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REACTIONS OF $Cp_2M(CO)_2$ AND $Cp_2M(CO)(PPh_3)$ (M = Zr, Hf) WITH ACETYLENES: FORMATION OF SOME METALLACYCLOPENTADIENE COMPLEXES OF ZIRCONOCENE AND HAFNOCENE

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Summary

The photolysis of $Cp_2Zr(CO)_2$ with diphenylacetylene or 3-hexyne yields the respective zirconacyclopentadiene complexes $Cp_2Zr(C_4R_4)$ (R = Ph, Et). The thermolysis of $Cp_2Zr(CO)_2$ with 3-hexyne or bis(pentafluorophenyl)acetylene also leads to the formation of $Cp_2Zr(C_4R_4)$ (R = Et, C_6F_5). HCl degradation of $Cp_2Zr[C_4(C_6F_5)_4]$ yields 1,2,3,4-tetrakis(pentafluorophenyl)-1,3-butadiene and Cp_2ZrCl_2. When $Cp_2Zr(CO)_2$ is heated with diphenylacetylene in a closed vessel, tetraphenylcyclopentadienone is formed along with $Cp_2Zr(C_4Ph_4)$. The hafnacyclopentadiene complexes $Cp_2Hf(C_4R_4)$ (R = Ph, C_6F_5, Et) are obtained when $Cp_2Hf(CO)_2$ is thermolyzed with the respective acetylene in refluxing octane. Complexes $Cp_2Hf(C_4R_4)$ (R = Ph, Et) are also formed when $Cp_2Hf(CO)_2$ is photolyzed with diphenylacetylene or 3-hexyne, respectively. The monocarbonyl-triphenylphosphine complexes $Cp_2M(CO)(PPh_3)$ (M = Zr, Hf) can be prepared via the irradiation of hydrocarbon solutions of $Cp_2M(CO)_2$ and triphenylphosphine. These complexes react readily with diphenylacetylene and 3-hexyne at 55–60 °C to afford the corresponding metallacyclopentadiene complexes $Cp_2M(C_4R_4)$ (M = Zr, Hf; R = Ph, Et). The metallocene dicarbonyls $Cp_2M(CO)_2$ (M = Zr, Hf) are readily prepared via the reduction of Cp_2MCl_2 (M = Zr, Hf) with amalgamated magnesium metal in THF solution under one atmosphere of carbon monoxide.

Introduction

While bis(η^5-cyclopentadienyl)dicarbonyltitanium has enjoyed a relatively extensive chemistry regarding its reactions with both acetylene and phosphine ligands [1–10], corresponding reactions involving bis(η^5-cyclopentadienyl)dicarbonylzirconium and -hafnium have remained relatively obscure [8,11]. As part of our continuing program regarding the chemistry of Group IVB $Cp_2M(CO)_2$ complexes (M = Ti, Zr, Hf) [4,5,9–11], we now report on both thermally and photochemically

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induced reactions of the metallocene dicarbonyls $Cp_2M(CO)_2$ (M = Zr, Hf) as well as the metallocene monocarbonyl-triphenylphosphine complexes $Cp_2M(CO)(PPh_3)$ (M = Zr, Hf) with various acetylenes. We also describe new, convenient syntheses for $Cp_2Zr(CO)_2$ and $Cp_2Hf(CO)_2$ along with photochemical preparations of $Cp_2Zr(CO)(PPh_3)$ and $Cp_2Hf(CO)(PPh_3)$.

Results and discussion

Since the first report in 1961 of a metallacyclopentadiene complex of a Group IVB metal, namely, 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylzirconacyclopentadiene (I) [12], various new methods for the preparation of this and related zirconacycles have appeared in the literature. Common to all these preparations is the reaction of two acetylene molecules with a zirconocene precursor. Table 1 gives a summary of such preparations. In contrast to the numerous methods of preparation and variety of acetylenes used for the synthesis of zirconacyclopentadienes, only one hafnacyclopentadiene complex has so far been described in the literature. Rausch et al. have prepared 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylhafnacyclopentadiene (II) via the photolysis of Cp_2HfMe_2 with diphenylacetylene [14,15] and by the photolysis or thermolysis of $Cp_2Hf(CO)_2$ with diphenylacetylene [11]. In this paper, we report the details of the latter syntheses, together with the preparations of two new hafnacyclopentadienes, 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraethylhafnacyclopentadiene (III) and 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetrakis(pentafluorophenyl)hafnacyclopentadiene (IV). We have also found that 1,1-bis(η^5-cyclopentadienyl)tetraethylzirconacyclopentadiene (V) can be prepared both photochemically or thermally from $Cp_2Zr(CO)_2$ and EtC≡CEt. Irradiation of a benzene solution of $Cp_2Zr(CO)_2$ with PhC≡CPh leads to formation of the zirconacyclopentadiene (I). A new zirconacycle, 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetrakis(pentafluorophenyl)zirconacyclopentadiene (VI) results from the thermolysis of $Cp_2Zr(CO)_2$ and bis(pentafluorophenyl)acetylene in refluxing heptane.

TABLE 1

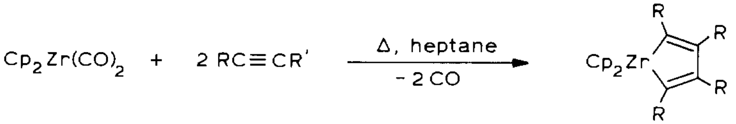
SYNTHETIC ROUTES TO ZIRCONACYCLOPENTADIENES

Complex	Zirconocene precursor	Acetylene	Ref.
$Cp_2Zr(C_4Ph_4)$	Cp_2ZrCl_2 [a]	PhC≡CPh	13
	Cp_2ZrMe_2 [b]		14,15
	$Cp_2Zr(CO)_2$ [c]		8
	Cp_2ZrCl_2 [d]		16
$(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4Ph_4)$	$[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu(H)]_2$ [c]	PhC≡CPh	17
$Cp_2Zr(C_4Ph_2H_2)$	$Cp_2Zr(CO)_2$ [c]	PhC≡CH	8
	Cp_2ZrPh_2 [b]		18
$Cp_2Zr(C_4Et_4)$	$Cp_2Zr(Me)(H)$ [c]	EtC≡CEt	19
	$Cp_2Zr(PMePh_2)_2$ [e]		20,21
	Cp_2ZrCl_2 [d]		16
$Cp_2Zr(C_4Me_4)$	Cp_2ZrCl_2 [d]	MeC≡CMe	16
$Cp_2Zr[C_4Me_2(\text{iso-Pr})_2]$	$Cp_2Zr(Me)(H)$ [c]	$MeC{\equiv}CCHMe_2$	19
$Cp_2Zr[C_4(SiMe_3)_2H_2]$	Cp_2ZrPh_2 [b]	$Me_3SiC{\equiv}CH$	18
$Cp_2Zr[C_4(CMe_3)_2H_2]$	Cp_2ZrPh_2 [b]	$Me_3CC{\equiv}CH$	18

[a] Addition of sodium naphthalenide. [b] Photochemically induced. [c] Thermally induced. [d] Addition of $Mg/HgCl_2$. [e] Room temperature.

Of the early transition metals, the Group IVB metals appear to exhibit the greatest propensity toward the formation of metallocene-containing metallacyclopentadiene complexes on reaction with acetylenes, in contrast to the Group VB and VIB metals, which almost exclusively tend to form metallocene-monoacetylene complexes [22–25]. Only recently has the first acetylene-derived metallacyclopentadiene complex of a Group VB metal been reported *. Irradiation of a toluene solution of Cp_2NbH_3 and $CF_3C{\equiv}CCF_3$ led to the formation of 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetrakis(trifluoromethyl)niobacyclopentadiene [26]. To the best of our knowledge, no bis(η^5-cyclopentadienyl)-metallacyclopentadiene complexes have been reported for Group VIB metals, although several novel bimetallacyclopentadiene complexes of these metals have recently been described [28–30].

Based on the studies of Demerseman et al. [8] and ours presented here, it appears that the thermolysis of $Cp_2Zr(CO)_2$ with various acetylenes provides a general route to the corresponding zirconacyclopentadienes. The tetraethyl derivative exhibited spectral properties similar to those previously reported [19]. The new zirconacyclopentadiene (VI) was formed in 74% yield as a lemon yellow solid, and was characterized by its spectral properties, elemental analysis, and its hydrogen chloride degradation products. Complex VI exhibits a sharp singlet in the ^1H NMR spectrum at δ 6.52 ppm (acetone-d_6) assignable to the cyclopentadienyl protons, while the mass spectrum shows a parent ion at m/e 936. The compound, while insoluble in aliphatic and aromatic solvents, exhibits good solubility in ethyl ether and in acetone. It gradually decomposes on exposure to air (most probably hydrolysis due to moisture). Further structural information was obtained by the degradation of VI with hydrogen chloride in ethyl ether solution. Zirconocene dichloride was identified by ^1H NMR as the only organometallic product, while the only isolable organic product was characterized by elemental analysis and its mass spectrum (M^+, m/e 718) as 1,2,3,4-tetrakis(pentafluorophenyl)-1,3-butadiene (VII).



(I, R = R' = Ph,
Ia, R = Ph, R' = H (or R = H, R' = Ph) [8]
V, R = R' = Et (this work),
VI, R = R' = C_6F_5(this work))

In an attempt to prepare the tetramethylzirconacyclopentadiene complex, a heptane solution of $Cp_2Zr(CO)_2$ and 2-butyne (b.p. 27 °C) was heated to 100 °C. Unlike the previous thermolyses, however, this reaction was performed in a closed vessel due to the low boiling point of 2-butyne. The resulting product was found not to be the zirconacycle, but rather a presently uncharacterized compound, which possessed a complex ^1H NMR spectrum, ketonic bands in the IR spectrum, and zirconocene and tetramethylcyclopentadienone fragments in the mass spectrum.

Based on this observation, $Cp_2Zr(CO)_2$ and diphenylacetylene were similarly thermolyzed in a sealed vessel. In addition to the formation of the zirconacycle I, a

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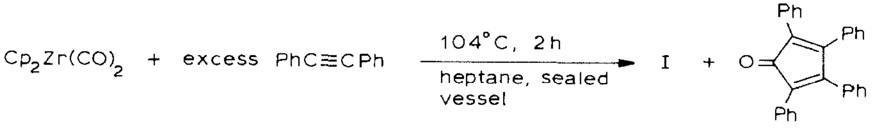
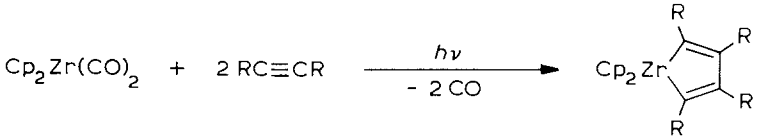
* Teuben et al. have prepared $Cp_2V(C_4Ph_4)$ via Cp_2VCl_2 and 1,4-dilithiotetraphenylbutadiene [27].

significant amount (20%) of tetracyclone could also be isolated.



Such an observation, while common to metal carbonyl/acetylene interactions [31–34], is significant here since it represents the first example of unsaturated cyclic ketone formation from a Group IVB metal carbonyl/acetylene reaction. In contrast, tetracyclone is not observed when $Cp_2Zr(CO)_2$ and diphenylacetylene are thermolyzed in an open reflux system at similar temperatures [8] *. Under the latter reaction conditions, the orange crystalline tetraphenylzirconacyclopentadiene precipitates from the refluxing reaction mixture over the course of a few hours. In the closed system, precipitation of the purple tetracyclone is observed. Suppression of CO evolution in the closed system may promote the formation of a zirconacyclobutenone intermediate. Similar complexes have been postulated as intermediates to cyclopentadienones and cyclopentadienonemetal complexes [32,35]. When $Cp_2Zr(CO)_2$ and bis(pentafluorophenyl)acetylene were thermolyzed in a closed reaction system, the zirconacyclopentadiene complex (VI) was identified in the ^1H NMR spectrum, but no perfluorotetracyclone could be detected.

We have also found that labilization of the carbon monoxide ligands of $Cp_2Zr(CO)_2$ by photochemical means in the presence of diphenylacetylene or 3-hexyne leads to the respective zirconacyclopentadienes I and V. While yields of



(I, R = Ph,
V, R = Et)

complex I are comparable by either the thermal or photochemcial route, substantially higher yields of complex V can be obtained via thermolysis (77 vs. 45%). Also, a drier and more tractable product is obtained by the thermal preparation.

In 1974, Rausch and Alt described the formation of the hafnacyclopentadiene II via the photolysis of Cp_2HfMe_2 and diphenylacetylene [14,15]. In 1979, we subsequently reported in communication form the formation of II via the thermolysis or photolysis of $Cp_2Hf(CO)_2$ with diphenylacetylene [11]. Since that time, we have extended the thermal method to include the new complexes 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraethylhafnacyclopentadiene (III) and 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetrakis(pentafluorophenyl)hafnacyclopentadiene (IV). Similarly, the irradiation of a heptane solution of $Cp_2Hf(CO)_2$ and 3-hexyne leads to the forma-

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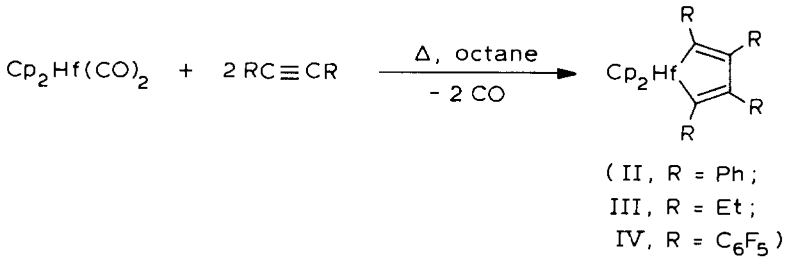
* The molar ratio of $Cp_2Zr(CO)_2$ to diphenylacetylene in ref. 8 was 1/2. Since the ratio of $Cp_2Zr(CO)_2$ to diphenylacetylene in our closed vessel experiment was 1/4, we ran a reaction according to the conditions in ref. 8 but with a 1/4 molar ratio. We obtained the same results as in ref. 8 (see Experimental section).



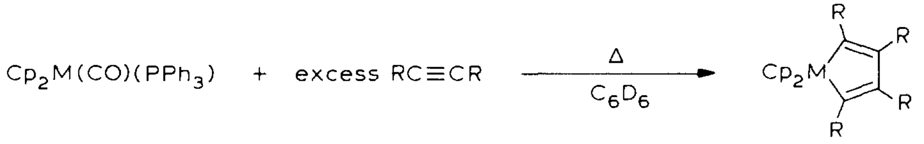
tion of III. Like the zirconium analogues, the yields of the tetraphenylhafnacyclopentadiene II are comparable by either the thermal or photochemical route, although substantially higher yields and a more tractable tetraethylhafnacyclopentadiene are obtained by thermolysis (74 vs. 42%).

The new complexes III and IV were characterized by their respective ^{1}H NMR and mass spectra, and by elemental analysis. The tetraethyl derivative is golden-yellow like its tetraphenyl counterpart II, and can be readily sublimed at 70 °C/10^{-2} Torr. It exhibits a sharp singlet in C_6D_6 at δ 5.87 ppm, assignable to the ten equivalent cyclopentadienyl protons. The inequivalent methylene protons are observed as overlapping quartets extending from δ 2.62 to 2.05 ppm (8H, J(H–H) 7.5 Hz), while the inequivalent methyl protons appear as overlapping triplets extending from δ 1.08 to 0.74 ppm (12H, J(H–H) 7.5 Hz). The mass spectrum shows a parent ion at m/e 474 together with fragments at m/e 392 and m/e 310 due to successive losses of 3-hexyne. The hydrolytic sensitivity of this complex requires storage in an inert atmosphere.

The tawny-colored perfluorinated phenyl complex IV, like its zirconium analogue VI, is readily soluble in diethyl ether and acetone, but insoluble in aliphatic and aromatic solvents. Its ^{1}H NMR spectrum (acetone-d_6) shows a sharp singlet at δ 6.67 assignable to the ten equivalent cyclopentadienyl protons, while the mass spectrum exhibits a parent ion at m/e 1026. On prolonged exposure to the atmosphere, complex IV turns white. The hafnacyclopentadiene structure is assigned to IV based on its spectral similarities to VI and the method of preparation, which in all other cases has led to metallacyclopentadiene formation.

While we have no evidence for intermediates leading to the described metallacyclopentadiene complexes, one could postulate successive substitution of the carbonyl ligands by the acetylene, resulting in the respective complexes $Cp_2M(CO)(\eta^2\text{-}RC{\equiv}CR)$ and $Cp_2M(\eta^2\text{-}RC{\equiv}CR)_2$ (M = Zr, Hf). Oxidative coupling in the bis(π-acetylene) complex would lead to the observed metallacyclopentadienes. In this regard, $Cp_2Ti(CO)(\eta^2\text{-}PhC{\equiv}CPh)$ has been shown to be an intermediate in the formation of 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenyltitanacyclopentadiene [2,3].

Based on our recent studies concerning the formation of various monocarbonyl-η^2-acetylene complexes of titanocene derived from $Cp_2Ti(CO)(PR_3)$ (R = Et, Ph) and the appropriate acetylene [10,36], we treated the metallocene carbonyl-phosphine complexes $Cp_2M(CO)(PPh_3)$ (M = Zr (VIII); M = Hf (IX)) [11] with diphenylacetylene and with 3-hexyne in hopes of detecting an elusive $Cp_2M(CO)(\eta^2\text{-}RC{\equiv}CR)$ complex (M = Zr, Hf). However, NMR tube reactions of the above showed only the disappearance of the carbonyl-phosphine cyclopentadienyl doublet with concurrent appearance of the cyclopentadienyl singlet due to the corresponding metallacyclopentadiene.



(VIII, M = Zr,
IX, M = Hf)

(I, M = Zr, R = Ph,
V, M = Zr, R = Et,
II, M = Hf, R = Ph,
III, M = Hf, R = Et)

Unlike the titanium analogues, no instantaneous reactions occurred on mixing VIII or IX with diphenylacetylene of 3-hexyne, as indicated by a lack of color change in the solution and by the absence of any new cyclopentadienyl resonances in the ^1H NMR spectrum. Based on these observations, the solutions were heated. Complex VIII on heating with either diphenylacetylene or 3-hexyne at 55 °C changed color from dark red to orange within 15 min. The ^1H NMR spectrum at this time showed a singlet corresponding to the cyclopentadienyl protons of the respective zirconacyclopentadiene. On heating IX with either of these acetylenes at 60 °C for 15 min, the cyclopentadienyl doublet remained unchanged and no new cyclopentadienyl resonances appeared. On further heating at 60 °C, the color of the solution lightened and gas evolution was observed. A spectrum recorded after 45 min showed resonances corresponding to both IX and the hafnacyclopentadiene. Schwartz and Gell have similarly reported that they were unable to observe in the ^1H NMR spectrum the postulated intermediate $Cp_2Zr(PPh_2Me)(\eta^2\text{-}EtC{\equiv}CEt)$ in the formation of V from the reaction of $Cp_2Zr(PPh_2Me)_2$ and EtC≡CEt [21].

Qualitatively, however, the monocarbonyl-triphenylphosphine complexes of zirconocene and hafnocene appear more reactive toward acetylenes than do the corresponding dicarbonyl complexes $Cp_2M(CO)_2$ (M = Zr, Hf). In this regard, when a C_6D_6 solution of $Cp_2Hf(CO)_2$ and diphenylacetylene of similar concentration to that of the $Cp_2Hf(CO)(PPh_3)$/diphenylacetylene mixture was heated in an NMR tube for 3.0 h at 60 °C, no resonance for the hafnacyclopentadiene II could be detected, nor was there any change in the intensity of the cyclopentadienyl proton singlet due to $Cp_2Hf(CO)_2$.

Studies on the photochemical behavior of $Cp_2Zr(CO)_2$ and $Cp_2Hf(CO)_2$ in aliphatic solvents have also been conducted. The irradiation of $Cp_2M(CO)_2$ (M = Zr, Hf) in heptane resulted in gas evolution, a lightening of the color of the solution, and the deposition of light brown (Zr) or yellow (Hf) precipitates which were usually found to be pyrophoric. These precipitates were moderately soluble in benzene, giving red solutions. After a short time, however, the benzene solutions also produced solid precipitates which could not be redissolved. The solutions exhibit similar ^1H NMR spectra in that they both (Zr and Hf) show a broad unresolvable resonance centered at ca. δ 6.20 ppm. The $Cp_2Zr(CO)_2$ photoproduct frequently exhibited a singlet at δ 6.22 ppm emerging out of the broad resonance. These resonances are assignable to cyclopentadienyl protons. The IR spectrum (Nujol) of these precipitates do not exhibit any absorptions in the vicinity of 1250 cm^{-1} which could be attributed to bridging metal hydrides [37], but do exhibit strong bands at ca. 780 and 1005 cm^{-1}, consistent with a metallocene-type structure [38]. These spectra appear to be very similar to those of the photodegradation products of $Cp_2M(CH_3)_2$ (M = Zr, Hf) [15,39]. One very notable spectral feature of the photochemically-generated precipitate from $Cp_2Hf(CO)_2$, absent in the spectrum of the zirconium product, is the presence of a strong, sharp band at 2055 cm^{-1} which is tentatively assigned as a terminal metal carbonyl stretching frequency. These precipitates are probably best described as oligomeric forms of zirconocene and hafnocene.

The photolyses of $Cp_2Zr(CO)_2$ or $Cp_2Hf(CO)_2$ with triphenylphosphine in aliphatic solvents invariably led to generation of the aforementioned precipitates together with formation of small dark red crystals and a change in the color of the solution to red-orange. Workup of these reactions resulted in $Cp_2Zr(CO)(PPh_3)$ (VIII) and $Cp_2Hf(CO)(PPh_3)$ (IX) in yields of 28 and 31%, respectively. The moderate yields of these products can be attributed in part to the competing photodecomposition of $Cp_2Zr(CO)_2$ and $Cp_2Hf(CO)_2$ with the desired photo-induced substitution processes.

Phosphine complexes VIII and IX are both extremely air-sensitive and turn pale yellow on such exposure. Both exhibit doublets in their ^1H NMR spectra at δ 4.93 and 4.75 ppm ($J(H-P)$ 1.8 Hz), respectively, assignable to the cyclopentadienyl protons coupled with the ^{31}P nucleus. Their IR spectra in THF show low frequency metal carbonyl bands at 1842 and at 1830 cm^{-1}, respectively.

During the course of this research program, we also investigated new synthetic routes to $Cp_2M(CO)_2$ (M = Zr, Hf), since we found existing syntheses to be of low yield, producing only very small amounts of material [40], or requiring high pressure equipment [41,42]. Our new, facile route involves the reduction of the commercially available metallocene dichlorides Cp_2ZrCl_2 and Cp_2HfCl_2 with amalgamated magnesium under one atmosphere of CO pressure [43].

$$Cp_2MCl_2 + Mg/HgCl_2 + 2CO \xrightarrow[\text{THF, 1 atm}]{25\,^\circ\text{C, 24 h}} Cp_2M(CO)_2 + MgCl_2$$

(M = Zr, Hf)

The yields are reasonably good (Zr, 53%; Hf, 30%) and the preparations give ample amounts of product for further investigations. The ^1H NMR, IR, and mass spectra are in accord with those previously reported [40].

Experimental

All manipulations of air-sensitive compounds were performed under a purified argon atmosphere using Schlenk techniques. The argon was dried with H_2SO_4 and P_2O_5, while trace amounts of oxygen were removed by means of a heated BTS catalyst column. Pentane, hexane, heptane, octane, benzene, and toluene were dried over calcium hydride and freshly distilled prior to use. Diethyl ether was predried over sodium wire and finally distilled under argon from the sodium ketyl of benzophenone. The tetrahydrofuran (THF) was predried over potassium hydroxide flakes, dried further over sodium wire, and then finally distilled under argon from the sodium ketyl of benzophenone. CAMAG neutral grade alumina was heated under high vacuum on a rotary evaporator for 2 h and then allowed to cool to room temperature under an argon atmosphere. Five percent by weight of degassed, distilled water was added to the alumina, and the flask was shaken until no clumping was observed. All photolyses were performed in water-jacketed Pyrex Schlenk tubes using a 250-W G.E. sunlamp. Cp_2ZrCl_2 was purchased from Arapahoe Chemical Co. while Cp_2HfCl_2 was prepared by a literature method [44] and recrystallized from hot toluene. Diphenylacetylene [45] and bis(pentafluorophenyl)acetylene [46] were prepared by literature methods, and 3-hexyne and 2-butyne were purchased from the Farchan Division of Chemsampco, Inc. Triphenylphosphine and tetracyclone were purchased from Eastman Kodak Co. Magnesium turnings were purchased from Fisher Scientific Co., while magnesium powder (RMC-50/100-UM) was obtained from Reade Manufacturing Co., Ridgeway Blvd., Lakehurst, NJ 08733. ^1H NMR spectra were recorded on a Varian A-60 spectrometer and all resonances are reported relative to an external TMS standard. In order to make accurate comparisons between the chemical shifts of various spectra, the C_6D_6 resonance at δ 7.20 ppm was used as an internal standard. IR spectra were recorded on a Beckman IR-10 or a Perkin–Elmer 237-B infrared spectrophotometer and were calibrated relative to the 1601 cm^{-1} band of polystyrene. Mass spectra were recorded by Mr. Eugene Guzik using a Perkin–Elmer Hitachi RMU-6L mass spectrometer. The most abundant isotopes (Zr = 90, Hf = 180) were used in calculations. Microanalyses were performed by the Microanalytical Laboratory, Office of of Research Services, University of Massachusetts, Amherst, MA 01003.

Preparation of $Cp_2Zr(CO)_2$

Bis(η^5-cyclopentadienyl)dichlorozirconium (2.00 g, 6.84 mmol) together with magnesium turnings (0.83 g, 34.1 mmol) and 50 ml of THF were placed into a 100-ml Schlenk tube and magnetically stirred. On dissolution of the Cp_2ZrCl_2, mercuric chloride (1.85 g, 6.81 mmol) was added to the mixture, at which time carbon monoxide was allowed to flow slowly over the solution through the side-arm stopcock and out to a mercury-filled overpressure valve. The solution was stirred in the CO atmosphere for 24 h at room temperature, during which time the solution changed from colorless to dark green and finally to dark red. The reaction vessel was then flushed with argon and the solution poured into a fritted funnel containing a plug (3 × 10 cm) of 5% deactivated alumina covered with 1.5 cm of sea sand. The plug was eluted with pentane until the eluate was colorless. It should be noted that the dark red solution appears green when passing through the alumina, and on exiting appears dark reddish-green, depending on how the solution is viewed. The THF/pentane solution was then concentrated to dryness, leaving a dark solid. The product was further purified by dissolving it in ca. 75 ml of hexane and passing the solution through another plug (3 × 5 cm) of 5% deactivated alumina. The plug was eluted with fresh hexane until the solution emerging from the fritted funnel was colorless. The hexane solution was then concentrated in vacuo until black needle-like crystals began to form. At this point, the solution was cooled to $-20\,^\circ C$, resulting in further crystal formation. The hexane was decanted from the crystals into another Schlenk tube and further concentrated and cooled. The resulting black crystal crops were dried under vacuum and combined, yielding 1.00 g (53%) of $Cp_2Zr(CO)_2$. IR (hexane): $\nu(CO)$ 1975, 1885 cm^{-1}; (THF) $\nu(CO)$ 1967, 1872 cm^{-1}. ^1H NMR (C_6D_6): δ (ppm) 4.95, s, C_5H_5.

Preparation of $Cp_2Hf(CO)_2$

Bis(η^5-cyclopentadienyl)dichlorohafnium (2.00 g, 5.27 mmol) together with magnesium powder * (0.50 g, 20.6 mmol) and 50 ml of THF were placed into a 100-ml Schlenk tube and magnetically stirred. On stirring, a deep narrow vortex is desirable (bubbling CO through the solution did not result in higher yields). This can be accompleshed with a small stir bar. On dissolution of the Cp_2HfCl_2, mercuric chloride (1.00 g, 3.68 mmol) was added to the mixture, at which time carbon monoxide was allowed to flow slowly over the solution throught the sidearm stopcock and out to a mercury-filled overpressure valve. The solution was stirred in the CO atmosphere for 24 h at room temperature, during which time the color changed from colorless to dark green and finally to dark red. The reaction vessel was then flushed with argon and the solution poured into a fritted funnel containing a plug (3 × 10 cm) of 5% deactivated alumina covered with 1.5 cm of sea sand. The plug was eluted with pentane until the eluate was colorless. The purple THF/pentane mixture was then concentrated to dryness, leaving a purple solid. The product was further purified by dissolving it in ca. 75 ml of hexane and passing this solution through another plug (3 × 5 cm) of 5% deactivated alumina. The plug was eluted with fresh hexane until the solution emerging from the fritted funnel was colorless. The hexane was then concentrated in vacuo until purple needle-like crystals began to form. At this point, the solution was cooled to $-20\,^\circ C$, resulting in additional crystal formation. The hexane was decanted from the crystals into another Schlenk tube and further concentrated and cooled. The resulting crystal crops were dried under vacuum and combined, yielding 0.58 g (30%) of $Cp_2Hf(CO)_2$. IR (hexane): $\nu(CO)$ 1969, 1878 cm^{-1}; (THF): $\nu(CO)$ 1960, 1861 cm^{-1}. ^1H NMR (C_6D_6): δ (ppm) 4.81, s, C_5H_5.

Photolysis of $Cp_2Zr(CO)_2$ with diphenylacetylene

A solution of $Cp_2Zr(CO)_2$ (0.44 g, 1.59 mmol) and diphenylacetylene (0.57 g, 3.20 mmol) in 130 ml of benzene was irradiated in a water-jacketed Schlenk tube with stirring for 3 h at 15 °C. The solution gradually turned orange with noticeable gas evolution observed at the oil bubbler. The benzene was then removed under reduced pressure, leaving an orange powder. In order to insure that any unreacted starting materials had been removed, the orange solid was washed with three 15-ml portions of hexane. After drying under high vacuum, 0.53 g (58%) of 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylzirconacyclopentadiene was obtained. An analytically pure sample was prepared by recrystallization of the product from a benzene/hexane mixture at room temperature. After 2 days, bright orange crystals appeared on the walls of the Schlenk tube. The solvent was decanted, and the crystals were washed with pentane and dried under high vacuum. (Found: C, 79.16; H, 5.33. $C_{38}H_{30}Zr$ calcd.: C, 78.98; H, 5.23%). ^1H NMR (C_6H_6): δ (ppm) 6.02, s, 10 H, C_5H_5; 6.60–7.14, m, 20 H, C_6H_5.

Thermolysis of $Cp_2Zr(CO)_2$ with bis(pentafluorophenyl)acetylene

A 100-ml, 3-necked flask was fitted with a condenser and gas inlet and outlet valves. Bis(η^5-cyclopentadienyl)dicarbonylzirconium (0.30 g, 1.08 mmol), bis(pentafluorophenyl)acetylene (0.80 g, 2.23 mmol), and 50 ml of heptane were added to the

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* The use of magnesium powder as opposed to magnesium turnings is essential for the success of this reaction. The use of magnesium powder for the preparation of $Cp_2Zr(CO)_2$, however, was found to result in lower yields of product.

flask with stirring. The solution was then heated to reflux for 3 h, during which time a lemon-yellow precipitate formed. The reaction mixture was cooled to room temperature and the heptane was carefully decanted from the precipitate. The latter was then washed with two 15-ml portions of hexane and dried under high vacuum, leaving 0.75 g (74%) of 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetrakis(pentafluorophenyl)zirconacyclopentadiene. An analytically pure sample was obtained by recrystallization of the product from diethyl ether at $-20\,°C$. (Found: C, 48.67; H, 1.33. $C_{38}H_{10}F_{20}Zr$ calcd.: C, 48.68; H, 1.07%). MS: *m/e* 936 (M^+), 716 [$(C_6F_5C{\equiv}CC_6F_5)_2{}^+$], 578 ($M - C_6F_5C{\equiv}CC_6F_5{}^+$), 358 ($C_6F_5C{\equiv}CC_6F_5{}^+$), 239 ($Cp_2ZrF^+$), 220 ($Cp_2Zr^+$), 193 ($CpZrF_2{}^+$). ^1H NMR (acetone-d_6): δ 6.52 ppm (s, C_5H_5). IR (KBr): 1510s, 1488s, 1109w, 1081w, 1018m, 987s, 931m, 884m, 809s cm^{-1}.

HCl degradation of $Cp_2ZrC_4(C_6F_5)_4$

Hydrogen chloride was bubbled through a 75-ml diethyl ether solution of 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetrakis(pentafluorophenyl)zirconacylopentadiene (1.20 g, 1.28 mmol) for ca. 10 min at room temperature, during which time the solution changed from yellow to colorless. After standing overnight at room temperature, white crystals precipitated from the solution. The solution was decanted into a 500-ml beaker and allowed to evaporate, leaving a brown gummy residue. Treatment of the residue with pentane yielded 20 mg of white crystals and a yellow solution. These crystals together with those initially obtained were washed with pentane and dried, giving a total weight of 1.15 g. A small amount of this material was dissolved in $CDCl_3$ and a ^1H NMR spectrum was recorded, which showed only a sharp singlet at δ 6.50 ppm assignable to Cp_2ZrCl_2. All of the white crystalline solid was then placed onto a dry-packed column of 5% deactivated alumina (20 × 1.5 cm) and eluted with 350 ml of acetone in order to separate the organic product from the Cp_2ZrCl_2 (the latter is not eluted). The acetone solution was allowed to slowly evaporate, during which time small white needles began to appear. When all the solvent had evaporated, the white crystals were washed with pentane and dried, leaving 0.49 g (53%) of 1,2,3,4-tetrakis(pentafluorophenyl)-1,3-butadiene. A ^1H NMR spectrum of this material in $CDCl_3$ showed that Cp_2ZrCl_2 was not present. No resonances assignable to the vinylic protons of the diene could be detected, however, this was not surprising since the product is virtually insoluble in $CDCl_3$ *. An analytically pure sample (m.p. 257–258 °C) was obtained by three successive sublimations at $180\,°C/10^{-3}$ Torr. (Found: C, 47.08; H. 0.22. $C_{28}H_2F_{20}$ calcd.: C, 46.82; H, 0.28%). MS: *m/e* 718 (M^+), 699 ($M - F^+$), 551 ($M - C_6F_5{}^+$), 360 [$(C_6F_5CH)_2{}^+$], 358 [$(C_6F_5C)_2{}^+$].

Thermolysis of $Cp_2Zr(CO)_2$ with 3-hexyne

A 50-ml, 3-necked flask was fitted with a condenser and gas inlet and outlet valves. Bis(η^5-cyclopentadienyl)dicarbonylzirconium (0.26 g, 0.94 mmol), 3-hexyne (0.79 g, 9.62 mmol), and 25 ml of heptane were added to the flask with stirring. The mixture was then heated to reflux for 3,5 h, after which time the solution was bright red and contained a small amount of precipitate. The mixture was filtered and the heptane was removed under reduced pressure, leaving a reddish-orange solid. The latter was dried under high vacuum overnight. yielding 0.28 g (77%) of 1,1-bis(η^5-

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* Note added in proof see page 37.

cyclopentadienyl)-2,3,4,5-tetraethylzirconacyclopentadiene. MS: m/e 384 (M^+). ^{1}H NMR (C_6D_6): δ 5.97 (s, 10H, C_5H_5), 2.07–2.57 (overlapping quartets, 8H, CH_2, J(H–H) 7.5 Hz), 0.80–1.15 ppm (overlapping triplets, 12H, CH_3, J(H–H) 7.5 Hz).

Photolysis of $Cp_2Zr(CO)_2$ with 3-hexyne

A 75-ml hexane solution of $Cp_2Zr(CO)_2$ (0.27 g, 0.97 mmol) and 3-hexyne (0.29 g, 3.53 mmol) was irradiated with stirring in a water-jacketed Schlenk tube for 2.5 h at 15 °C. During this time gas evolved and the solution color changed from dark red to orange. The reaction mixture was then filtered in order to remove oligomeric zirconocene, and the hexane was removed under reduced pressure, leaving a gummy, reddish-orange residue. This material was placed under high vacuum with slight heating (40–50 °C) for 24 h and then cooled at −20 °C for 2 days. The dry orange solid, 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraethylzirconacyclopentadiene, was isolated in 45% yield (0.17 g). The ^{1}H NMR spectrum (C_6D_6) was identical to that of the product obtained via thermolysis.

Thermolysis of $Cp_2Zr(CO)_2$ with diphenylacetylene in a closed vessel

Into a heavy-walled Schlenk tube equipped with a 15-mm threaded connector and nylon plug (Ace Glass) and a pressure stopcock (Eck and Krebs) were placed $Cp_2Zr(CO)_2$ (0.37 g, 1.33 mmol), diphenylacetylene (0.95 g, 5.33 mmol), and 20 ml of heptane. The tube was placed in an oil bath at 104 °C and heated for 2 h. During this time, the initial black solution had lightened to red with the formation of a purple precipitate. On cooling to room temperature, the red solution was decanted from the precipitate into a Schlenk tube. The precipitate was washed with two 10-ml portions of fresh heptane, and these portions were added to the original reaction solution. The purple precipitate was then dried under high vacuum and identified as tetracyclone (0.20 g, 20%) by comparison of its ^{1}H NMR, IR, and mass spectra with those of an authentic sample. The red heptane solution on standing at room temperature precipitated a brownish-orange solid, which was collected on a frit and dried, leaving 0.21 g of material. A ^{1}H NMR spectrum of the solid exhibited singlet resonances at δ 6.02 and 5.54 ppm in the ratio of ca. 2/1. The former resonance was readily assignable to 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylzirconacyclopentadiene while the latter resonance was not identified. The filtrate was taken to dryness under reduced pressure, leaving a yellow powder which was added to a dry-packed column of 5% deactivated alumina (20 × 1.5 cm). Elution with ca. 150 ml of pentane produced 0.28 g of diphenylacetylene corresponding to 29% of the original starting material.

Thermolysis of $Cp_2Zr(CO)_2$ with 4 equivalents of diphenylacetylene in an open system

A 50-ml, 3-necked flask was fitted with a condenser and gas inlet and outlet valves. Bis(η^5-cyclopentadienyl)dicarbonylzirconium (0.37 g, 1.33 mmol), diphenylacetylene (1.00 g, 5.61 mmol), and 19 ml of heptane were added to the flask with stirring. The mixture was then heated to reflux for 3.0 h, during which time a bright orange solid formed. On cooling to room temperature, the solution was decanted and the solid was washed once with a 10-ml portion of fresh heptane. After drying under high vacuum, 0.57 g (74%) of 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylzirconacyclopentadiene was obtained, as identified by its ^{1}H NMR spectrum. No tetracyclone could be detected and 0.55 g of diphenylacetylene was recovered.

Thermolysis of $Cp_2Zr(CO)_2$ with bis(pentafluorophenyl)acetylene in a closed vessel

Into a heavy-walled Schlenk tube equipped with a 15-mm threaded connector and nylon plug and a pressure stopcock were placed $Cp_2Zr(CO)_2$ (0.23 g, 0.83 mmol), bis(pentafluorophenyl)acetylene (1.20 g, 3.35 mmol), and 15 ml of heptane. The tube was placed in an oil bath and heated to 100 °C for 2.5 h, producing a brownish-yellow precipitate and a yellow solution. On cooling to room temperature, the solution was decanted from the precipitate into a Schlenk tube. The precipitate was washed with fresh heptane, and then dried under high vacuum. The washings were added to the original reaction solution and the heptane was removed under reduced pressure, leaving a pale yellow solid. A ^1H NMR spectrum of this solid in acetone-d_6 showed no distinct resonances. On subliming the material at 90 °C/10^{-2} Torr, 0.50 g (42%) of bis(pentafluorophenyl)acetylene was recovered. A ^1H NMR spectrum of the precipitate in acetone-d_6 exhibited a sharp singlet at δ 6.52 ppm due to 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetrakis(pentafluorophenyl)zirconacyclopentadiene. Also present in the spectrum was a broad resonance at δ 6.13–6.70 ppm. An IR spectrum of the product (KBr) showed no ketonic band at 1730 cm^{-1} [46,47], thus precluding the presence of 2,3,4,5-tetrakis(pentafluorophenyl)cyclopentadienone.

Thermolysis of $Cp_2Hf(CO)_2$ with diphenylacetylene

A 50-ml, 3-necked flask was fitted with a condenser and gas inlet and outlet valves. Bis(η^5-cyclopentadienyl)dicarbonylhafnium (0.41 g, 1.12 mmol), diphenylacetylene (1.00 g, 5.61 mmol), and 20 ml of octane were added to the flask with stirring. The mixture was then heated to reflux for 26 h, during which time a yellow solid precipitated from the solution. On cooling to room temperature, the solvent was decanted and the solid was washed once with 10 ml fresh octane. After drying under high vacuum, 0.51 g (68%) of 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylhafnacyclopentadiene was obtained. MS: m/e 666 (M^+), 488 ($M - PhC{\equiv}CPh^+$), 356 [$(PhC{\equiv}CPh)_2{}^+$], 310 (Cp_2Hf^+), 178 ($PhC{\equiv}CPh^+$). ^1H NMR (C_6D_6): δ 5.97 (s, 10H, C_5H_5), 6.60–7.15 (m, 20H, Ph). IR (KBr): 1588m, 1477m, 1435m, 1250w, 1069w, 1013m, 799s, 695s cm^{-1}.

Photolysis of $Cp_2Hf(CO)_2$ with diphenylacetylene

A 120-ml toluene solution of $Cp_2Hf(CO)_2$ (0.35 g, 0.96 mmol) and diphenylacetylene (0.35 g, 1.96 mmol) was irradiated with stirring in a water-jacketed Schlenk tube for 5 h at 15 °C. The purple solution gradually turned yellow with notable gas evolution. The toluene was removed under reduced pressure, leaving a yellow-brown oil which when triturated with hexane produced a yellow precipitate. The hexane was decanted, the yellow solid was further washed with fresh hexane, and finally it was dried under high vacuum. To insure complete removal of the starting materials, a cold finger sublimer equipped with a 24/40 ST female joint was inserted into the Schlenk tube, and the tube was heated to 70 °C under high vacuum. A small amount of diphenylacetylene appeared on the probe at the end of the sublimation period. The yellow solid, 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylhafnacyclopentadiene, was obtained in 52% yield (0.33 g), and could be readily recrystallized from a toluene/hexane solution at −20 °C. The spectral properties of this hafnacycle were identical to those of the thermally-produced product.

Thermolysis of $Cp_2Hf(CO)_2$ with bis(pentafluorophenyl)acetylene

A 50-ml, 3-necked flask was fitted with a condenser and gas inlet and outlet valves. Into the flask were placed $Cp_2Hf(CO)_2$ (0.41 g, 1.12 mmol), bis(pentafluorophenyl)acetylene (0.89 g, 2.49 mmol), and 30 ml of octane. The solution was heated to reflux with stirring for 34 h. During this time, the solution changed from purple to pale yellow, with formation of a light brown precipitate. On cooling to room temperature, the octane was syringed away from the product, which was subsequently washed with hexane and finally dried under high vacuum, leaving 0.82 g (71%) of 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetrakis(pentafluorophenyl)hafnacyclopentadiene. An analytically pure sample was obtained by recrystallization of the product from diethyl ether at $-20\,°C$. (Found: C, 44.38; H, 1.16. $C_{38}H_{10}F_{20}Hf$ calcd.: C, 44.53; H, 0.98%). MS: m/e 1026 (M^+), 716 [$(C_6F_5C{\equiv}CC_6F_5)_2{}^+$], 358 ($C_6F_5C{\equiv}CC_6F_5{}^+$), 348 ($Cp_2HfF_2{}^+$), 329 ($Cp_2HfF^+$), 310 ($Cp_2Hf^+$), 283 ($CpHfF_2{}^+$). ^1H NMR (acetone-d_6): δ 6.67 ppm (s, C_5H_5). IR (KBr): 1510s, 1485s, 1108w, 1078w, 1015m, 980s, 935m, 882m, 810s cm^{-1}.

Thermolysis of $Cp_2Hf(CO)_2$ with 3-hexyne

A 50-ml, 3-necked flask was fitted with a condenser and gas inlet and outlet valves. Bis(η^5-cyclopentadienyl)dicarbonylhafnium (0.27 g, 0.74 mmol), 3-hexyne (0.80 g, 9.74 mmol), and 25 ml of octane were added to the flask with stirring. The purple solution was then heated to reflux for 26 h, during which time the color gradually changed to yellow. On cooling to room temperature, the solution was filtered to remove a small amount of pale yellow precipitate. The resulting bright yellow filtrate was taken to dryness, leaving 0.26 g (74%) of 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraethylhafnacyclopentadiene. An analytically pure sample was obtained by three successive sublimations at $70\,°C/10^{-2}$ Torr. (Found: C, 55.64; H, 6.47. $C_{22}H_{30}Hf$ calcd.: C, 55.87; H, 6.39%). MS: m/e 474 (M^+), 392 ($M-EtC{\equiv}CEt^+$), 363 ($392-Et^+$), 310 (Cp_2Hf^+). ^1H NMR (C_6D_6): δ 5.87 (s, 10H, C_5H_5), 2.05–2.62 (overlapping quartets, 8H, CH_2, J(H–H) 7.5 Hz), 0.74–1.08 ppm (overlapping triplets, 12H, CH_3, J(H–H) 7.5 Hz). IR (KBr): 1437m, 1355w, 1162w, 1001s, 788s cm^{-1}.

Photolysis of $Cp_2Hf(CO)_2$ with 3-hexyne

A 45-ml heptane solution of $Cp_2Hf(CO)_2$ (0.11 g, 0.30 mmol) and 3-hexyne (0.10 g, 1.22 mmol) was irradiated with stirring in a water-jacketed Schlenk tube for 2.0 h at 15 °C. During this time, the solution changed from purple to yellow with noticeable gas evolution. The solution was then filtered and the heptane was removed under reduced pressure, leaving a gummy yellow residue. The residue was dried under high vacuum with slight heating (40–50 °C) for 24 h and was then finally cooled at $-20\,°C$ for 2 days. The product, 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraethylhafnacyclopentadiene, could be obtained as a yellow solid in 42% yield (0.06 g). The ^1H NMR spectrum (C_6D_6) was identical to that of the product obtained via thermolysis, however, an unidentified signlet at δ 5.72 ppm was occasionally observed.

Photolysis of $Cp_2Zr(CO)_2$ with triphenylphosphine

A 75-ml heptane solution of $Cp_2Zr(CO)_2$ (0.25 g, 0.90 mmol) and triphenylphosphine (0.50 g, 1.91 mmol) was irradiated with stirring in a water-jacketed Schlenk tube for 4.5 h at 15 °C. During this time, gas evolution was observed at the oil bubbler, and the solution changed to a bright red-orange color. A yellow-brown precipitate (oligomeric zirconocene), which also formed during this period, coated the walls of the vessel and was scraped free once every hour. The reaction mixture was then filtered, concentrated to ca. 50 ml, and cooled to −20 °C. The original photolysis vessel contained a small amount of $Cp_2Zr(CO)(PPh_3)$ which had precipitated on the vessel walls during the reaction. The vessel was therefore rinsed with cold hexane to remove any residual oligomeric zirconocene. The crystals of $Cp_2Zr(CO)(PPh_3)$ adhering to the walls of the vessel were then dried under high vacuum. The original reaction filtrate, on cooling at −20 °C overnight, deposited additional dark red crystals of product. The now pale yellow filtrate was decanted, and the crystals were washed with cold hexane and dried under high vacuum. The resulting $Cp_2Zr(CO)(PPh_3)$ was then dissolved in ca. 20 ml of benzene, and the solution was used to extract the product originally remaining in the photolysis vessel. This deep red solution was filtered and the benzene was removed under reduced pressure, leaving a red-brown solid. In order to insure the removal of excess triphenylphosphine, a cold finger sublimer equipped with a 24/40 ST female joint was inserted into the Schlenk tube, and the tube was gently heated under vacuum (10^{-2} Torr) to 60–70 °C for ca. 2 h. The resulting yield of $Cp_2Zr(CO)(PPh_3)$ was 28% (0.13 g). ^1H NMR (C_6D_6): δ 4.93 (d, C_5H_5, J(H–P) 1.8 Hz), 6.95–7.39 ppm (m, Ph). IR (THF): ν(CO) 1842 cm^{-1}.

Photolysis of $Cp_2Hf(CO)_2$ with triphenylphosphine

A 100-ml octane solution of $Cp_2Hf(CO)_2$ (0.35 g, 0.96 mmol) and triphenylphosphine (0.30 g, 1.14 mmol) was irradiated with stirring in a water-jacketed Schlenk tube for 3.5 h at 15 °C. During this time, the solution changed from purple to orange, with the formation of a yellow precipitate (oligomeric hafnocene carbonyl) and deposition of dark red crystals of $Cp_2Hf(CO)(PPh_3)$ on the vessel walls. Also noteworthy was gas evolution at the oil bubbler. The solution was filtered through a frit into another water-jacketed Schlenk tube. The photolysis vessel was rinsed with cold hexane and the adhering $Cp_2Hf(CO)(PPh_3)$ was dried under vacuum. The filtrate was then photolyzed further for another hour, again filtered, concentrated to ca. one-half its volume, and finally cooled to −20 °C. After 2 days, additional crystals of $Cp_2Hf(CO)(PPh_3)$ precipitated. The octane was decanted and the crystals were washed with cold hexane and dried under high vacuum. Approximately 20 ml of benzene was then added to the crystals, giving a deep red solution. This solution was added to the crystals contained in the original photolysis vessel, and the combined solution was filtered. The benzene was removed under reduced pressure, leaving a dry, red-brown, air-sensitive solid. In order to insure the removal of any remaining triphenylphosphine, a cold finger sublimer equipped with a 24/40 ST female joint was inserted into the Schlenk tube, and the tube was gently heated under vacuum (10^{-2} Torr) to 60–70 °C for ca. 2 h. The yield of $Cp_2Hf(CO)(PPh_3)$ was 31% (0.18 g). An analytically pure sample was obtained by recrystallization from heptane at −20 °C (Found: C, 57.34; H, 4.60; P, 4.81. $C_{29}H_{25}HfPO$ calcd.: C, 58.16; H, 4.21; P, 5.16%). ^1H NMR (C_6D_6): δ 4.75 (d, C_5H_5, J(H–P) 1.8 Hz), 6.95-7.33 ppm (m, Ph). IR (THF): ν(CO) 1830 cm^{-1}.

Thermolysis of $Cp_2Zr(CO)(PPh_3)$ with diphenylacetylene in an NMR tube

Into an NMR tube were placed $Cp_2Zr(CO)(PPh_3)$ (18.7 mg, 0.037 mmol) and 0.60 ml of C_6D_6. Diphenylacetylene (16.0 mg, 0.09 mmol) was then dissolved in the solution at room temperature; no apparent color change was observed. A ^{1}H NMR spectrum was recorded and exhibited a doublet at δ 4.93 ppm assignable to $Cp_2Zr(CO)(PPh_3)$. The NMR tube was then connected to a glass T-tube by means of a short piece of Tygon tubing. The other legs of the T-tube were attached to an oil bubbler and to an argon line. The latter leg was equipped with a stopcock. The NMR tube was placed in an oil bath at 55 °C and the solution color changed from dark red to gold-orange after only 15 min. The tube was removed from the bath and quickly cleaned with hexane. The ^{1}H NMR spectrum was recorded and exhibited a singlet at δ 6.02 ppm assignable to 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylzirconacyclopentadiene. The original doublet due to $Cp_2Zr(CO)(PPh_3)$ was absent.

Thermolysis of $Cp_2Zr(CO)(PPh_3)$ with 3-hexyne in an NMR tube

Into an NMR tube were placed $Cp_2Zr(CO)(PPh_3)$ (21.1 mg, 0.041 mmol) and 0.65 ml of C_6D_6. Three drops of 3-hexyne were then added to the solution at room temperature, and no apparent color change was observed. A ^{1}H NMR spectrum was recorded and exhibited a doublet at δ 4.93 ppm assignable to $Cp_2Zr(CO)(PPh_3)$. The NMR tube was attached to an oil bubbler as described above, and then placed in an oil bath at 55 °C. After 15 min, the color had changed from dark red to gold-orange. The tube was withdrawn from the bath and quickly cleaned with hexane. A ^{1}H NMR spectrum was recorded and showed the original doublet due to $Cp_2Zr(CO)(PPh_3)$ to be absent. However, a singlet at δ 5.97 ppm assignable to 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraethylzirconacyclopentadiene was observed.

Thermolysis of $Cp_2Hf(CO)(PPh_3)$ with diphenylacetylene in an NMR tube

Into an NMR tube were placed $Cp_2Hf(CO)(PPh_3)$ (26.4 mg, 0.044 mmol) and 0.70 ml of C_6D_6. Diphenylacetylene (20.0 mg, 0.11 mmol) was then dissolved in the solution at room temperature, and no apparent color change was observed. A ^{1}H NMR spectrum was recorded, and exhibited a doublet at δ 4.75 ppm assignable to $Cp_2Hf(CO)(PPh_3)$. The NMR tube was attached to an oil bubbler as described above and then placed in an oil bath at 60 °C. Spectra were again recorded after 15, 45, 75 and 90 min of heating. The spectrum after 15 min showed only the doublet at δ 4.75 ppm. After 45 min, a singlet at δ 5.97 ppm assignable to 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylhafnacyclopentadiene was observed. Its intensity was approximately equal to that of the remaining doublet of $Cp_2Hf(CO)(PPh_3)$. After 75 min, the doublet was barely perceptible, and the singlet at δ 5.97 ppm had grown in intensity. After 90 min, the singlet was the only observable peak in the spectrum, and the solution was yellow.

Thermolysis of $Cp_2Hf(CO)_2$ with diphenylacetylene in an NMR tube

Into an NMR tube were placed $Cp_2Hf(CO)_2$ (32.8 mg, 0.09 mmol), diphenylacetylene (40.0 mg, 0.22 mmol), and 1.40 ml of C_6D_6. A ^{1}H NMR spectrum of the purple solution exhibited the singlet of $Cp_2Hf(CO)_2$ at δ 4.81 ppm. The NMR tube was attached to an oil bubbler as described above, and was then placed in an oil bath at 60 °C. Spectra were recorded after 30, 90, and 180 min of heating. Throughout this time the singlet remained unchanged, and no additional resonances could be observed.

Thermolysis of $Cp_2Hf(CO)(PPh_3)$ with 3-hexyne in an NMR tube

Into an NMR tube were placed $Cp_2Hf(CO)(PPh_3)$ (27.5 mg, 0.046 mmol) and

0.75 ml of C_6D_6 together with three drops of 3-hexyne. A ^{1}H NMR spectrum of the solution was recorded and exhibited a doublet at δ 4.75 ppm assignable to $Cp_2Hf(CO)(PPh_3)$. The NMR tube was attached to an oil bubbler as described above and then placed in an oil bath at 60 °C. Spectra were recorded after 15, 45, and 75 min of heating. The spectrum after 15 min showed only the doublet at δ 4.75 ppm. After 45 min, a singlet at δ 5.87 ppm assignable to 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraethylhafnacyclopentadiene was observed. Its intensity was approximately equal to that of the remaining doublet of $Cp_2Hf(CO)(PPh_3)$. After 75 min, the doublet was barely perceptible, the singlet at δ 5.87 ppm had grown in intensity, and the solution was now yellow.

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* *Note added in proof*: When the ^{1}H NMR spectrum of this product is recorded at 400 MHz on a Bruker WP-400 spectrometer in acetone-d_6, a resonance assignable to the vinylic protons is observed at δ 6.99 ppm. We thank Prof. D.W. Macomber of Kanses State University for this measurement.