)methylzirconium(IV) $[Zr(\eta^5\text{-}C_5H_5)_2(Bu\text{-}n\{CH(SiMe_3)_2\}]$. To a solution of $[Zr(\eta^5\text{-}C_5H_5)_2(Cl)\{CH(SiMe_3)_2\}]$(3.5 g, 8.4 mmol) in ether (50 mL) was added LiBu-*n* (12 mmol) in ether (25 mL) at −20 °C. The mixture was stirred overnight at room temperature and then volatiles were removed. The residue was extracted with hexane, filtered, and concentrated. Cooling to −30 °C gave yellow crystals of *n*-butylbis(η^5-cyclopentadienyl)bis(trimethylsilyl)methylzirconium(IV) (2.9 g, 78%). Anal. Calcd for $C_{21}H_{39}SiZr$: C, 57.6; H, 8.8. Found: C, 57.1; H, 8.7.

X-Ray Data Collection and Structure Determination for $[Hf(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$. Single crystals of the air-sensitive compound were sealed in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of the angular settings for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table VI. The space group was uniquely determined to be $P2_1/n$, an alternate setting of $P2_1/c[C_{2h}{}^5$, No. 14], from the systematic absences in $0k0$ for $k = 2n + 1$ and in $h0l$ for $h + l = 2n + 1$.

Details of the data collection procedure, using an Enraf-Nonius CAD-4 diffractometer with graphite crystal monochromated molybdenum radiation, are included in the supplementary material.

The existence of four molecules per unit cell in the space group $P2_1/n$ imposed no crystallographic symmetry on the molecule. The position of the hafnium atom was revealed by the inspection of a Patterson map, and a difference Fourier map phased on the hafnium atom readily afforded the positions of all 36 carbon atoms. Isotropic refinement led to a discrepancy factor of $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.13$. Anisotropic refinement of the hafnium atom gave $R_1 = 0.11$. The hydrogen atoms were then placed at calculated positions 0.98 Å from the bonded carbon atoms, and the carbon atoms were refined anisotropically. The R factor was lowered to 0.091, but the thermal parameters of some of the cyclopentadienyl carbon atoms were not positive definite. The treatment of the cyclopentadienyl carbon atoms in an isotropic fashion led to $R_1 = 0.094$ and $[\Sigma(|F_o| - |F_c|)^2/\Sigma(F_o)^2]^{1/2} = 0.099$. The refinement difficulties and the relatively high R factor were probably due to either a scaling difficulty or an absorption problem (or both). The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference Fourier showed no feature greater than 0.8 e/Å^3. The standard deviation of an observation of unit weight was 1.00. Unit weights were employed at all stages of refinement. No systematic variation of $w(|F_o| - |F_c|)$ vs. F_o or $(\sin\theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Table VIII.

X-Ray Data Collection and Structure Refinement for $[Zr(\eta^5\text{-}C_5H_5)_2(CHPh_2)_2]$. Following the data collection procedures given above, 2989 unique reflections in the range $2\theta < 50°$ were obtained. No absorption correction was applied because of the low linear absorption coefficient ($\mu = 4.15\ cm^{-1}$) and the rather cylindrical shape of the crystal.

Isotropic refinement of all nonhydrogen atoms, using at first the positions from the hafnium analogue, gave $R_1 = 0.097$. Inclusion of the hydrogen atoms at calculated positions 1.00 Å from the bonded carbon atoms, and anisotropic refinement of the nonhydrogen atoms, resulted in final R values of $R_1 = 0.064$ and $R_2 = 0.062$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference Fourier map showed no feature greater than 0.4 e/Å^3. The standard deviation of an observation of unit weight was 0.87.

The final values of the positional and thermal parameters for the two compounds are given in Tables VII and VIII and the least-squares planes are in Tables IX and X.

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Supplementary Material Available: Tables VII and VIII (final values of the positional and thermal parameters), and IX and X (least squares planes); structure factor amplitudes; details of the data collection procedure (33 pages). Ordering information is given on any current masthead page.

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Geometry of Cycloheptane Conformers. Crystal Structure of 1-Dimethylphosphono-1-hydroxycycloheptane[1]

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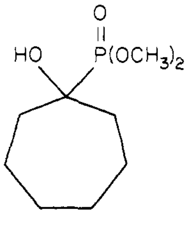
Abstract: In order to establish the conformation of 1-dimethylphosphono-1-hydroxycycloheptane (**1**) in the solid state we carried out an x-ray analysis. Crystals of **1** belong to the triclinic space group $P\bar{1}$ with cell dimensions a = 8.443, b = 11.346, c = 6.785 Å; α = 101.30, β = 111.21, γ = 98.41°. Intensity data were measured on a diffractometer with Mo radiation. The structure was solved by direct methods and refined by block-diagonal least squares. The final agreement index R is 0.045 for 2351 reflections. A difference Fourier map revealed that two atoms in the cycloheptane ring, C(6) and C(7), are disordered, each of them occupying two distinct positions. Consequently, both the twist-chair and the chair conformers occur in the crystal structure; their relative abundance, as determined by a refinement of occupancy factors, is 0.93 and 0.07. In the twist-chair the two substituents occupy isoclinal positions at C(1), while in the chair conformer the dimethylphosphonate group is equatorially oriented. Bond angles and torsion angles in the twist-chair conformer agree very well with those calculated with Allinger's force field. The chair form agrees best with the model obtained from Boyd's field. The ratio of the two conformers corresponds to ΔE = 1.5 kcal/mol. From this one can calculate that moving a hydroxyl group from an isoclinal to an axial position at C(1) raises the energy by 0.5 kcal/mol.

Recent efforts in one of these laboratories have been directed toward a clarification of geometries of medium-ring compounds, using ^{13}C NMR spectroscopy.[3,4] In the course of examining a series of cyclic hydroxyphosphono compounds, it became apparent that x-ray data for the cycloheptane derivative would be desirable in view of apparent anomalies between the expected geometry and the observed ^{13}C-C-C-^{31}P coupling constants. Experimental information about the conformation of cycloheptane rings is rather limited.[5] Many crystal structures have been determined in which seven-membered rings are fused to others[6] and such results have been used to discuss the conformation of these rings.[7,8] However, when we started this study we were aware of only one published x-ray analysis of a compound containing an isolated cycloheptane ring.[9a] For various reasons, including extensive disorder and the presence of a bromine atom, the precision of that structure analysis was rather low. Consequently, it appeared worthwhile to determine the crystal structure of 1-dimethylphosphono-1-hydroxycycloheptane (**1**). Very recently, after our work was completed, the structure of calcium cycloheptane carboxylate pentahydrate was published.[9b] Owing to pseudorotation all ring atoms were found to be disordered and it was not possible to obtain precise results.



1

Experimental Section

Colorless crystals of **1** were obtained from ethyl acetate (mp 106.0-107.5 °C). Precession photographs indicated triclinic symmetry; in the absence of chiral centers the space group was expected, and later confirmed, to be $P\bar{1}$. A crystal fragment measuring 0.5 × 0.5 × 0.5 mm was mounted along the a^* axis on a card-controlled Picker four-circle diffractometer. Cell dimensions were determined from angular settings of 15 high-angle reflections and both Cu Kα_1 (λ 1.54051 Å) and Cu Kα_2 (λ 1.54433 Å) radiations were used. The following crystal data were obtained: a = 8.443 (1), b = 11.346 (1), c = 6.785 (1) Å; α = 101.30 (2), β = 111.21 (2), γ = 98.41 (2)°; V = 577.2 Å^3; D_x = 1.28 g cm^{-3}; Z = 2; $F(000)$ = 240; μ(Mo Kα) = 2.20 cm^{-1}.