

data left 1983 unique data in the final data set.

The zirconium and sulfur atoms were located from a Patterson map: all remaining non-hydrogen atoms were obtained from Fourier maps. The data were refined as described for the structures discussed above. All non-hydrogen atoms were handled as described earlier. Final refinement of this solution yielded an R value of 2.33% ($R_w = 2.98\%$). Generation of the other enantiomorph and subsequent refinement converged to an R value of 2.26%, indicating that the second choice of polarity was correct.

The final residuals for 324 variables refined against 1773 data for which $F^2 > 3\sigma(F^2)$ were $R = 2.26\%$, $R_w = 2.89\%$, and $GOF = 1.17$. The R value for all 1983 data was 2.77%. The quantity minimized by the least-squares program, p factor, and corrections for anomalous dispersion were also handled as described above. The largest peaks in the final difference Fourier map had an electron density of $\pm 0.23 \text{ e}/\text{\AA}^3$. There was no indication of secondary extinction in the high-intensity, low-angle data.

Synthesis of $\text{Cp}^*_2\text{Zr}(\text{SC}(p\text{-C}_6\text{H}_4\text{CH}_3)=\text{C}(p\text{-C}_6\text{H}_4\text{CH}_3))$ (13c). As in the preparation of 13b, a benzene solution of complex 11a (100 mg, 0.21 mmol) and 130 mg (0.63 mmol) of di-*p*-tolylacetylene was thermolyzed in a degassed Pyrex bomb at 85 °C for 12 h. Excess alkyne was removed by sublimation at 85 °C onto a cold finger (under vacuum). Extraction of the red-orange

residue into a minimum of benzene, filtration, and layering with hexane yielded 83 mg (65%) of microcrystalline material: IR (C_6H_6) 2907, 2888, 1518, 1248, 1178, 672 cm^{-1} . Anal. Calcd for $\text{C}_{36}\text{H}_{44}\text{SZr}$: C, 72.06; H, 7.39. Found: C, 71.62; H, 7.46.

Preparation of $(\text{Cp}^*_2(\text{SH})\text{Zr})_2(\mu\text{-S})$ (14). $\text{Cp}^*_2\text{ZrPh}_2$ (500 mg, 0.97 mmol) was dissolved in 30 mL of toluene and the solution placed in a Pyrex bomb, frozen in liquid nitrogen, and thoroughly degassed. H_2S (1.50 equiv) was condensed into the bomb via a known volume bulb, and this mixture was thawed and heated at 80 °C for 12 h. The resulting yellow reaction mixture was filtered and taken to dryness in vacuo and the residue washed with 10 mL of ether, yielding 252 mg (63%) of bright yellow solid: IR (C_6H_6) 2951, 2906, 1378, 1248, 1178, 673 cm^{-1} . Anal. Calcd for $\text{C}_{40}\text{H}_{62}\text{S}_3\text{Zr}_2$: C, 58.48; H, 7.61; S, 11.71. Found: C, 58.42; H, 7.67; S, 11.49.

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(Diphenylphosphino)methyl Complexes of Titanium and Zirconium: Synthesis and Characterization. Molecular Structure of $\text{CpCp}^*\text{Ti}(\text{CH}_2\text{PPh}_2)_2$ ($\text{Cp} = \text{C}_5\text{H}_5$; $\text{Cp}^* = \text{C}_5\text{Me}_5$)

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The reaction of $[\text{C}_5(\text{CH}_3)_5](\text{C}_5\text{H}_5)\text{MCl}_2$ ($\text{M} = \text{Ti}, \text{Zr}$) with 2 equiv of $\text{LiCH}_2\text{PPh}_2 \cdot \text{TMEDA}$ offers a convenient method for the preparation of the corresponding dialkyl derivatives $[\text{C}_5(\text{CH}_3)_5](\text{C}_5\text{H}_5)\text{M}(\text{CH}_2\text{PPh}_2)_2$ where $\text{M} = \text{Ti}$ and Zr in 95–100% yield. However, when this reaction is carried out with 1 equiv of $\text{LiCH}_2\text{PPh}_2 \cdot \text{TMEDA}$ in the same conditions, the chloro alkyl complex of titanium $[\text{C}_5(\text{CH}_3)_5](\text{C}_5\text{H}_5)\text{TiCl}(\text{CH}_2\text{PPh}_2)$ is formed, whereas a mixture of the starting material and the dialkyl derivative is obtained for zirconium. These new complexes have been characterized by ^1H , ^{13}C , and $^{31}\text{P}\{^1\text{H}\}$ NMR measurements and elemental analysis. The ^1H NMR spectra show a clear diastereotopic behavior for the methylene protons of the CH_2 groups. The molecular structure of $[\text{C}_5(\text{CH}_3)_5](\text{C}_5\text{H}_5)\text{Ti}(\text{CH}_2\text{PPh}_2)_2$ as determined by X-ray diffraction methods is reported. The complex crystallizes in the space group $P2_1/c$ (No. 14), $a = 17.323$ (2) Å, $b = 12.549$ (1) Å, $c = 16.497$ (2) Å, $\beta = 103.71$ (2)°, $Z = 4$. The geometry around the Ti atom is normal. A weak agostic interaction $\text{Ti} \cdots \text{H}(4)$ can be proposed to be present in the structure of the solid state of this compound.

Introduction

Many important industrial processes¹ have been devised by using cyclopentadienyltitanium and -zirconium derivatives. An interesting class of complexes is those con-

taining remote phosphine ligands with a M–C–P framework in which a functionalized tertiary phosphine is present. They were initially prepared as precursors to access the heterodinuclear compounds formed by group 4 metals and mainly late-transition-metal centers.² These

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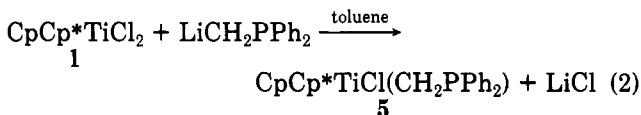
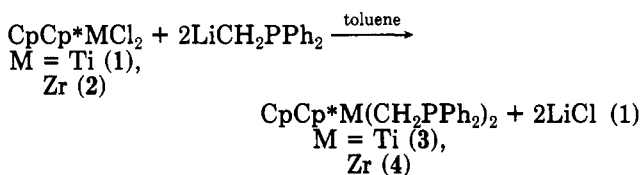
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particular complexes activate C–H bonds³ and show catalytic activity in selective hydrogenation of olefin substrates.⁴ The majority of studies has been related to complexes with unsubstituted^{1–4} or monosubstituted^{2b} cyclopentadienyl rings.

We are interested in studying the regio- and stereo-specific hydrogenation of olefins and the stereoregular propagation of polypropylene chains in Ziegler-Natta processes by using complexes containing chiral metal centers or precursors of chiral active species. We decided to obtain [(diphenylphosphino)methyl]titanium and -zirconium derivatives containing two electronically and sterically different cyclopentadienyl rings. Here we report the synthesis of complexes $\text{CpCp}^*\text{MR}(\text{CH}_2\text{PPh}_2)$ ($\text{Cp} = \text{C}_5\text{H}_5$; $\text{Cp}^* = \text{C}_5\text{Me}_5$; $\text{M} = \text{Ti}, \text{Zr}$; $\text{R} = \text{Cl}, \text{CH}_2\text{PPh}_2$), their structural characterization by NMR spectroscopy, and the X-ray crystal structure of the complex $\text{CpCp}^*\text{Ti}(\text{CH}_2\text{PPh}_2)_2$.

Results and Discussion

The reaction of a toluene solution of $\text{CpCp}^*\text{MCl}_2$ [$\text{M} = \text{Ti}$ (1), Zr (2)] at -78°C with 2 equiv of $\text{LiCH}_2\text{PPh}_2$. TMEDA leads to red (Ti) or orange (Zr) solutions from which $\text{CpCp}^*\text{M}(\text{CH}_2\text{PPh}_2)_2$ [$\text{M} = \text{Ti}$ (3), Zr (4)] were obtained according to eq 1.



When the same reaction was carried out by using only 1 equiv of the alkylating agent, the titanium derivative 1 leads to the formation of chloro alkyl complex 5, whereas the zirconium complex 2 gave a mixture of the starting dichloro complex and the dialkyl derivative which could not be isolated as a pure sample.

Complexes 3 and 5 (both red) and 4 (yellow) were crystalline solids. They are very soluble in benzene, toluene, and THF but only slightly soluble in hydrocarbons. They remain as unchanged solids for a week in the presence of air.

The ^1H NMR spectra of complexes 3–5 show the expected singlets due to the protons of the cyclopentadienyl ring and to the methyl protons of the permethylated ring (see Experimental Section). The most significant feature of all the three complexes is the behavior of the methylene group of the phosphinoalkyl ligand. The presence of two different cyclopentadienyl Cp and Cp^* rings around the metal center makes the two diastereotopic methylene protons nonequivalent.⁵ The same behavior has been observed for the methylene protons of the CH_2SiMe_3 ligand in cyclopentadienyl fulvalene titanium and zirconium derivatives,⁶ whereas they are equivalent in metallocenes

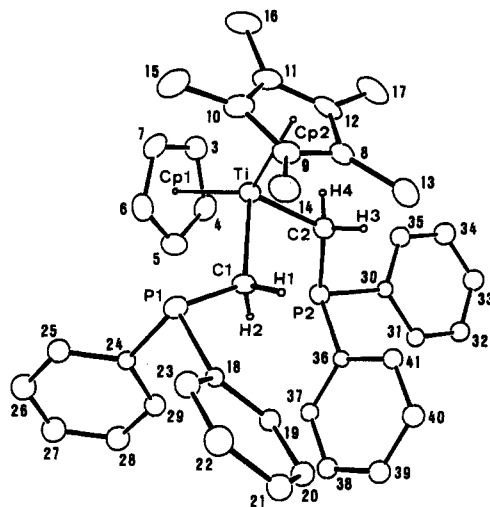


Figure 1. ORTEP view of the structure of $\text{CpCp}^*\text{Ti}(\text{CH}_2\text{PPh}_2)_2$ (3). Hydrogens are omitted for clarity, except for the methylene moiety.

with two equal rings. The two diastereotopic protons in 4 give rise to two pseudodoublets at δ 0.22 and 0.81 with a high coupling constant $J_{\text{HH}} = 11$ Hz, similar to those found for analogue diastereotopic systems.⁶ Both of these signals are split by coupling with the phosphorus atom, giving a doublet, which is only well resolved for the low-field doublet with $^2J_{\text{PH}} = 3.0$, similar to that found for dialkyl analogues containing the same two unsubstituted^{2a-c} or *t*-Bu-substituted^{2b} rings, which show only one doublet with $^2J_{\text{PH}} = 3.0$ – 3.5 Hz.

Only one pseudodoublet at δ 0.20 with $J = 10.8$ Hz was observed for complex 3 in benzene- d_6 , whereas in CDCl_3 3 shows one pseudodoublet at δ 0.04 ($J = 11.72$ Hz) and a quartet at δ 1.38 ($J = 5.9$ Hz) with an intensity ratio 1/1 and 2/2/15/5 in relation to the signals of the Cp^* and Cp rings, respectively. A $\{^1\text{H}, ^1\text{H}\}$ COSY 2D NMR spectrum was made in benzene- d_6 to localize the second doublet which is overlapped by the methyl Cp^* resonance at δ 1.65. The spectrum shows the expected correlation between both H_A and H_B protons of the CH_2 groups, the second being observed exactly at the same position corresponding to the methyl Cp^* resonance.

A similar behavior is observed for compound 5. In this case the presence of two different cyclopentadienyl rings introduces a chiral ligand arrangement about the Ti center. As a result the diastereotopic pair of protons produces a symmetric quartet at δ 2.47 ($J = 5.5$ Hz) and a pseudodoublet at δ 1.35 ($J = 10.7$ Hz) with an intensity ratio corresponding to one proton for each group of signals. To complete the assignment of these signals, a $\{^1\text{H}, ^1\text{H}\}$ COSY 2D NMR was carried out for compound 5. The $\{^1\text{H}, ^1\text{H}\}$ COSY 2D NMR spectrum shows that H_A correlates with H_B .

The ^{13}C NMR spectra in benzene- d_6 show doublets with $J_{\text{PC}} = 54.3$ Hz for 3, 49.3 Hz for 4, and 54.90 Hz for 5, the methylene carbon atoms which appear as two triplets with $J_{\text{CH}} = 121.2$ Hz for (3) and 115.0 Hz for (4) with the same

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Table I. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses^a

Ti-Cp(1)	2.086 (3)	Ti-Cp(2)	2.113 (3)
Ti-C(1)	2.183 (3)	Ti-C(2)	2.203 (3)
Cp(1)-Ti-Cp(2)	132.8 (1)	Cp(1)-Ti-C(1)	106.1 (1)
Cp(1)-Ti-C(2)	105.6 (1)	Cp(2)-Ti-C(1)	107.2 (1)
Cp(2)-Ti-C(2)	105.79 (9)	C(1)-Ti-C(2)	91.79 (9)
C(1)-P(1)	1.827 (2)	C(2)-P(2)	1.822 (3)
C(1)-H(1)	0.97 (2)	C(2)-H(3)	0.97 (1)
C(1)-H(2)	0.97 (2)	C(2)-H(4)	0.97 (2)
Ti...H(1)	2.71 (2)	Ti...H(3)	2.72 (2)
Ti...H(2)	2.62 (2)	Ti...H(4)	2.46 (2)
Ti...P(1)	3.5339 (8)	Ti...P(2)	3.5869 (9)
Ti-C(1)-P(1)	123.4 (1)	Ti-C(2)-P(2)	125.8 (1)
Ti-C(1)-H(1)	113 (1)	Ti-C(2)-H(3)	112 (1)
Ti-C(1)-H(2)	106 (1)	Ti-C(2)-H(4)	93 (1)
P(1)-C(1)-H(1)	98.3 (9)	P(2)-C(2)-H(3)	107 (1)
P(1)-C(1)-H(2)	111 (1)	P(2)-C(2)-H(4)	111 (1)
H(1)-C(1)-H(2)	104 (1)	H(3)-C(2)-H(4)	106 (1)

^a Cp(1) and Cp(2) are the centroids of the C(3)C(4)C(5)C(6)C(7) and C(8)C(9)C(10)C(11)C(12) rings, respectively.

Table II. Crystal Data and Data Collection Details for 3

Crystal Data	
formula	C ₄₁ H ₄₄ P ₂ Ti
fw	646.65
cryst syst	monoclinic
space group	P2 ₁ /c (No. 14)
a, Å	17.323 (2)
b, Å	12.549 (1)
c, Å	16.497 (2)
β, deg	103.71 (2)
V, Å ³	3484 (1)
Z	4
D _{calcd} , g/cm ³	1.23
F(000)	1368
μ(Mo Kα), cm ⁻¹	3.6
Data Collection	
temp, °C	20 ± 1
λ(Mo Kα radiation, graphite monochromator), Å	0.71073
attenuator	Zr foil, factor 12.8
takeoff angle, deg	3.45
detector aperture	4.0-4.0 mm horizontal 4.0 mm vertical
θ(min-max), deg	1.5-22.0
scan mode	ω-2θ
scan range, deg	0.80 + 0.35 tan θ
scan speed, deg/min	1.1-5.5
no. of refls measd	4426 total, 4257 unique
R _{av}	0.021 (on I)
corrections	Lorentz-polarization

J_{PC} observed in the ¹H coupled spectrum. The chemical shifts observed in the ³¹P NMR spectra, in C₆D₆ (referenced to H₃PO₄ in D₂O; see Experimental Section), are similar to those reported for analogous titanium and zirconium derivatives,^{2a,c,d} indicating that the phosphorus atom is not coordinated to the metal center.

The IR spectra of the new compounds show the expected absorptions for the Cp ligands¹⁰ and alkyl groups. The mass spectra are also in agreement with the proposed formulation.

Complex 3 was studied by X-ray diffraction methods. Selected interatomic distances and angles for 3 are given in Table I. The ORTEP drawing is shown in Figure 1.

In general, the structure of 3 is very similar to that previously described for Cp₂Ti(CH₂PPh₂)₂^{2c} and confirms the pseudotetrahedral nature of the Ti coordination sphere. As an effect of replacement of one C₅H₅ ligand

Table III. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å² × 100) with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U _{eq} ^a /U _{iso}
Ti	0.32328 (3)	0.58766 (3)	0.15710 (3)	3.63 (7)
P(1)	0.33725 (4)	0.36506 (5)	0.29101 (4)	4.1 (1)
P(2)	0.13268 (4)	0.68962 (5)	0.16842 (4)	4.1 (1)
C(1)	0.2753 (1)	0.4562 (2)	0.2167 (2)	3.8 (4)
H(1)	0.2476 (9)	0.404 (1)	0.177 (1)	5.0
H(2)	0.2337 (8)	0.487 (2)	0.240 (1)	5.0
C(2)	0.2038 (2)	0.6544 (2)	0.1073 (1)	4.2 (5)
H(3)	0.175 (1)	0.615 (1)	0.0591 (7)	5.0
H(4)	0.224 (1)	0.718 (1)	0.085 (1)	5.0
C(3)	0.3864 (2)	0.7526 (2)	0.2018 (2)	4.9 (5)
C(4)	0.3226 (2)	0.7462 (2)	0.2393 (2)	5.0 (5)
C(5)	0.3349 (2)	0.6626 (2)	0.2941 (2)	5.9 (6)
C(6)	0.4073 (2)	0.6169 (2)	0.2925 (2)	5.1 (5)
C(7)	0.4403 (2)	0.6725 (2)	0.2375 (2)	5.2 (5)
C(8)	0.2926 (2)	0.4919 (2)	0.0238 (1)	4.5 (5)
C(9)	0.3542 (2)	0.4356 (2)	0.0769 (2)	4.7 (5)
C(10)	0.4217 (2)	0.5007 (2)	0.0986 (2)	5.5 (5)
C(11)	0.4032 (2)	0.5975 (2)	0.0562 (2)	5.9 (6)
C(12)	0.3238 (2)	0.5934 (2)	0.0111 (2)	5.4 (5)
C(13)	0.2133 (2)	0.4462 (2)	-0.0181 (2)	5.9 (5)
C(14)	0.3514 (2)	0.3189 (2)	0.0941 (2)	6.3 (6)
C(15)	0.5016 (2)	0.4640 (3)	0.1463 (2)	8.0 (7)
C(16)	0.4600 (2)	0.6852 (3)	0.0452 (2)	9.2 (8)
C(17)	0.2804 (2)	0.6747 (2)	-0.0501 (2)	7.8 (7)
C(18)	0.27529 (8)	0.2432 (1)	0.2801 (1)	3.66 (6)
C(19)	0.19242 (8)	0.2428 (1)	0.2576 (1)	4.41 (6)
C(20)	0.15119 (8)	0.1464 (1)	0.2470 (1)	4.96 (7)
C(21)	0.19282 (8)	0.0503 (1)	0.2589 (1)	5.19 (7)
C(22)	0.27569 (8)	0.0506 (1)	0.2815 (1)	6.22 (8)
C(23)	0.31693 (8)	0.1470 (1)	0.2921 (1)	5.37 (7)
C(24)	0.32574 (7)	0.4150 (1)	0.3931 (1)	3.90 (6)
C(25)	0.39420 (7)	0.4213 (1)	0.4576 (1)	5.38 (7)
C(26)	0.38953 (7)	0.4583 (1)	0.5360 (1)	6.56 (8)
C(27)	0.31639 (7)	0.4891 (1)	0.5499 (1)	6.58 (8)
C(28)	0.24792 (7)	0.4829 (1)	0.4855 (1)	6.22 (8)
C(29)	0.25260 (7)	0.4458 (1)	0.4070 (1)	5.14 (7)
C(30)	0.05151 (9)	0.7520 (1)	0.08956 (9)	4.02 (6)
C(31)	-0.02795 (9)	0.7346 (1)	0.08986 (9)	4.75 (7)
C(32)	-0.08794 (9)	0.7863 (1)	0.03185 (9)	5.45 (7)
C(33)	-0.06847 (9)	0.8555 (1)	-0.02646 (9)	6.15 (8)
C(34)	0.01100 (9)	0.8729 (1)	-0.02676 (9)	6.69 (8)
C(35)	0.07099 (9)	0.8212 (1)	0.03126 (9)	5.58 (7)
C(36)	0.08286 (9)	0.5639 (1)	0.18171 (8)	3.75 (6)
C(37)	0.06642 (9)	0.5451 (1)	0.25927 (8)	4.33 (6)
C(38)	0.02269 (9)	0.4556 (1)	0.27110 (8)	5.00 (7)
C(39)	-0.00460 (9)	0.3847 (1)	0.20538 (8)	5.36 (7)
C(40)	0.01183 (9)	0.4035 (1)	0.12783 (8)	5.33 (7)
C(41)	0.05556 (9)	0.4931 (1)	0.11599 (8)	4.81 (7)

^a U_{eq} = one-third the trace of U.

by C₅Me₅ from Cp₂Ti(CH₂PPh₂)₂, increasing both steric hindrance and electron density at the metal, the C(1)-Ti-C(2) angle, 91.79 (9)° is smaller than in Cp₂Ti(CH₂PPh₂)₂, 97.7 (1)° whereas Ti-C(2)-P(2), 125.8 (1)° is greater than in the analogous nonsubstituted cyclopentadienyl complex 122.9 (2)°. The Ti-P distances, 3.5339 (8) and 3.5869 (9) Å, rule out any direct bonding between these atoms.^{2c}

The most relevant feature of the molecular structure is the value of the Ti-C(2)-H(4) angle, 93 (1)°, lower than the remaining similar angles which are between 106 and 113°. On the other hand, despite the limitation of the X-ray diffraction method for the determination of the hydrogen positions, the Ti-H(4) distance, 2.46 (2) Å is shorter than the remaining Ti-H distances. An analogous behavior was found for [TiBz₃] (μ-η⁵-η⁵-C₁₀H₈),⁷ this distance being intermediate between that known for agostic CH...Ti systems (2.35 Å) and for CH₂ groups without a Ti...H interaction (2.63 Å).^{7,8} Thus a weak agostic interaction can also be postulated for complex 3, although it presents a fluxional behavior in solution, as confirmed by

^1H and ^{13}C NMR spectroscopy without normal J_{CH} coupling constants.

Conclusions

Bis(diphenylphosphino)methyl complexes of titanium and zirconium containing two different cyclopentadienyl rings have been prepared. These compounds can be considered interesting precursors of chiral active species which must present interesting properties in olefin hydrogenation or polymerization processes. The analogous chloro[(diphenylphosphino)methyl] derivative of titanium presents a chiral ligand arrangement about the titanium center. The ^1H NMR spectra of these compounds show a clear diastereotopic behavior of the methylene protons of the CH_2 groups imposed by the presence of the different cyclopentadienyl rings around the metal atom. On the other hand, a weak agostic interaction $\text{Ti}\cdots\text{HC}$ is observed in the molecular structure of $\text{CpCp}^*\text{Ti}(\text{CH}_2\text{PPh}_2)_2$.

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Experimental Section

All manipulations were performed under an inert atmosphere (dinitrogen or argon) by using Schlenk and high-vacuum line techniques or a vacuum atmosphere drybox Model HE-63-P PEDETROL. Solvents were purified by initial distillation from an appropriate drying agent (sodium/benzophenone for THF, sodium for hexane, and sodium/potassium alloy for toluene) and deoxygenated before use. $\text{CpCp}^*\text{MCl}_2$ ($\text{M} = \text{Ti}^{9a}$, Zr^{9b}) and $\text{LiCH}_2\text{PPh}_2\text{TMEDA}^{9c}$ were prepared according to literature methods. ^1H , ^{13}C , and ^{31}P NMR spectra were obtained on a Varian FT-80 Å and Varian Unity FT-300 instruments. Chemical shifts are reported in units of δ referenced to tetramethylsilane. Mass spectra were recorded on a Hewlett-Packard 5890 spectrometer. Elemental C and H analyses were performed by a Perkin-Elmer 240B microanalyzer.

Preparation of $\text{CpCp}^*\text{Ti}(\text{CH}_2\text{PPh}_2)_2$ (3). A solution of $\text{LiCH}_2\text{PPh}_2\text{TMEDA}$ (8.13 g, 25.50 mmol) in toluene (20 mL) was added to a suspension of $\text{CpCp}^*\text{TiCl}_2$ (3.83 g, 12.00 mmol) in toluene (100 mL) cooled to -78°C . Upon warming slowly to room temperature, the reaction mixture was stirred for 6 h to give a red solution. After filtration to remove the LiCl the resulting solution was evaporated in vacuum to give an oil which was twice washed (50 mL) with cold hexane. After extraction with toluene/hexane (1/1), the mixture was concentrated to a small volume. Red crystals of 3 suitable for X-ray diffraction precipitated upon cooling at -30°C (7.5 g, 11.6 mmol, 97% yield). Anal. Calcd (found) for $\text{C}_{41}\text{H}_{44}\text{TiP}_2$: C, 76.18 (76.43); H, 6.81 (6.98). ^1H NMR (300 MHz, C_6D_6 , 25°C): δ 0.20 (br d, 2 H, CH_2 , $J = 10.8$ Hz), 1.65 (s, 17 H, $\text{C}_5\text{Me}_5 + \text{CH}_2$), 5.89 (s, 5 H, C_5H_5), 7.00–7.25 (m), 7.35–7.42 (t), 7.73–7.82 (t) (20 H, Ph). ^1H NMR (300 MHz, CDCl_3 , 25°C): δ 0.04 (br d, 2 H, CH_2 , $J = 11.72$ Hz), 1.38 (q, 2 H, CH_2 , $J = 5.9$ Hz), 1.90 [s, 15 H, $\text{C}_5(\text{CH}_3)_5$], 5.84 (s, 5 H, C_5H_5), 7.05–7.78 (m, 20 H, Ph). ^{13}C NMR (75 MHz, C_6D_6 , 25°C): δ 12.92 [q, $\text{C}_5(\text{CH}_3)_5$, $J_{\text{CH}} = 125.4$ Hz], 58.33 [dt, CH_2 , $J_{\text{CH}} = 121.2$ Hz, $J_{\text{PC}} = 54.32$ Hz], 115.33 (d, C_5H_5 , $J_{\text{CH}} = 173.21$ Hz), 122.23 [s, $\text{C}_5(\text{CH}_3)_5$], 126.1–149.93 (Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , referenced to H_3PO_4 in D_2O): δ 6.1 (s). EI/MS (70 eV): $m/z = 643.5$ [$\text{M}]^+$, 247 [$\text{CpCp}^*\text{Ti}]^+$ (100%).

Preparation of $\text{CpCp}^*\text{Zr}(\text{CH}_2\text{PPh}_2)_2$ (4). It was prepared as described above for compound 3 using $\text{CpCp}^*\text{ZrCl}_2$ (6.11 g, 16.9 mmol) and $\text{LiCH}_2\text{PPh}_2\text{TMEDA}$ (11.41 g, 35.4 mmol) in 150 mL of toluene. Compound 4 was obtained as a pale yellow solid (11.63 g, 16.9 mmol, 100% yield). Anal. Calcd (found) for $\text{C}_{41}\text{H}_{44}\text{ZrP}_2$: C, 71.38 (70.99); H, 6.38 (6.26). ^1H NMR (300 MHz, C_6D_6 , 25°C): δ 0.22 (br d, 2 H, CH_2 , $J = 11.5$ Hz), 0.81 (dd, 2 H, CH_2 , $J = 11$ Hz, $J_{\text{PH}} = 3.00$ Hz), 1.69 (s, 15 H, C_5Me_5), 5.77 (s, 5 H, C_5H_5), 7.05–7.16 (m), 7.24–7.45 (m), 7.60 (m, 20 H, Ph). ^{13}C NMR (75 MHz, C_6D_6 , 25°C): δ 11.95 [q, $\text{C}_5(\text{CH}_3)_5$, $J_{\text{CH}} = 126.5$ Hz], 45.66

[dt, CH_2 , $J_{\text{CH}} = 115$ Hz, $J_{\text{PC}} = 49.35$ Hz], 112.31 (d, C_5H_5 , $J_{\text{CH}} = 172.23$ Hz), 119.98 [s, $\text{C}_5(\text{CH}_3)_5$], 127.0–148.3 (Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , referenced to H_3PO_4 in D_2O): δ -3.30 (s).

Preparation of $\text{CpCp}^*\text{TiCl}(\text{CH}_2\text{PPh}_2)$ (5). To a solution of $\text{CpCp}^*\text{TiCl}_2$ (2.49 g, 7.82 mmol) in toluene (50 mL) cooled to -40°C was added dropwise a solution of $\text{LiCH}_2\text{PPh}_2\text{TMEDA}$ (2.52 g, 7.82 mmol) in THF with vigorous stirring. After the addition, the reaction mixture was slowly warmed to room temperature and stirred over a period of 3 h. The color turned dark red within 3 h. The resulting solution was evaporated to dryness in vacuum. Washing with hexane was twice repeated. The residual solid was recrystallized from toluene (50 mL). Cooling the solution to -30°C yielded compound 5 as a microcrystalline red solid (1.84 g, 3.81 mmol). A second fraction was obtained from the mother liquor (0.43 g, 0.89 mmol) (60% yield). Anal. Calcd (found) for $\text{C}_{28}\text{H}_{32}\text{TiClP}$: C, 69.66 (70.05); H, 6.63 (6.88). ^1H NMR (300 MHz, C_6D_6 , 25°C): δ 1.35 (br d, 1 H, CH_2 , $J = 10.7$ Hz), 1.72 [s, 15 H, $\text{C}_5(\text{CH}_3)_5$], 2.47 (q, 1 H, CH_2 , $J = 5.5$ Hz), 5.92 (s, 5, C_5H_5), 7.07–7.24 (m, 10 H, Ph). ^{13}C NMR (75 MHz, C_6D_6 , 25°C): δ 12.8 [s, $\text{C}_5(\text{CH}_3)_5$], 59.35 [d, CH_2 , $J_{\text{PC}} = 54.9$ Hz], 116.6 (s, C_5H_5), 125.04 [s, $\text{C}_5(\text{CH}_3)_5$], 128.0–148.0 (Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , referenced to H_3PO_4 in D_2O): δ 24.63 (s). EI/MS (70 eV): $m/z = 283$ [$\text{CpCp}^*\text{TiCl}]^+$.

X-ray Crystal Structure Determination for $[\text{C}_5(\text{CH}_3)_5][\text{C}_5\text{H}_5]\text{Ti}(\text{CH}_2\text{PPh}_2)_2$ (3). Collection and Reduction of X-ray Data. A red parallelepipedic crystal of size $0.50 \times 0.45 \times 0.15$ mm was mounted on a glass fiber on an Enraf-Nonius CAD4 diffractometer. Systematic absences were found for $0k0$ reflections for which $k \neq 2n$ and $h0l$ reflections for which $l \neq 2n$. Cell parameters were determined from a least-squares fit of 25 accurately centered reflections ($9.4 < \theta < 13.4^\circ$). These parameters are summarized in Table II. Three intense reflections were monitored every 2 h. Only random fluctuations were observed. Data were corrected for Lorentz and polarization effects by using SDP.¹¹ No absorption corrections were made. A total of 4257 unique reflections were collected ($\pm h, k, l$); 3071 were considered observed ($I > 3\sigma(I)$) and used for structure refinement.

Solution and Refinement. Atoms were located by use of SHELXS 86.¹² Refinement and Fourier difference calculations were made with SHELXL 76.¹³ Phenyl rings were refined as isotropic rigid groups ($\text{C}-\text{C} = 1.395$ Å). Anisotropic temperature factors were refined for all other non-H atoms. All H atoms were located on a ΔF map. They were included in calculated positions ($\text{C}-\text{H} = 0.97$ Å) in structure factor calculations with an assigned U value of 0.05 Å² for cyclopentadienyl and phenyl H and 0.07 Å² for methyl H. Methylene H atoms were allowed to vary; their U value was first refined and then kept fixed to 0.05 Å².

Scattering factors for H were obtained from Stewart et al.¹⁴ and for other atoms from ref 15. In the last full-matrix least-squares cycle the greatest shift/esd was 0.03 on a H parameter and the final R value was 0.023; $[\sum w(|F_o| - |F_c|)^2 / (n - m)]^{1/2}$ was equal to 0.96 ($R_w = 0.024$) with unit weights, $n = 3071$ observations and $m = 241$ variables. A final Fourier difference map showed a residual electron density of 0.17 e/Å³. Final positional and equivalent or isotropic temperature factors are listed in Table III. All calculations were performed on a DEC Microvax 3400 computer.

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Supplementary Material Available: Figures of $\{^1\text{H}, ^1\text{H}\}$ COSY 2D NMR spectra for compounds 3 and 5 and tables of fractional atomic parameters, thermal parameters, all bond lengths and angles, and least-squares plane equations for 3 (9 pages); a table of observed and calculated structure factors for 3 (15 pages). Ordering information is given on any current masthead page.

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