Energy, is gratefully acknowledged. We thank J. Allshouse and L. Lopez for assistance in two experiments.

Supplementary Material Available: Complete tables of data collection parameters, bond distances and angles, and displacement parameters for 7, a figure giving an alternate view of 7, and a 300-MHz ^1H NMR spectrum of $[(CpMo)(S_2CH_2)(\mu\text{-}SH)(\overline{SCH_2)Mo}Cp]SO_3CF_3$ (4) in CD_2Cl_2 (12 pages). Ordering information is given on any current masthead page.

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Elimination Process from the [(Diphenylphosphino)methyl]zirconium Hydride $[Cp_2ZrH(CH_2PPh_2)]_n$†

Yveline Raoult, Robert Choukroun,* and Claudine Blandy

Laboratoire de Chimie de Coordination, UPR 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique de Toulouse, 205 Route de Narbonne, 31077 Toulouse Cedex, France

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The synthesis of $[Cp_2ZrH(CH_2PPh_2)]_n$, 1, and its chemical behavior toward different organic or organometallic substrates are described. The chemical reduction of the hydride 1 produced a paramagnetic Zr(III) species formulated as $[CpZr(\eta^2\text{-}CH_2PPh_2)_2]$, and a redistribution reaction from the unstable $[Cp_2ZrH(CH_2PPh_2)]^-$ is suggested. The thermolytic experiment of 1 led to the Zr(III) species "Cp_2ZrH" and $[Cp_2Zn(\eta^2\text{-}CH_2PPh_2)]$, and a mechanistic pathway implying the reductive elimination of the phosphine CH_3PPh_2 is proposed. Indirect evidence comes from the thermolysis of $[Cp_2ZrD(CH_2PPh_2)]_n$ and $[(C_5D_5)_2ZrD(CH_2PPh_2)]_n$ or from the reactivity of 1 with PhC≡CPh, $Cp_2Zr(Ph)_2$, or $Cp_2Zr(\eta^4\text{-butadiene})$. A Zr(IV)–Zr(II) homodimetallic hydride $[Cp_2Zr(\mu\text{-}H)(\mu\text{-}CH_2PPh_2)ZrCp_2]$ is postulated as an intermediate in the decomposition scheme of 1.

Introduction

The organometallic chemistry of Zr(IV) containing a Zr–H bond provides many examples of thermally and photolytically unstable products.[1–5] Mechanisms have been investigated, and their decomposition pathways have proved difficult to establish due to cyclopentadienyl CH activation, which complicates the nature of the reaction.[4a,5e,f,6,7] Intramolecular reductive elimination of the alkyl and hydride ligand, as RH, with formation of the zirconocene species "Cp_2Zr", which in some instances can be trapped, is one proposed mechanism for the autodecomposition of hydride alkyl complexes.[5a,b,d,e] Early work in this area introduced the paramagnetic Zr(III) species $Cp_2Zr(\eta^2\text{-}CH_2PPh_2)$ in the activation of cyclopentadienyl C–H bonds.[8] The related compound, $[Cp_2ZrH(CH_2PPh_2)]_n$ (1), has shown by thermolysis at 60 °C the formation of a zirconium(III) hydride species, "Cp_2ZrH" (2), and the [(diphenylphosphino)methyl]zirconium $Cp_2Zr(\eta^2\text{-}CH_2PPh_2)$ (3).[9] The catalytic hydrogenation properties of 1 were investigated, and the presence of 3 was revealed during the hydrogenation of various organic unsaturated substrates.[10] Consequently, we were intrigued by the formation of species 3 when 1 was mixed with olefins, even at room temperature.

Herein we present a study on the chemical properties of 1, to learn as much as possible about the formation of Zr(III) species observed in the thermolytic experiments as well as toward olefinic substrates and to propose a picture about the decomposition of 1.

Scheme I

$$(1/n)[Cp_2ZrH(CH_2PPh_2)]_n \xrightarrow{Na(np)} [Cp_2ZrH(CH_2PPh_2)]^- + Na^+ + Np$$

$$[Cp_2ZrH(CH_2PPh_2)]^- \longrightarrow {}^1/_2[Cp_2ZrH_2]^- + {}^1/_2[Cp_2Zr(CH_2PPh_2)_2]^-$$

$${}^1/_2[Cp_2Zr(CH_2PPh_2)_2]^- \longrightarrow {}^1/_2[Cp_2Zr(\eta^2\text{-}CH_2PPh_2)_2]^- \; (+{}^1/_2Cp^-)$$

Results and Discussion

Synthesis, Chemical Reduction, Photolysis, and Thermolysis of $[Cp_2ZrH(CH_2PPh_2)]_n$, 1. The reaction of $Cp_2ZrCl(CH_2PPh_2)$ with $LiAlH(O\text{-}t\text{-}Bu)_3$ in THF or $NaAlH_2(OCH_2CH_2OMe)_2$ in toluene produces the insoluble polymeric white hydride complex $[Cp_2ZrH(CH_2PPh_2)]_n$, 1, in 60% yield.[9] Complex 1 is also accessible in a one-pot synthesis, with the same yield, starting from a mixture of Cp_2ZrCl_2 and $LiCH_2PPh_2(TMEDA)$ in THF at −78 °C,[13b]

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† In memory of Prof. D. Gervais.

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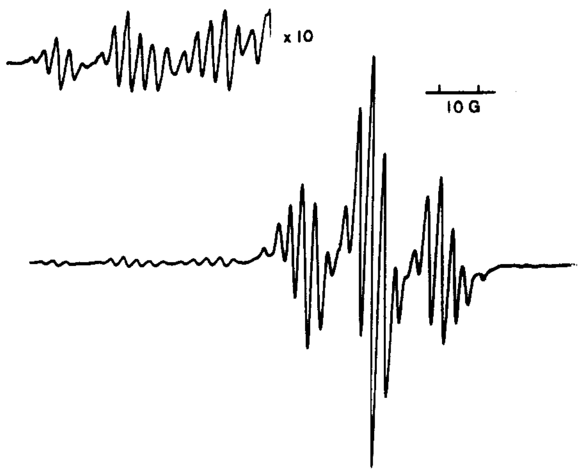


Figure 1. ESR spectrum of the reduced solution of $[Cp_2ZrH(CH_2PPh_2)]_n$ with Na(np) in THF.

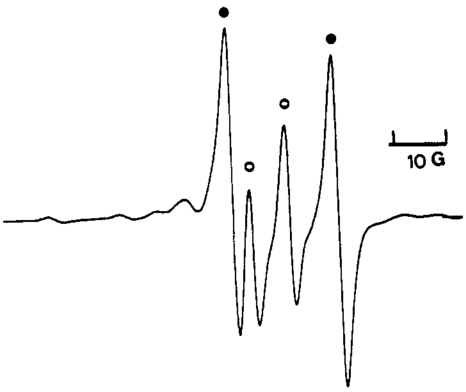


Figure 2. ESR spectrum of the photolysis of $[Cp_2ZrH(CH_2PPh_2)]_n$ after 5 min in THF: (○) 2, (●) 3.

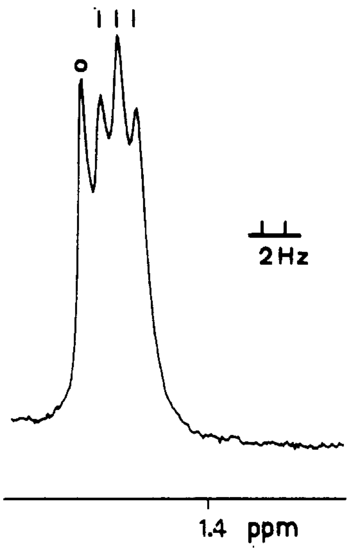
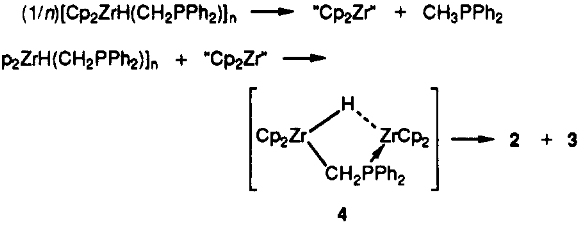


Figure 3. 250-MHz $^1H\{^{31}P\}$ NMR spectrum of the thermolysis of $[Cp_2ZrD(CH_2PPh_2)]_n$ in C_6D_6 at 60 °C showing the methyl region of PPh_2Me: (○) Me, (|) CH_2D.

Scheme II



and adding $LiAlH(O\text{-}t\text{-}Bu)_3$ at room temperature. The deuterated analogous complex is synthesized from $LiAlD(O\text{-}t\text{-}Bu)_3$, in the same manner as described above. The insolubility of 1 precludes any NMR characterization, but the IR spectrum shows a broad strong absorption at 1355 cm^{-1} (and 970 cm^{-1} for the deuteride) for the bridging hydride.

Chemical reduction of 1 with 1 equiv of sodium naphthalenide (Na(np)) leads to a Zr(III) species characterized by its ESR spectra as the (monocyclopentadienyl)zirconium $CpZr(\eta^2\text{-}CH_2PPh_2)_2$ (this species was obtained independently from the chemical reduction of $Cp_2Zr(CH_2PPh_2)_2$ and Na(np)[11]): each line of a central 1:2:1 triplet, due to the coupling to two equivalent phosphorus atoms, is split by coupling to four equivalent protons ($g = 1.987$, $a(^{31}P) = 16.1$ G, $a(^1H) = 2.8$ G, $a(^{91}Zr) = 22.5$ G) (Figure 1). The formation of $CpZr(\eta^2\text{-}CH_2PPh_2)_2$ from a Zr complex containing only one CH_2PPh_2 ligand could be due to a redistribution reaction from the unstable $[Cp_2ZrH(CH_2PPh_2)]^-$ formed during the first step of the reaction (Scheme I). Keeping in mind that anionic $[Cp'_2ZrH_2]^-$ ($Cp' = C_5H_4SiMe_3$, $C_5H_4\text{-}t\text{-}Bu$) has a precedent in zirconium chemistry,[12] we were unable to detect in our experimental conditions the unkwown $[Cp_2ZrH_2]^-$, due maybe to the short lifetime of this species.

Photolysis of 1 in toluene (or C_6D_6) was performed in the ESR cavity, and immediate formation of the well-known zirconium(III) hydride species[1,14b] Cp_2ZrH (2; $g = 1.987$, ($a(^1H) = 8$ G) and of the chelated [(diphenylphosphino)methyl]zirconium $[Cp_2Zr(\eta^2\text{-}CH_2PPh_2)]$ (3; $g = 1.985$, $a(^{31}P) = 19.5$ G), already reported by Schore et al., is observed (Figure 2).[9] A longer irradiation period complicates the ESR spectra and gives inextricable ESR features with ill-defined species.

Thermolytic experiments on 1 were followed by ESR spectroscopy in deuterated or undeuterated solvants (benzene, toluene, tetrahydrofuran) and led to 60 °C to the Zr(III) species 2 and 3. Thermolytic experiments on $[Cp_2ZrD(CH_2PPh_2)]_n$ in various deuterated solvants ($C_6D_5CD_3$, C_6D_6, THF-d_8) did not give the expected Cp_2ZrD species, but 2 and 3 were observed by ESR. A rapid exchange between the deuterated hydride position and the hydrogen of the cyclopentadienyl ligand is suggested according to already investigated mechanisms.[14]

At this stage, the ^1H and $^1H\{^{31}P\}$ NMR spectra of the solution show evidence for the formation of CH_2DPPh_2[13b] (1:1:1 triplet; $\delta = 1.43$ ppm, $J_{(PH)} = 3.9$, $J_{(HD)} = 1.9$ Hz) with the concomitant presence of a low amount of undeuterated phosphine (CH_2D/CH_3 ratio equal to 4; see Figure 3). The existence of CH_2DPPh_2 involves a reductive elimination pathway and allows us to propose a mechanism which proceeds through a thermally generated Cp_2Zr zirconocene intermediate species which takes up 1 to give a transitional homodimetallic hydride bridge complex, $[Cp_2Zr(\mu\text{-}H)(\mu\text{-}CH_2PPh_2)ZrCp_2]$, 4, formally (Zr(IV)–Zr(II) which dissociates into two Zr(III) species (Scheme II).

The ^{31}P NMR does not reveal the presence of $Cp_2Zr(PPh_2Me)_2$ observed by Schwartz et al. from Cp_2ZrHR in the presence of phosphines[5] (^{31}P: $\delta = 60.9$ ppm). Nevertheless, some amount of $[Cp(\eta^1{:}\eta^5\text{-}C_5H_4)Zr(PPh_2Me)]_2$ (^{31}P: $\delta = 32.5$ ppm) is observed and can be due to the decomposition pathway from $Cp_2Zr(PPh_2Me)_2$ or, in our opinion, preferentially from 3[8] (the formation of $[Cp(\eta^1{:}\eta^5\text{-}C_5H_4)Zr(PPh_2Me)]_2$ is faster from 3 than from

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[14] (a) Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *167*, 136. (b) Samuel, E. *J. Am. Chem. Soc.* **1983**, *22*, 2967.

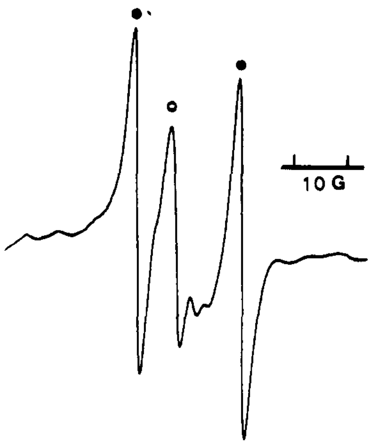


Figure 4. ESR spectrum of the thermolysis of [$(C_5D_5)_2ZrD(CH_2PPh_2)$]$_n$ in THF-d_8: (○) $(C_5D_5)_2ZrD$, (●) **3**.

Scheme III

$$Cp_2ZrPh_2 \xrightarrow{h\nu} \text{"}Cp_2Zr\text{"} + PhPh$$

$$(1/n)[Cp_2ZrH(CH_2PPh_2)]_n + \text{"}Cp_2Zr\text{"} \longrightarrow [4] \longrightarrow 2 + 3$$

$Cp_2Zr(PPh_2Me)_2$, where several days are needed).[5e] From the nonisotopically pure [$(C_5D_5)_2ZrD(CH_2PPh_2)$]$_n$, thermolytic experiments in toluene or C_6D_6 at 60 °C give a mixture of **2** and **3** and a new broad singlet signal attributed to $(C_5D_5)_2ZrD$ (g = 1.988) (Figure 4).

Considering this pathway, which strongly implicates the zirconocene species, the same results are afforded by combining **1** with $Cp_2Zr(Ph)_2$, which is able to generate zirconocene species by photolysis.[15] The stoichiometric mixture of **1** and $Cp_2Zr(Ph)_2$ in C_6D_6 was monitored by ^1H NMR and EPR in a sealed tube. Species **2** and **3** were produced with progressive disappearance of $Cp_2Zr(Ph)_2$ (^1H NMR: δ(Cp) = 6.12 ppm) and formation of biphenyl characterized by GC analysis. No detectable free phosphine was observed, and the reaction sequence suggested in Scheme III describes the trapping of **1** by Cp_2Zr generated from the diphenylzirconium complex.

Reactivity of 1 with Unsaturated Organic Substrates. In our previous studies on the catalytic hydrogenation of olefins,[10a,b] we observed that the reaction mixture between **1** and olefins develops a red color, which proves that paramagnetic species, mainly **3**, are formed. The facile circumstances of the readily accessible **3** led us to a systematic study of the reaction of **1** toward various olefins, in a stoichiometric way, to get insight into the mechanistic formation of **3**.

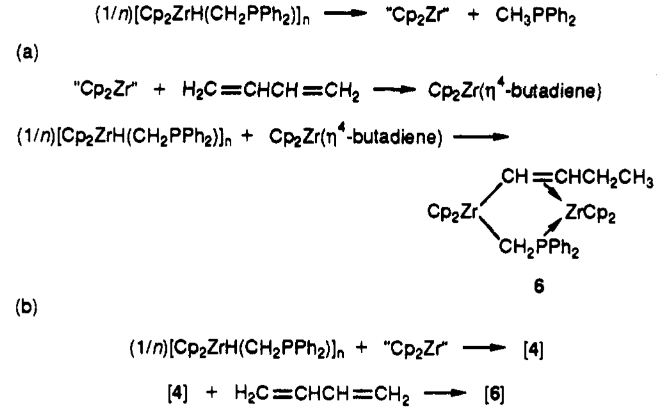
In the presence of a monoolefin such as 1-hexene, **1** reacts slowly at room temperature in C_6D_6 to give a homogeneous solution analyzed by ^1H and ^{31}P NMR as $Cp_2Zr(n\text{-hexyl})(CH_2PPh_2)$ (**5**) (^1H NMR: δ(Cp) = 5.84 ppm, ^{31}P NMR: δ = −5.4 ppm). The formation of the linear hexyl group is confirmed by its conversion into n-heptanal (characterized by GC), obtained conventionally via CO insertion into the metal–alkyl bond and hydrolysis. Complex **5** synthesized in situ from **1** and 1-hexene (1 equiv) in a sealed tube develops within a few days at room temperature or within 1 h at 80 °C a red paramagnetic solution in which **3** is identified by ESR. The ^1H NMR analysis of the solution shows the disappearance of the Cp signal attributed to **5** (no ^{31}P resonance is observed) and

Scheme IV

$$(1/n)[Cp_2ZrH(CH_2PPh_2)]_n + \text{1-hexene} \longrightarrow \underset{\mathbf{5}}{Cp_2Zr(n\text{-hexyl})(CH_2PPh_2)}$$

$$(1/n)[Cp_2ZrH(CH_2PPh_2)]_n + \text{1-hexene} \longrightarrow 3 + \text{hexane} + \text{1-hexene}$$

Scheme V



Scheme VI

$$(1/n)[Cp_2ZrH(CH_2PPh_2)]_n \longrightarrow \text{"}Cp_2Zr\text{"} + CH_3PPh_2$$

$$\text{"}Cp_2Zr\text{"} + 2PhC{\equiv}CPh \longrightarrow Cp_2Zr(C_4Ph_4)$$

the formation of new peaks identified as 1-hexene and n-hexane by GC analysis (Scheme IV).

The same reaction is observed with **1** and cyclohexene or 1,3-COD and affords, monitored by ^1H NMR and ESR techniques in a sealed tube, **3** and a mixture of cyclohexene/cyclohexane or cyclobutane/cyclooctane (identified by GC), but no formation of the cyclohexylzirconium(IV) species is detected during the course of the reaction. The same scheme as Scheme IV could be drawn, and the alkylzirconium species are presumably far too unstable for their observation.

We recently reported[16] the reaction with **1** and butadiene leading to the homodimetallic [Zr(IV)–Zr(II)]species [$Cp_2Zr(\mu\text{-}CH_2PPh_2)(\mu\text{-}CH{=}CHCH_2CH_3)ZrCp_2$], **6**. In light of the above results, we can now rationalize the formation of **6**. The release of PPh_2Me in the reaction implies the reductive elimination of the phosphine and generation of Cp_2Zr, which can be trapped (i) by the butadiene to give the formation of the well-known $Cp_2Zr(\eta^4\text{-butadiene})$ complex (Scheme Va) or (ii) by **1** to give **4** (Scheme Vb).

Confirmation of Scheme Va comes from the direct reaction between **1** and $Cp_2Zr(\eta^4\text{-butadiene})$, a source of zirconocene species[17] leading to **6** without evolution of PPh_2Me.[16]

Alkynes are also well-known to trap Cp_2Zr zirconocene species and to give a large variety of zirconacyclopentadiene complexes.[18] The reaction of **1** with PhC≡

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CPh follows this scheme and gives $Cp_2Zr(C_4Ph_4)$, identified by ^1H and ^{13}C NMR by comparison with an authentic sample, and free PPh_2Me (Scheme VI). The formation of a labile Zr(III) species, $Cp_2ZrH(PhC{\equiv}CPh)$ (g = 1.992, $a(^1H)$ = 5.5 G, $a(^{91}Zr)$ = 24 G), as a side product, is detected at the beginning of the reaction and disappears rapidly.[1a]

Concluding Remarks

We demonstrate that, considering the different works on Cp_2ZrHR, the hydridozirconium complex **1** has a classic sequence of decomposition via the reductive elimination of phosphine PPh_2Me and the formation of the zirconocene intermediate Cp_2Zr, which may be trapped by butadiene or diphenylacetylene. Although these mechanistic schemes are based upon indirect proof, an intermediate Zr(IV)–Zr(II) binuclear hydride, $[Cp_2Zr(\mu\text{-}H)(\mu\text{-}CH_2PPh_2)ZrCp_2]$, **4**, is postulated. Complex **4** could play an important role toward the selective catalytic hydrogenation of 1,5- or 1,3-cyclooctadiene in cyclooctene and is a good candidate to explain the reactivity we previously observed with diolefins[10b] and $PhC{\equiv}CPh$[10a,19] in catalysis.

Experimental Section

General Methods. All manipulations were carried out using high-vacuum-line and Schlenk techniques. Solvents were purified from sodium benzophenone ketyl under argon and degassed before use. ^1H and ^{31}P NMR spectra were recorded on Bruker WH90 and WM200 spectrometers. The GC tests were performed on an Intersmat IGC 121 apparatus. ESR spectra were recorded on a Bruker ER200 T spectrometer, equipped with a 200-W Oriel Hg lamp and an optic fiber for the transmission in the X cavity. The photolysis reactions were conducted with a 200-W Hanovia medium-pressure vapor photochemical lamp.

Several reactions were carried out in sealed NMR tubes and monitored by NMR as well as ESR spectroscopy. A glovebox (V.A.C.) was used for preparative works in NMR tubes.

The zirconium complexes $Cp_2ZrCl(CH_2PPh_2)$,[13] $Cp_2Zr(Ph_2)$,[2] $Cp_2Zr(C_4Ph_4)$,[18] and $Cp_2Zr(\eta^4\text{-butadiene})$[17] were prepared according to literature procedures. Elemental analyses were performed by the Service Central de Microanalyse du CNRS.

Preparation of $[Cp_2ZrH(CH_2PPh_2)]_n$, 1. To a solution of $Cp_2ZrCl(CH_2PPh_2)$ (3.5 g, 76.8 mmol) in 20 mL of THF was added a slight excess of $LiAlH(OCMe_3)$ (2.34 g, 92.1 mmol) in 20 mL of THF (or 1.5 mL of $NaAlH_2(OCH_2CH_2OMe)_2$ (70% in toluene)). The mixture was stirred for 1 day at room temperature and the white precipitate filtered and washed several times with THF (3 × 20 mL). Yield 60%. Anal. Calcd for $C_{23}H_{23}PZr$: C, 65.52; H, 5.46; Zr, 21.65. Found: C, 65.42; H, 5.40; Zr, 21.70.

The procedure described above was used to synthesize $[Cp_2ZrD(CH_2PPh_2)]_n$ and deuterated $[(C_5D_5)_2ZrD(CH_2PPh_2)]_n$ from $LiAlD(OCMe_3)$ and Cp_2ZrCl_2 or $(C_5D_5)_2ZrCl_2$, respectively.

Chemical Reduction of 1 with Na(np). To **1** (70 mg, 16.6 mmol) in 0.5 mL of THF was added 1.5 equiv of a freshly prepared green solution of sodium naphthalenide (Na(np)) dropwise via a syringe and the final red-brown solution transferred in a NMR tube, sealed, and monitored by ESR and ^1H and ^{31}P NMR.

Thermolytic or Photolytic Experiments. A NMR tube (or a quartz ESR tube) containing a weighted amount of **1** with or without substrate was filled with deuterated or undeuterated solvant (THF, toluene, benzene). The NMR tube was then sealed and the reaction monitored by ^1H NMR and ESR techniques. For example, **1** (95 mg, 22.5 mmol) was introduced in a NMR tube and 0.6 mL of C_6D_6 was added. The tube was sealed and heated with a sand bath at 60 °C. ^1H and ^{31}P NMR and ESR spectra were monitored from time to time to follow the evolution of the reaction.

Reaction of 1 with $Cp_2Zr(Ph)_2$. **1** (70 mg, 16.6 mmol) and $Cp_2Zr(Ph)_2$ (63 mg, 16.6 mmol) were introduced with 0.5 mL of C_6D_6 in a NMR tube. The tube was sealed, and the mixture was photolyzed and monitored by ^1H NMR and ESR from time to time. The cyclopentadienyl ligand signal of $Cp_2Zr(Ph)_2$ (δ = 6.12 ppm) decreased within a few hours with the appearance of PPh_2Me and bibenzyl, while paramagnetic signals for **2** and **3** appeared. PhPh was characterized by GC analysis.

Reactivity of 1 with 1-Hexene. **1** (185 mg, 43.9 mmol) and an excess of 1-hexene (74 mg, 88.0 mmol) were mixed together in THF. After stirring until the disappearance of insoluble **1**, evaporation of the solvant afforded an oily product, analyzed by ^1H and ^{31}P NMR (^1H: δ = 5.84 ppm; the resonance of the methylene group of CH_2PPh_2 was not observed, overlapped by the hexyl ligand, ^{31}P: δ = −5.4 ppm). Addition of CO followed by hydrolysis gave *n*-heptanal at the only product (GC analysis). The same experiment was repeated in a NMR tube (**1**: 85 mg, 20.1 mmol, 1-hexene:. 17 mg, 20.0 mmol) and monitored by ^1H NMR and ESR. After 1 h at 80 °C, $Cp_2Zr(\eta^2\text{-}CH_2PPh_2)$ was identified by ESR. The tube was broken, and GC analysis showed the presence of 1-hexene and hexane.

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Registry No. 1, 96645-33-9; 2, 86569-04-2; 3, 87184-10-9; $Cp_2ZrCl(CH_2PPh_2)$, 74380-49-7; $[Cp_2ZrD(CH_2PPh_2)]$, 141438-68-8; $[(C_5D_5)_2ZrD(CH_2PPh_2)]$, 141438-69-9; $(C_5D_5)_2ZrCl_2$, 141438-70-2; Cp_2ZrCl_2, 1291-32-3; $CpZr(\eta^2\text{-}CH_2PPh_2)_2$, 141438-71-3; $Cp_2Zr(Ph)_2$, 51177-89-0; 1,3-COD, 1700-10-3; $Cp_2Zr(\eta^4\text{-butadiene})$, 75374-50-4; $PhC{\equiv}CPh$, 501-65-5; $Cp_2Zr(C_4Ph_4)$, 53433-58-2; $Cp_2ZrH(PhC{\equiv}CPh)$, 96645-38-4; 1-hexene, 592-41-6; cyclohexene, 110-83-8.

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