

The Synthesis of Organometallic Ylides

Interaction of Methylenetriphenylphosphorane with Bis(η^5 -cyclopentadienyl)-zirconium and -hafnium Dichlorides and the Molecular Structure of Bis(η^5 -Cyclopentadienyl)chlorozirconylmethylenetriphenylphosphorane

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Dedicated to Prof. Dr. h. c. H. Behrens on his 65th birthday

The interaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{MCl}_2$ ($\text{M} = \text{Zr}, \text{Hf}$) with excess $\text{CH}_2=\text{P}^+\text{Ph}_3$ in THF gives $(\eta^5\text{-C}_5\text{H}_5)_2\text{MCl}(\text{CH}=\text{P}^+\text{Ph}_3)$ as yellow orange needles. Nuclear magnetic resonance spectra show hindered rotation about the P^+-C bond with $\Delta G^\ddagger = 8.6$ kcal/mole for $\text{M} = \text{Zr}$ and 8.3 kcal/mole for $\text{M} = \text{Hf}$, respectively. The X-ray molecular structure of the zirconium complex shows a relatively short Zr–C bond length of 2.152 Å and a long P^+-C bond length of 1.716 Å.

Introduction

Organometallic complexes of the Group IV B transition metals have recently become important in a variety of significant chemical processes. For example, bis(η^5 -cyclopentadienyl)zirconium hydride-chloride is a versatile reagent for functionalization of alkenes, dienes, and alkynes [1]. Other complexes of zirconium serve as model compounds for the reduction of carbon monoxide [2], and titanium organometallic complexes play an important role in the Ziegler-Natta polymerization of alkenes [3].

Ylides are useful reagents which typically exchange carbonyl groups for olefinic units, because the ylidic bond can be readily cleaved. If ylides such as $\text{CH}_2=\text{P}^+\text{Ph}_3$ could be substituted with transition metal atoms, then cleavage of the carbon-metal and carbon-phosphorus bond could be accomplished with selected reagents.

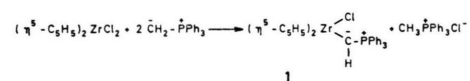
This paper describes the synthesis and X-ray structure of an ylide with a transition metal atom in place of the ylide hydrogen atom.

Results

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{MCl}(\text{CH}=\text{P}^+\text{Ph}_3)$
 $\text{M} = \text{Zr}, \text{Hf}$

When a colorless solution of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ is treated with four equivalents of $\text{CH}_2=\text{P}^+\text{Ph}_3$ in tetra-

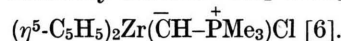
hydrofuran (THF), first at 0 °C for 3 days, then at ambient temperature for 7 days, one equivalent of $\text{CH}_3\text{PPh}_3^+\text{Cl}^-$ slowly forms as a white solid and a red solution is obtained after filtration. The white solid is identified by IR, ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy as $\text{CH}_3\text{PPh}_3^+\text{Cl}^-$ [4], and the crystallized product (THF/pentane) is a very air sensitive yellow-orange zirconium complex,



The reaction stoichiometry requires only two equivalents of $\text{CH}_2=\text{P}^+\text{Ph}_3$ per equivalent of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$; however, treatment of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ with only two equivalents of $\text{CH}_2=\text{P}^+\text{Ph}_3$ gives lower and less pure yields of **1**, even though one equivalent of $\text{CH}_3\text{P}^+\text{Ph}_3\text{Cl}^-$ is eventually produced. If $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ is treated with $\text{Ph}_3\text{P}^+-\text{CH}_2$ in benzene at 40 °C, the mixture becomes deep red and very low yields of **1** are obtained. A $^{31}\text{P}\{^1\text{H}\}$ analysis of the reaction mixture shows the presence of free triphenylphosphine and as yet unidentified zirconium species.

When one equivalent of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrCl}_2$ [5] in THF is treated with two equivalents of $\text{Ph}_3\text{P}^+-\text{CH}_2$ for 5 days at 20 °C and 9 days at reflux, only 21% $\text{CH}_3\text{P}^+\text{Ph}_3\text{Cl}^-$ can be isolated. However, no new compounds could be detected in the filtrate excep-

recovered $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrCl}_2$. The sluggish reaction is apparently almost stopped by the bulky pentamethylcyclopentadienyl ligands, although the less sterically hindered $\text{CH}_2\text{-P}^+\text{Me}_3$ does give

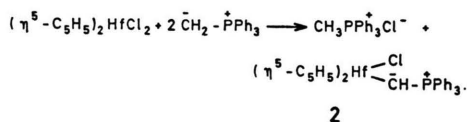


Further substitution of a halogen atom in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_2\text{-P}^+\text{Ph}_3)\text{Cl}_2$ by $\text{CH}_2\text{-P}^+\text{Ph}_3$ does not occur probably because the ylide is too bulky. Transylidation [7] occurs instead to give

$(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH-P}^+\text{Ph}_3)\text{Cl}$. Moreover, additional substitution of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH-P}^+\text{Ph}_3)\text{Cl}$ by $\text{CH}_2\text{-P}^+\text{Ph}_3$ does not occur because of steric crowding around the zirconium atom.

Similar results occur when $\text{CH}_2\text{-P}^+\text{Ph}_3$ is treated with $[(\text{CH}_3)_3\text{CCH}_2]_4\text{TaCl}$. The alkylidene species $[(\text{CH}_3)_3\text{CCH}_2]_3\text{Ta-CHC}(\text{CH}_3)_3$ is generated rather than substitution of the halogen [8].

In a similar fashion $(\eta^5\text{-C}_5\text{H}_5)_2\text{HfCl}_2$ when treated with two equivalents of $\text{CH}_2\text{-P}^+\text{Ph}_3$ in THF for 14 days at room temperature gives one equivalent of $\text{CH}_3\text{P}^+\text{Ph}_3\text{Cl}^-$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}(\text{CH-P}^+\text{Ph}_3)\text{Cl}$,



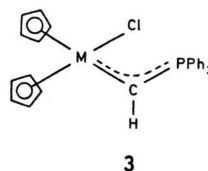
Infrared Spectra

The infrared spectrum of **1** consists essentially of the infrared spectrum of $\text{CH}_2\text{-P}^+\text{Ph}_3$ superimposed over that of the appropriate $(\eta^5\text{-C}_5\text{H}_5)_2\text{MCl}_2$ complex. The band designated as $\nu_{\text{P-C}}$ in $\text{Ph}_3\text{P}^+\text{-CH}_2$ appears at 885 cm^{-1} (lit. 900 cm^{-1}) [9]. The spectrum of $\text{Ph}_3\text{P}^+\text{-CH}_2$ where the methylene carbon is approximately 14 atom-% ^{13}C -enriched, shows an 885 cm^{-1} band reduced in intensity and the appearance of a weak band at 861 cm^{-1} ($\nu_{\text{P-}^{13}\text{C}}$). The zirconium complex has no 885 cm^{-1} band, but a band at 939 cm^{-1} . A sample of **1** prepared with ^{13}C -enriched ylide also has the 939 cm^{-1} band and a weaker one at 917 cm^{-1} ($\nu_{\text{P-}^{13}\text{C}}$). The estimated isotopic shift for a change from ($\nu_{\text{P-}^{13}\text{C}}$) is -26 cm^{-1} [10], the observed shift is -22 cm^{-1} . The analogous isotopic shift in the spectrum of the free ylide is -24 cm^{-1} , estimated at -25 cm^{-1} .

Nuclear Magnetic Resonance

The ^1H , ^{13}C and ^{31}P NMR spectral data are entirely consistent with the formulation of the complexes **1** and **2**.

It is interesting to note the parallels between ^1H and ^{13}C chemical shifts of the ylide proton and carbon atoms in **1** and **2** and the corresponding $\nu_{\text{P-C}}$ vibrations. The ylide proton resonances of **1** (5.92δ) and **2** (4.37δ) are both well downfield from the resonances of the highly shielded methylene protons of $\text{CH}_2\text{-P}^+\text{Ph}_3$ ($+0.74$, $d^2J_{\text{PH}} = 6.5 \text{ Hz}$ in C_6D_6) just as the free ylide $\nu_{\text{P-C}}$ band is at the lowest frequency. The ylide carbon atoms of **1** (107.8δ) and **2** (97.4δ) are also deshielded with respect to the carbanionic methylene carbon of the free ylide (-4.2δ). The following type of structure can account for the magnetic resonance data observed for **1** and **2**.



This would imply an sp^2 hybrid at the ylide carbon atom. The free ylide $\text{CH}_2\text{-P}^+\text{Ph}_3$ is apparently sp^2 hybridized at the methylene carbon, judging from the crystal structure [11] and the $^1J_{\text{CH}}$ coupling constant of the carbon atom (153 Hz). (The $^1J_{\text{CH}}$ coupling constant of ethylene is 156.2 Hz). In contrast, the analogous $^1J_{\text{CH}}$ coupling constants of **1** and **2** are 122 and 120 Hz respectively; these are lower than those generally observed for sp^3 hybrid carbon atoms ($> 125 \text{ Hz}$) [12].

In the alkylidene complexes of Ta(V) , $^1J_{\text{CH}}$ values are uncommonly small for ($\text{Ta} = \text{CHR}$, $^1J_{\text{CH}} = 90 \text{ Hz}$) [8]; such small values are unreliable indicators of carbon hybridization in these compounds. Lower values than expected for $^1J_{\text{CH}}$ in organolithium compounds [13] have also been reported due to the charge density on the carbon atoms.

Although less is known about changes in the $\text{P}^+\text{-C}$ coupling constants, one can note that $^1J_{\text{PC}}$ for the ylide carbon in **1** and **2** is about $1/3$ the value for $^1J_{\text{PC}}$ in $\text{CH}_2\text{-P}^+\text{Ph}_3$. This could suggest there is less electron density in the $\text{P}^+\text{-C}$ bond in **1** and **2** if the

Fermi contact mechanism is dominant in the coupling interaction [14].

X-Ray Molecular Structure of

$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\bar{\text{C}}\text{H}-\text{P}^+\text{Ph}_3)$

The X-ray molecular structure of the zirconium ylide complex is shown in Figure 1 with the atom numbering schemes. Details concerning the structural analysis can be found in the experimental section. The final positional and thermal parameters are available from the authors on request [36]; pertinent interatomic distances (Å) and angles are listed in Table I with some dihedral angles between planes.

Table I. Intramolecular bond distances (Å) and bond angles (degrees)^a.

Zr - Cl	2.518(3)
Zr - C50	2.152(8)
C50 - H50	0.861(74)
C50 - P	1.708(6)
P - C21	1.834(6)
P - C31	1.825(7)
P - C41	1.836(6)
Zr - Cl	2.518(3)
Zr - C2	2.530(7)
Zr - C3	2.554(7)
Zr - C4	2.528(7)
Zr - C5	2.556(7)
Zr - C11	2.543(7)
Zr - C12	2.527(7)
Zr - C13	2.495(8)
Zr - C14	2.504(8)
Zr - C15	2.549(8)

Distance of atom H(50) from plane defined by three other atoms.

H(50) 0.067 Å

Cl - Zr - C50	100.69(18)
Zr - C50 - H50	114.17(487)
Zr - C50 - P	135.87(34)
H50 - C50 - P	109.81(488)
C50 - P - C21	111.88(30)
C50 - P - C31	113.41(29)
C50 - P - C41	116.88(30)
C21 - P - C31	107.17(29)
C21 - P - C41	101.44(28)
C31 - P - C41	104.95(2a)

Dihedral angle between planes each defined by three atoms.

H(50) - C(50) - P	4.76°
Zr - C(50) - P	
P - C(50) - Zr	95.54°
Cl - Zr - C(50)	

^a Standard deviations of least significant figures given in parenthesis, Standard deviations unavailable for rigid-group atoms.

Each cyclopentadienyl ring is η^5 -bonded to a zirconium atom. The rings are bent away from the horizontal mirror plane which contains the alkylidenetriphenylphosphorane and chlorine atom, with a centroid-Zr-centroid angle of 130.09°. This is in the range frequently observed for η^5 -cyclopentadienyl complexes of zirconium [15].

An average Zr-C(η^5) length of 2.54 Å compares favorably with other compounds that have bulky ligands bonded to the α -carbon atom attached to zirconium; $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{C}_6\text{H}_5)[\text{CH}(\text{SiMe}_3)_2]$, 2.543 Å; $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_2\text{CMe}_3)_2$, 2.56 Å; $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{ZrClCH}(\text{SiMe}_3)_2$, 2.513 Å [16]. The bulk of the triphenylphosphine group in the ylide complex apparently does not markedly affect the average Zr-C(η^5) distance.

The most notable features in the structure of the complex are the particularly long Zr-Cl bond, 2.51 Å, the very short Zr-C(50) bond, 2.152 Å, and the relatively long C(50)-P bond, 1.716 Å.

Normal Zr-Cl bonds range from 2.309 Å to 2.44 Å [17]. This suggests a partially labilized Zr-Cl bond which could be a consequence of the short Zr-C(50) σ -bond. A similar effect is observed in the structure of bis(η^5 -cyclopentadienyl)(η^2 -acetyl)methylzirconium [18]. Here, the methyl zirconium σ -bond is much longer than typical zirconium-carbon sp^3 bond lengths.

Another noted feature in the structure is the relatively short Zr-C(50) bond length of 2.152 Å. This is the shortest Zr-C bond length thus far reported and suggests that there is a structural basis for hindered Zr-C bond rotation observed in the ^1H NMR spectrum (*cf. vide infra*). A comparison with data taken from the literature [34] shows that the Zr-C(50) bond in the ylide complex is considerably shorter than other Zr-C systems with sp^2 bonded carbon atoms.

A consequence of the short Zr-C(50) bond is the elongated $\bar{\text{C}}\text{-P}^+$ bond, 1.716 Å. This bond in $\bar{\text{C}}\text{H}_2\text{-P}^+\text{Ph}_3$ is 1.661(8) Å, which is close to the sum of the atomic radii, 1.665 Å [19]. An ylide $\bar{\text{C}}\text{-P}^+$ bond which compares to that observed in the zirconium complex is $\text{Ph}_3\text{P}^+\text{-C}(\text{I})\text{COPh}$ (1.71 Å) [19].

The relationship of the triphenylphosphorylidene moiety to the rest of the molecule deserves comparison with the alkylidene complexes of tantalum which it resembles [20].

The $\angle[C(50)-Zr-Cl]$ is $100.69(18)^\circ$ which compares well with $TaCp_2(CHCMe_3)Cl$, $97.63(18)^\circ$; $TaCp_2(CH_3)(CH_2)$, 95.6° and $TaCp_2(CHPh)(CH_2Ph)$, $95.2(5)^\circ$ [21]. Similarly the $\angle[P-C(50)-Zr]$ is $135.87(34)^\circ$, which is close to the same angle $Ta-C_\alpha-C_\beta$ (in the alkylidene moiety) in $TaCp_2(CHPh)(CH_2Ph)$, $135.2(7)^\circ$. This same angle is greatly increased in $TaCp_2(CHCMe_3)Cl$ to $150.4(5)^\circ$, probably because of steric interactions between the $-CMe_3$ and $\eta^5-C_5H_5$ groups [22]. By comparison, the $Ta-C_\alpha-H$ angle in $TaCp_2(CH_3)(CH_2)$ [20] is $126(5)^\circ$.

The hydrogen atom H(50) is not significantly out of the $Zr-C(50)-P$ plane ($0.0672 \text{ \AA}$). This means that there is a $2p_z$ orbital on C- α which is perpendicular to the $Zr-C(50)-P$ plane. However, computations of the dihedral angle between the $Zr-C(50)-P$ and $Zr-C(50)-Cl$ planes give a value of 95.54° , *i.e.* the triphenylphosphorylidene moiety is displaced from the perpendicular by approximately 5.54° to the "inside". Similar displacements from the perpendicular are observed for $TaCp_2(CHPh)(CH_2Ph)$ 5.7° [21], $TaCp_2(CHCMe_3)Cl$ [22], 10.3° and $TaCp_2(CH_3)(CH_2)$ 0° [20]. The lower $\Delta G_{rot}^\ddagger$ is related to the extent of displacement from the perpendicular. Thus $TaCp_2(CHCMe_3)Cl$ has the lowest $\Delta G_{rot}^\ddagger$ value (16.8 kcal/mole) [22, 23].

Rotation about the $\bar{P}-\bar{C}$ Bond in

$\eta^5-(C_5H_5)_2MCl(\bar{C}H\bar{P}PPh_3)$, $M = Zr, Hf$

The 1H NMR spectra of **1** and **2** show sharp singlets for the cyclopentadienyl hydrogen atoms at room temperature. These resonances broaden into two singlets with a separation of 73 Hz (-116°) in a 21.3 K Gauss field. Coalescence for the zirconium complex occurs at -95°C ($k_1 = 170 \text{ sec}^{-1}$). The cyclopentadienyl resonance for the hafnium complex coalesces at -102°C ($k_1 = 150 \text{ sec}^{-1}$), in $THF-d_8$. No change, other than slight broadening of all lines due to viscosity occur for the other resonances in 1H and $^1H\{^{31}P\}$ NMR spectra; $P-H$ coupling is maintained throughout. The dynamic NMR data most closely fit an intramolecular two-site exchange [24] mechanism in which the symmetry of the molecule as a whole is lowered by hindered rotation about the metal-ylide, $M-C$ bond, Figure 1.

Examination of a model, built by using approximate bond distances, and angles from the structure

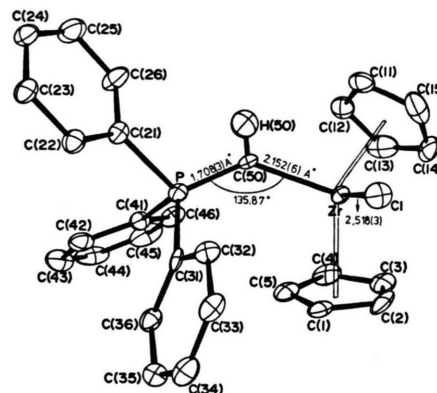


Fig. 1. The X-ray molecular structure of $(\eta^5-C_5H_5)_2ZrCl(\bar{C}H\bar{P}PPh_3)$. The hydrogen atoms on the benzene and cyclopentadienyl rings are omitted for clarity.

of $(\eta^5-C_5H_5)_2ZrCl_2$ [25], shows that there is an unfavorable steric interaction between the phenyl rings of the PPh_3 moiety of the ylide, and the cyclopentadienyl rings. The conformer of least steric interactions is **5**, Figure 2. However, in **5** as well as **6** the cyclopentadienyl rings are symmetric with respect to the $Cl-M-\bar{C}-\bar{P}$ plane and should therefore appear as one resonance if **5** or **6** is the predominant structure, at low temperature. Structures **4** and **7**, which are enantiomeric, most closely fit the stopped exchange, low temperature 1H NMR spectra. The model, when rotated into conformation **4** or **7**, shows that the phenyl rings of the PPh_3 moiety are very close to one of the cyclopentadienyl rings. The cyclopentadienyl hydrogen atoms of this ring are likely to be more shielded than those of the other cyclopentadienyl ring due to ring currents in the phenyl ring in close proximity, an effect

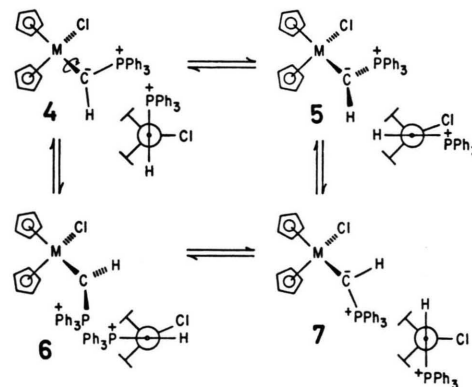
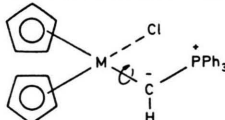


Fig. 2. Rotamers of $(\eta^5-C_5H_5)_2ZrCl(\bar{C}H\bar{P}PPh_3)$.

Table II. Arrhenius Activation Parameters for Rotation about M-C Bond.
 T_c = Coalescence temperature in THF- d_8 , used to calculate $\Delta G^\ddagger$ and $\Delta H^\ddagger$.

	T_c °K	E_a kcal/mole	$\text{Log } A$	$\Delta G^\ddagger$	$\Delta H^\ddagger$ kcal/mole	$\Delta S^\ddagger$ cal/° mole
						
M = Zr	178	9.3	13.73	8.6	9.0	2.3
M = Hf	171	8.2	12.70	8.3	7.9	-2.4
error limits	± 1	± 0.4	± 0.9	± 0.4	± 0.4	± 2

observed for hydrogen atoms above an aromatic ring in paracyclophanes [26], for example. Thus, these resonances are shifted to higher field (5.51 δ), whereas the remote cyclopentadienyl ring hydrogen atom resonances are shifted downfield (6.24 δ) closer to the resonances of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$. Structures **4** and **7** are the conformers formed electronically because they offer the best possible overlap of the filled ylide carbon p -orbital with the empty metal a_1 frontier orbital [23].

The activation parameters for the rotational process in **1** and **2** are calculated from first order rate constants obtained from the ^1H NMR spectra of **1** and **2** at specific temperatures via a band shape analysis of the two-site exchange using the DNMR 3 program [27]. The calculated values appear in Table II.

There is no useful data to gauge the steric effect of the PPh_3 moiety in changing the barrier to rotation [28]. The slight change in enthalpies of activation between **1** and **2** (~ 1 Kcal/mole) is in line with the IR and NMR observations that the M-C bond is weaker, *i.e.* has less double bond character for the hafnium complex than the zirconium one.

$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\text{CH-PPh}_3)$ and CO

Ordinarily CO will not interact with alkylidene-phosphoranes; there is no addition across the double bond. Transition metal substituted ylides can alter the non-reactivity of ylides to CO by interacting with the metal-carbon bond. When purified carbon monoxide is bubbled through a solution of **1** in THF, the solution is slowly decolorized over a 3 h period, and a white solid is obtained. The IR spec-

trum shows a strong band at 1550 cm^{-1} which is similar to that of the product obtained by Floriani when $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrMe}_2$ is treated with CO ($\nu_{\text{CO}} = 1550\text{ cm}^{-1}$) [18]. The remainder of the IR spectrum consists of bands that are typical for cyclopentadienyl and ylide moieties. A ^1H NMR spectrum shows a doublet at 4.79 δ ($^2J_{\text{PH}} = 30.5\text{ Hz}$ 1H) for the ylide proton, a singlet at 5.85 δ (10H) for the cyclopentadienyl hydrogen atoms and two overlapping multiplets at 7.51 δ and 7.62 δ for the aromatic hydrogen atoms,

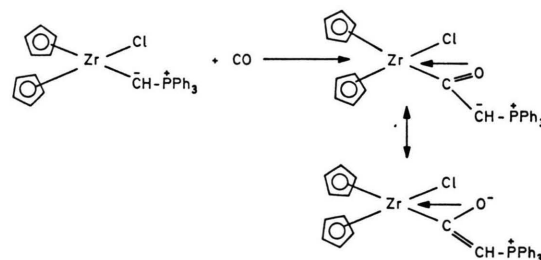


Table III. Crystal data.

Space group $P2_1/n$; $Z = 4$
Lattice parameters (115 K)
$a = 12.627(7)$, $b = 18.713(21)$, $c = 10.742(8)$
$\beta = 103.45(5)$
Radiation $\text{MoK}\alpha$ crystal monochromatized (0.7107 Å)
Crystal Dimensions $0.5 \times 0.5 \times 0.15\text{ mm}$
Absorption coefficient 6.25 cm^{-1} ;
$T_{\text{mix}} = 0.76$, $T_{\text{max}} = 0.89$
Scan range 1.0 below $K\alpha_1$ to 1.0 above $K\alpha_2$
Scan rate 8.0 degrees per minute
Scan mode $\theta/\text{two } \theta$, Two θ max = 50.0°
Background time = Scan time
Observed reflections (I greater than $3.0\sigma(I)$) 3036
$R = 0.048$; $R_w = 0.061$
Error in observation of unit weight 1.78

There is no evidence that elimination of triphenylphosphine oxide occurs at room temperature. Similar results are observed for other ylide transition metal complexes [29].

Experimental

All operations are performed under dry, oxygen-free nitrogen or argon. Reagents and products are manipulated in an argon-filled dry box under conditions where a sodium-potassium alloy mirror persists for at least 30 s. The zirconium complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ is purchased from Alpha Ventron, Danvers, Mass. and sublimed twice (130–140 °C, 0.01 Torr) prior to use. The hafnium complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{HfCl}_2$ is purchased from Research Organic Inorganic, Sun Valley, Calif. and sublimed twice (150 °C, 0.01 Torr) prior to use. The ylide $^{13}\text{C}\bar{\text{H}}_2\text{-P}^+\text{Ph}_3$ is synthesized as follows. Triphenylphosphine (purified by distillation under vacuum), 0.084 mmole, is treated with a mixture of 2.0 g (0.014 mmole) 90-atom-% ^{13}C -enriched methyl iodide (Merck and Co.) and 4.4 ml (0.070 mmole) of reagent grade methyl iodide. The resultant phosphonium salt (31.5 g, 0.0779 mole) is treated with potassium hydride (3.28 g, 0.082 mole, 5% excess) in THF. After the solution is stirred for 2 h is filtered from KI and the THF removed to give a yellow crystalline mass which is further purified by recrystallization from heptane or hexane (96%). The integral ratio of ^{13}C -satellites to the major doublet due to the CCH_2 protons indicates 14 atom-% ^{13}C enrichment.

Solvents. Tetrahydrofuran (THF), benzene, and pentane are distilled from sodium benzophenone-ketyl under argon; diphenyl ether is added to the solvents other than THF to aid in the formation of benzophenone ketyl. Pentane refers to a 30–38 °C fraction of low boiling hydrocarbons from 30–60 °C petroleum ether after removal of olefins. Benzene- d_6 , methylene chloride- d_2 , and 1,4-dioxane- d_8 are used as purchased from Aldrich Chemical Company, Milwaukee, Wisconsin. The THF- d_8 is from Aldrich or Merck and is vacuum distilled from LiAlH_4 before use.

Instrumentation. NMR spectra are obtained from samples prepared in a dry box and flame sealed under vacuum. Proton NMR spectra: Varian T-60, and XL-100/Nicolet TT-100 PFT (chemical shifts in ppm downfield from TMS). Carbon-13 NMR spectra: Varian CFT-20 (chemical shifts in ppm from TMS, downfield positive). Phosphorus-31 NMR spectra: Varian XL-100/Nicolet TT-100 (chemical shifts in ppm downfield positive, from external H_3PO_4 (85% of H_3PO_4) from capillary). Infrared spectra: Perkin Elmer 337 and 283. Melting points are determined with a Thomas Hoover capillary

melting point apparatus and are uncorrected. Mass spectra are obtained on an AEI-MS-902 double focusing mass spectrometer. Samples are sent to Chemalytics, Inc., Tempe, Arizona for elemental analyses.

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\text{CH-PPh}_3)$

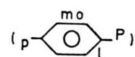
To a colorless solution of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ (2.50 g, 8.55 mmole) in 25 ml of dry THF chilled to 0 °C under nitrogen (chilling produces a slight turbidity) is added a bright yellow solution of $\bar{\text{C}}\text{H}_2\text{-P}^+\text{Ph}_3$ (9.45 g, 34.21 mmole) in 150 ml THF over 2 h at 0 °C. The turbid yellow-orange mixture is left to stir under nitrogen in ice for 3 days. A white solid gradually precipitates from the orange supernatant. After seven days at room temperature the white solid is removed by filtration and vacuum dried (20 °C, 0.01 Torr). The yield of phosphonium salt is 2.88 g (108% as $(\text{Ph}_3\text{PCH}_3)\text{Cl}$, 97% as $(\text{Ph}_3\text{PCH}_3)\text{Cl} \cdot 1/2 \text{ THF}$). The material is identified by proton NMR and IR spectroscopy [4].

The yellow residue is taken up in 100 ml of THF to give a yellow solution which is filtered to remove a trace of insoluble material, then vacuum evaporated to the point of crystallization at about 50 ml. A volume of pentane (450 ml) is added at room temperature with stirring to precipitate the product as fine yellow crystals. The crystals are washed twice with pentane and vacuum dried (1 h, 20 °C, 0.01 Torr), 3.42 g (75%), m.p. 199–200 °C, dec. with darkening 120 °C (and sintering at 194 °C), sealed tube.

Anal.: [30] Calculated for $\text{C}_{29}\text{H}_{26}\text{ClPZr}$: [30] 65.45%, 4.92%, 6.66% Cl, 5.82% P. Found: 63.89% C, 5.40% H, 5.77% P. Second analysis: 63.48% C, 5.23% H, 6.74% Cl, 5.45% P. Mass Spectrum: calcd. for $\text{C}_{29}\text{H}_{26}^{35}\text{ClP}^{90}\text{Zr}$: m/e 530. Observed: 530.

^1H NMR (C_6D_6): δ = 5.92 (d, 1 H, $^2J_{\text{PH}} = 11.1 \text{ Hz}$), 5.87 ($^5\text{HC}_5\text{H}_5$; THF- d_8 —5.72, $^2J_{\text{PH}} = 11.0 \text{ Hz}$), 7.07 (m, $p\text{-C}_6\text{H}_5\text{P}$), 7.71 (0, $\text{C}_6\text{H}_5\text{P}$). $^{31}\text{P}\{^1\text{H}\}$ NMR: +15.1 (s).

^{13}C NMR (C_6D_6): δ 107.8 (CHPPH_3 , $J_{\text{P-C}} = 31 \text{ Hz}$, $J_{\text{CH}} = 122 \text{ Hz}$), 110.1 ($J_{\text{CH}} = 172 \text{ Hz}$, $^{2+3}J_{\text{CH}} = 7 \text{ Hz}$, C_5H_5), 131.5 (s, $^4J_{\text{PC}} = 0 \text{ Hz}$, PC_6H_5), 129.9 (d, $^3J_{\text{PC}} = 12 \text{ Hz}$, m, C_6H_5), 134.0 (d, $^2J_{\text{PC}} = 9 \text{ Hz}$, 0, C_6H_5), 134.9 (d, $J_{\text{PC}} = 81 \text{ Hz}$, C_1)



The peaks above the molecular ion cluster at m/e 530 $\text{C}_{29}\text{H}_{26}^{35}\text{ClP}^{90}\text{Zr}$ correspond to traces of the hafnium complex. Hafnium compounds are very difficult to separate from the zirconium analogs due to the close similarity in properties.

Temperatures and rate Constants for the rotational process in $\text{Cp}_2\text{ZrCl}(\bar{\text{C}}\text{HPPH}_3)$.

T (°K)	k (sec ⁻¹)	T (°K)	k (sec ⁻¹)
156.3	5.0	174.5	110
161.9	14.0	175.6	135
163.7 ?	30.0	177.8 ?	170
168.0 ?	35.0	180.2	275
170.9	65.0	184.8	600
172.2	85.0	186.9	700

Preparation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{HfCl}(\bar{\text{C}}\text{H}-\ddot{\text{P}}\text{Ph}_3)$

In a flask is placed $\eta^5\text{Cp}_2\text{HfCl}_2$ (0.50 g, 1.32 mmole) and $\bar{\text{C}}\text{H}_2-\ddot{\text{P}}\text{Ph}_3$ (0.729 g, 2.64 mmole) with 40 ml of THF. The turbid mixture is stirred under argon for 14 days at ambient temperature, then filtered. The white solid is identified as $(\text{Ph}_3\text{PCH}_3)\text{Cl}$ by its IR spectrum. The filtrate is stirred for another 15 days at ambient temperature. More of the white solid gradually precipitates. The mixture is re-filtered to give another 0.064 g of $(\text{Ph}_3\text{PCH}_3)\text{Cl}$ (86% total). The yellow-orange filtrate is vacuum evaporated to give, a foamy yellow solid.

The solid is dissolved in 30 ml of dry THF; the solution is filtered to remove slight turbidity, then vacuum evaporated to the point of crystallization at 3–4 ml. Pentane (100 ml) is added with swirling at room temperature to precipitate the product as fine yellow needles. The yellow crystals are washed once with a little pentane, then vacuum dried (20 °C, 0.01 Torr) 0.543 g (66.5%), m.p.: slow decomposition over 120 °C, black at 130 °C, sinters 140 °C, sealed tube.

Anal.: Calculated for $\text{C}_{29}\text{H}_{26}\text{ClHfP}$: 56.23% C, 4.23% H, 5.72% Cl, 5.00% P. Found: 50.23% C, 4.73% H, 5.42% Cl, 4.48% P.

$^1\text{H NMR}$ (C_6D_6): δ = 4.37 (d, 1H, $^2J_{\text{PH}} = 13.2$ Hz), 5.81 (s, 5H, C_5H_5 , Toluene- d_8 , 5.84 $^2J_{\text{PH}} = 11$ Hz), 7.07 (m, $p\text{-C}_6\text{H}_5\text{P}$), 7.74 (0, $\text{C}_6\text{H}_5\text{P}$). $^{31}\text{P}\{^1\text{H}\}\text{NMR}$: +20.5 (s).

$^{13}\text{C NMR}$ (C_6D_6): δ 97.4 (CHPPH_3), $J_{\text{PC}} = 37$ Hz, $J_{\text{CH}} = 120$ Hz), 109.5 ($J_{\text{CH}} = 174$ Hz, $^{2+3}J_{\text{CH}} = 7$ Hz, C_5H_5), 130.3 (s, $^4J_{\text{PC}} = 0$ Hz, $p\text{-C}_6\text{H}_5$), 127.8 (d, $^3J_{\text{PC}} = 11$ Hz, $m\text{-C}_6\text{H}_5$), 132.9 (d², $J_{\text{PC}} = 9.0$ Hz, 0, C_6H_5).

Temperatures and rate Constants for the rotational process in $\text{Cp}_2\text{HfCl}(\bar{\text{C}}\text{HPPH}_3)$.

T (°K)	k (sec ⁻¹)	T (°K)	k (sec ⁻¹)
161.3 ?	77.0	174.9	262.5
165.9	85.0	177.1	375
169.1 ?	100.0	179.4 ?	800
170.3 ?	85.0	185.7	1150
171.1	150	187.7	1400
173.1 ?	275		

$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\text{CH}-\text{PPh}_3)$ with HCl

Orange crystalline $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\bar{\text{C}}\text{H}-\ddot{\text{P}}\text{Ph}_3)$ (0.129 g, 0.242 mmole) dissolved in 15 ml of dry

THF is treated with hydrogen chloride gas HCl (Linde, technical grade), which is passed through a drying tube which contains anhydrous CaCl_2 . The orange solution immediately becomes colorless with evolution of heat. The solution is stirred for 5 h under nitrogen. The solvent is removed under vacuum and the brownish white solid is vacuum dried at room temperature. The residue is treated with 15 ml of dry benzene and the pale yellow supernatant is decanted from a faintly brownish-white solid. The solid is washed with benzene and vacuum dried. 0.051 g. m.p. 280 °C in air. The material is identified as $(\text{CH}_3\text{PPh}_3)_2\text{ZrCl}_6$ (49%) by IR and NMR spectra and by its solubility behavior (KBr IR) cm^{-1} : 3055 m, 2990 m, 2904 m, 1585 m, 1480 m, 1434 m, 1405 (sh), 1335 m, 1320 m, 1189 w, 1162 w, 1111 vs, 1070 w (sh), 1023 w, 994 m, 890 m, 782 m, 741 s, 715 s, 684 s, 495 m, 429 m, 275 vs.

The benzene extract is evaporated to give an off-white solid 0.083 g (117% if all were $\eta^5\text{-Cp}_2\text{ZrCl}$. An IR (KBr pellet) spectrum of the off-white solid consists of bands which correspond to a mixture of $\eta^5\text{-Cp}_2\text{ZrCl}_2$ and silicon stopcock grease. A $^1\text{H NMR}$ spectrum benzene- d_6 also shows only resonances for $\eta^5\text{-Cp}_2\text{ZrCl}_2$ and stopcock grease.

$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\bar{\text{C}}\text{H}-\ddot{\text{P}}\text{Ph}_3)$ with CO

A yellow-orange solution of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\bar{\text{C}}\text{H}-\ddot{\text{P}}\text{Ph}_3)$ (0.217 g, 0.408 mmole) in 15 ml of dry THF is treated with CO (Linde, CP grade) which is first passed through a drying tube filled with NaOH pellets, then through activated Linde 4A molecular sieves at -78 °C. The solution becomes turbid fairly rapidly as the gas is bubbled through the solution, and the color gradually fades over 70–80 min. The white suspension then remains unchanged as the CO is bubbled through for another 2 h. The white solid is allowed to settle after 20 h stirring, the clear nearly colorless supernatant is filtered through a medium glass frit, and the solution evaporated to give crude $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\text{CO}-\text{PPh}_3)$. 0.137 g (60%), m.p. 155 dec; sealed tube.

Anal.: Calcd for $[\text{30}] \text{C}_{30}\text{H}_{26}\text{ClPOZr}$: 64.32% C, 4.68% H, 5.53% P. Found: 62.31% C, 5.16% H, 5.05% P.

KBr IR (cm^{-1}): 3050 w, 2960 m, 1448 m, 1340 m-s (br), 1260 m-s, 1105 vs, 1016 s, 885 m, 802 vs, 750 m, 722 m, 694 m, 560 m, 519 m, 485 w-m (sh).

Variable Temperature Study of

$(\eta^5\text{-C}_5\text{H}_5)_2\text{MCl}(\bar{\text{C}}\text{H}-\ddot{\text{P}}\text{Ph}_3)$ M = Zr and Hf

$^1\text{H NMR}$ spectra are obtained for solutions of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}(\bar{\text{C}}\text{H}-\ddot{\text{P}}\text{Ph}_3)$ or Hf in THF- d_8 in sealed 5 mm tubes at various temperatures. The temperature settings are stabilized by a Varian variable temperature controller and checked by a calibrated, copper-constantan thermocouple (Honeywell type

T # 9B1B8, size 30 AWG) [31] connected to a Leeds and Northrup temperature potentiometer.

X-Ray Data Collection

Under a nitrogen atmosphere an irregular crystal, $0.5 \times 0.5 \times 0.15$ mm is secured in a glass capillary with silicon grease.

Crystallographic data are obtained at 115 K with a Syntex PI diffractometer equipped with a locally constructed low temperature device [32]. Experimental and data handling techniques are analogous to those described previously [33]. Experimental parameters are summarized in Table III. Patterson, difference-Fourier, and least-squares refinement techniques are used in the solution of the structure. In the final refinement, positions and anisotropic

thermal parameters of all non-hydrogen atoms are refined along with the positions of the hydrogen atoms [35]. Isotropic temperature factors of the hydrogen atoms are fixed at 4.0 Angstroms squared, except for H(50) which is fixed at 3.0 Angstroms squared.

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