Reactivity of Substituted Acetylenes with $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$. Observation of Zirconacyclopentadiene Formation and Acetylene Hydrogenation[1]

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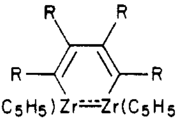
The reactivity of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ with various substituted acetylenes has been investigated. Diphenylacetylene and phenylacetylene react with $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ below 50 °C to yield primarily $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_4)$ and the 2,5-diphenyl-substituted isomer of $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_2H_2)$, respectively. Under appropriate conditions substantial hydrogenation of diphenylacetylene to *trans*-stilbene and phenylacetylene to ethylbenzene, respectively, is observed. These results suggest that at least two competing processes—zirconacyclopentadiene formation and acetylene hydrogenation—are present. Complementary EPR studies for the reactions of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ with diphenylacetylene, 1-phenylpropyne, and 2-butyne have further revealed the formation of a paramagnetic zirconocene species $(\eta^5\text{-}C_5H_4CH_3)_2Zr(H)(RC{\equiv}CR)$. The possible participation of this adduct in the acetylene chemistry of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ is discussed.

Introduction

The reactivity of zirconocene hydrides, such as $[(\eta^5\text{-}C_5H_5)_2Zr(H)Cl]_x$ and $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_x$, with acetylenes was originally investigated by Wailes and co-workers.[2] Recent efforts by Schwartz and co-workers[3] have shown that hydrozirconation of unsymmetrically substituted acetylenes by $[(\eta^5\text{-}C_5H_5)_2Zr(H)Cl]_x$ proceeds stereospecifically to the *cis*-alkenyl isomer with the sterically least-hindered substituent of the acetylene nearest the zirconocene center. Erker and co-workers[4] have examined the further reactivity of the corresponding substituted vinylzirconocene chlorides $(\eta^5\text{-}C_5H_5)_2ZrCl(CH{=}CHR)$, which are produced upon hydrozirconation of terminal acetylenes, with $[(\eta^5\text{-}C_5H_5)_2ZrH(Cl)]_x$. Their results have shown that the reaction of equivalent amounts of $(\eta^5\text{-}C_5H_5)_2ZrCl(CH{=}CHPh)$ and $[(\eta^5\text{-}C_5H_5)_2Zr(H)Cl]_x$, for example, proceeds with the formation of an equimolar mixture of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, $(\eta^5\text{-}C_5H_5)_2ZrCl(CH_2CH_2Ph)$, and an unusual dinuclear zirconocene complex, $(\eta^5\text{-}C_5H_5)_2ZrCl(CH{=}CHPh)Zr(\eta^5\text{-}C_5H_5)_2$. In contrast, early studies of acetylene chemistry of $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_x$ led collectively to several alternative observations. First of all, $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_x$[2b] and related zirconocene hydrides[5] have been found to act as catalysts for acetylene hydrogenation at temperatures from 80 to 120 °C and H_2 pressures of 50–100 atm. In the absence of H_2, Wailes et al.[2a] have reported that $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_x$ and $HC{\equiv}CPh$ react in refluxing benzene to form the bis(alkenyl) compound $(\eta^5\text{-}C_5H_5)_2Zr(CH{=}CHPh)_2$, with no indication of H_2 evolution. Their data for the same reaction using diphenylacetylene or di-*p*-tolylacetylene suggested the formation of an unprecedented dizirconacyclohexadiene complex, 1. The identities of these zirconium-containing products obtained from the reactions of $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_x$ with $HC{\equiv}CPh$ or $PhC{\equiv}CPh$, however, were not conclusively determined and thereby suggest the need for further work.



1, R = C_6H_5, *p*-$CH_3C_6H_5$

With this in mind, we have undertaken an investigation of the reactivity of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$, 2, with various substituted acetylenes. Preliminary results for reactions of 2 with phenylacetylene and diphenylacetylene have been communicated[6] and indicate that these reactions involve two competing processes—zirconacyclopentadiene formation and acetylene hydrogenation. McGlinchey and co-workers[7] have obtained independently $(\eta^5\text{-}C_5H_5)_2Zr(C_4(C_6H_5)_4)$ and *trans*-stilbene as the principal organometallic and hydrocarbon products, respectively, for the reaction of $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_x$ with diphenylacetylene. During the course of our investigations of the reaction of 2 with diphenylacetylene, we have further observed by EPR methods the presence of a paramagnetic zirconocene complex. A discussion of the possible participation of this paramagnetic species in this reaction is presented herein.

Experimental Section

General Considerations. All manipulations, unless otherwise described, were conducted under vacuum or an atmosphere of prepurified nitrogen or argon on a double-manifold, high-vacuum line or in a Vacuum Atmospheres drybox, respectively. Glassware was flame-dried under vacuum or oven-dried before use. Solvents were purified by standard methods and freshly distilled from benzophenone ketyl (toluene, THF, benzene, hexane), Na/K alloy (pentane), or phosphorus pentoxide (CH_2Cl_2, $CHCl_3$) prior to use. Diphenylacetylene (Eastman) was purified by recrystallization from 95% ethanol followed by vacuum sublimation. Phenylacetylene (Aldrich, 98%) was degassed and vacuum distilled. 1-Phenylpropyne (Aldrich, 99%) was degassed, stirred with $LiAlH_4$ overnight under argon, and then vacuum distilled. 2-Butyne

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[1] Based in part on a dissertation submitted by S. B. Jones to the Graduate School at West Virginia University in partial fulfillment of the requirement for the Ph.D. degree, Dec 1983.

[2] (a) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *27*, 373. (b) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *43*, C32.

[3] Schwartz, J.; Hart, D. W.; Blackburn, T. F. *J. Am. Chem. Soc.* **1975**, *97*, 679.

[4] Erker, G.; Kropp, K.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1982**, *2*, 1555.

[5] (a) Couterier, S.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1980**, *195*, 291. (b) Meunier, P.; Gatheron, B.; Couterier, S. *J. Organomet. Chem.* **1982**, *231*, C1.

[6] Jones, S. B.; Petersen, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 5502.

[7] Bickley, D. G.; Hao, N.; Bougeard, P.; Sayer, B. G.; Burns, R. C.; McGlinchey, M. J. *J. Organomet. Chem.* **1983**, *246*, 257.

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(Pfaltz and Bauer) was used as received. [(η^5-$C_5H_4CH_3$)$_2$ZrH(μ-H)]$_2$ was prepared by using published procedures.[8]

^1H and ^{13}C NMR spectra were recorded on a Varian CFT-20 NMR spectrometer operating in the FT mode, and unless otherwise indicated all spectra are referenced to internal tetramethylsilane. Infrared spectra were recorded on either a Beckman IR-8 or Beckman IR-20A spectrometer and were calibrated relative to polystyrene film. The EPR spectra were measured with an IBM/Bruker ER200D-SRC spectrometer under the control of an ASPECT computer system. The microwave frequency was monitored with a Hewlett-Packard 5340A frequency counter. The magnetic field of the spectrometer is calibrated by an internal NMR gaussmeter to within ±0.01 G. Gas chromatographic analyses were performed on a Perkin-Elmer Sigma 1 gas chromatograph using the flame ionization detector with N_2 as the carrier gas. Flow rates were determined with a soap bubble flow meter. Response factors for the various organic compounds were calculated relative to an appropriate alkane using authentic samples. Melting points were determined on a Mel-Temp (Laboratory Devices) apparatus in open capillaries and are uncorrected. The photolysis reactions were conducted with a 450-W Hanovia medium-pressure vapor photochemical lamp located in a quartz water-cooled immersion well. Elemental analyses were performed by Dornis and Kolbe Microanalytical Laboratories, Mulheim, West Germany.

General Procedure for the Reaction of 2 with Substituted Acetylenes. These reactions were conducted by using the same general experimental procedure. A 50-mL Schlenk tube containing a weighed amount of **2** was attached to a 500-mL expansion bulb. The solvent was then vacuum distilled into the Schlenk tube. Phenylacetylene was vacuum distilled onto the frozen solvent, whereas diphenylacetylene was added to the Schlenk tube via an addition arm. The reaction mixture was then degassed three times. Since these acetylene reactions with **2** are likely to generate significant amounts of H_2, the course of each reaction was monitored by periodic measurement of the evolved H_2. This analysis was accomplished by the submerging of the reaction vessel in liquid N_2 followed by the collection of any H_2 present into a calibrated volume with a Toepler pump. Reactions evolving H_2 were considered complete when no additional H_2 was collected. Reactions evolving very little H_2 were terminated when no visible change in the reaction mixture could be observed.

a. Reaction of 2 with Diphenylacetylene. This reaction was run three times under different reaction conditions. To maximize the amounts of zirconium-containing product and evolved H_2 obtained and to minimize the possibility of acetylene hydrogenation, reaction 1 was performed with frequent removal of the evolved H_2. Reaction 2 was carried out at higher temperatures to examine the extent of the hydrogenation of diphenylacetylene. H_2 was only sampled to determine if the reaction was complete. An analytically pure sample of the zirconium-containing product was not obtained from reactions 1 and 2, due to difficulties encountered during the removal of organic by-products and solvent from this product.

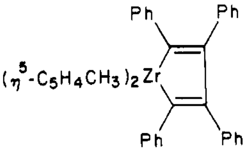
In an effort to solve this problem, an authentic sample of the suspected zirconium-containing product (η^5-$C_5H_4CH_3$)$_2$Zr($C_4(C_6H_5)_4$) was prepared.[9] This compound was used for NMR spectral comparison and to find a suitable column packing for chromatographic separation of the reaction products. After several materials were tested (including silica gel, Celite, and PG-75-200 controlled pore glass), Bio-beads (styrene-divinyl benzene copolymer beads) were found to be a suitable chromatographic medium. Subsequently, the reaction of **2** and diphenylacetylene was repeated on a larger scale (i.e., reaction 3) to isolate the organozirconium product.

Reaction 1. Diphenylacetylene (0.790 g, 4.43 mmol) was added to a suspension of **2** (0.554 g, 1.10 mmol) in 15 mL of THF. The reaction was heated between 45 and 50 °C for 58 h. During this time the color of the reaction mixture went from colorless to dark red orange, and 1.63 mmol of H_2 was collected. After an additional 43 h of heating at 56 °C, the reaction was stopped and the THF was removed. At this point a total of 2.05 mmol of H_2 had been collected. Unreacted diphenylacetylene (0.04 g, 0.22 mmol) was removed by sublimation at 50 °C from the oily red-orange residue.

The orange product was analyzed by hydrolysis and ^{13}C NMR measurements. Hydrolysis in H_2O/Et_2O was performed to identify the ligand attached to the $(C_5H_4CH_3)_2Zr$ fragment. The Et_2O layer was separated from the H_2O layer, which was washed twice with Et_2O. The combined Et_2O fractions were dried over $MgSO_4$. The Et_2O was evaporated leaving white needles covered by a tan impurity. Sublimation provided a white compound whose ^1H NMR and melting point (182–183 °C) were identical with those of an authentic sample of *cis,cis*-1,2,3,4-tetraphenyl-1,3-butadiene (181.5–183 °C). A mixture melting point of the two (181.5–182.5 °C) further confirmed the identity of the hydrolysis product. A ^{13}C NMR spectrum of the orange product was identical with that of an authentic sample of (η^5-$C_5H_4CH_3$)$_2$Zr($C_4(C_6H_5)_4$) except for several small impurity peaks.

Reaction 2. Diphenylacetylene (0.906 g, 5.08 mmol) was added to a suspension of **2** (0.639 g, 1.27 mmol) in 10 mL of toluene. The reaction mixture was heated between 55 and 58 °C for 216 h with samplings after 72, 132, and 216 h. A total of 1.40 mmol of H_2 was collected. All volatiles were sublimed at 50 °C into a received cooled with liquid N_2. Gas chromatographic analysis of the volatiles was performed by using a 6 ft × 2 mm i.d. gas column packed with 10% SE-30 on WHP 80/100 mesh which had been silanized. The oven was set a 175 °C, and the flow rate was 23 mL/min. Bibenzyl[11] (0.21 mmol) and *trans*-stilbene (1.03 mmol) were found. Hydrolysis of some of the reaction residue yielded *cis,cis*-1,2,3,4-tetraphenyl-1,3-butadiene.

Reaction 3. Diphenylacetylene (3.480 g, 19.53 mmol) was added to a suspension of **2** (2.456 g, 4.88 mmol) in 20 mL of benzene. The reaction temperature was slowly raised as follows: 25 °C (29 h), 30–35 °C (13 h), 40 °C (19 h), 50 °C (42 h), 55 °C (44.5 h), and 55–65 °C (68 h). A total of 7.34 mmol of H_2 was collected. The red-orange reaction mixture was concentrated to 10 mL, added to a 115 × 2 cm column packed with SX-8 Bio-Beads in benzene, and eluted with benzene in four fractions: colorless benzene preceding an orange band, an orange band, the tail of the orange band, and a colorless rinse. After solvent removal no residue remained from either the first or fourth fractions. The second fraction left a dark red orange viscous oil, and the third fraction left a mixture of an orange compound and colorless crystalline material. Gas chromatographic analysis of the colorless material from the third fraction yielded 0.049 mmol of *trans*-stilbene. The orange material from the second fraction was recrystallized from benzene/hexane yielding 4.51 g of large orange crystals. This orange compound was characterized by chemical analysis, ^1H and ^{13}C NMR measurements, and an X-ray structural analysis[12] and was found to be (η^5-$C_5H_4CH_3$)$_2$Zr($C_4(C_6H_5)_4$), **3**. On the basis of this formulation with (or without) a benzene of recrystallization, the isolated yield was 67.6% (or 76.3%).



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Anal. Calcd for $C_{40}H_{34}Zr$: C, 79.29; H, 5.66. Found: C, 79.37; H, 5.71.

NMR Data. ^1H and ^{13}C NMR spectra were identical with those of an authentic sample of **3** except for a benzene peak in the ^{13}C

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[8] Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889.

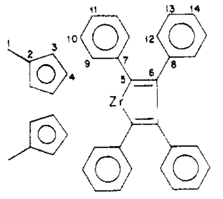
[9] This zirconacyclopentadiene compound was obtained from the metathetical reaction of bis(methylcyclopentadienyl)zirconium(IV) dichloride with dilithio-1,2,3,4-tetraphenyl-1,3-butadiene.[10]

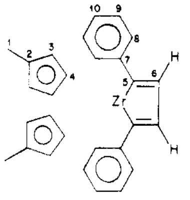
[10] Braye, E. H.; Hubel, W.; Caplier, I. *J. Am. Chem. Soc.* **1961**, *83*, 4406.

[11] Although bibenzyl and *cis*-stilbene have different melting points, they have essentially the same boiling points. Separate tests with authentic samples showed that they could not be separated on the SE-30 column. Although no condensable liquid was observed during the sublimation (*cis*-stilbene melts at −5 °C), the possibility that a small portion of the reported bibenzyl is actually *cis*-stilbene cannot be entirely ruled out.

[12] A complete description of the X-ray diffraction analysis of (η^5-$C_5H_4CH_3$)$_2$Zr($C_4(C_6H_5)_4$)·C_6H_6 and tables of the structural parameters are included as supplementary material.

Table I. ^{13}C Resonances ($^1J_{CH}$, Hz) for 3 and 4 in Ppm Downfield from Me_4Si





C_1:	15.17 (127.5)	C_1:	15.31 (127.9)
C_2:	124.73	C_2:	124.41
C_3:	115.17 (171.5)	C_3:	112.76 (171.3)
C_4:	109.39 (172.2)	C_4:	105.32 (171.3)
C_5:	194.51	C_5:	190.80
C_6:	143.43	C_6:	118.79 (149.2)
C_7:	149.25	C_7:	147.29
C_8:	142.54	C_8:	128.29 (158.3)
C_9-C_{14}:	131.23, 127.57, 127.39, 126.53, 124.43, 122.85	C_9:	126.51 (157.4)
		C_{10}:	125.59 (160.3)

spectrum. The ^{1}H NMR spectrum (benzene-d_6) exhibits resonances centered at δ 6.87 (complex multiplet, 10 H), 5.99 (t, J_{H-H} = 2.6 Hz, 2 H), 5.79 (t, J_{H-H} = 2.6 Hz, 2 H), and 2.10 (s, 3 H), which are readily assigned to the phenyl, MeCp ring, and methyl protons, respectively. The ^{13}C NMR decoupled and gated NOE spectra (CH_2Cl_2, D_2O capillary lock) were also measured. The peak positions were assigned by comparing the expanded decoupled and gated NOE spectra of 3, $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_2H_2)$ (vide infra), and $(\eta^5\text{-}C_5H_4CH_3)_2ZrCl_2$,[13] and are listed in Table I. The resonance for the carbons in the metallacycle ring which are attached to zirconium is shifted substantially downfield from the others. This shift is diagnostic of a metallacyclopentadiene structure and has been observed in similar systems.[14]

b. Reaction of 2 with Phenylacetylene. The reaction of phenylacetylene with 2 was performed three times under different reaction conditions. For reaction 1, the temperature was kept at 25 °C and then eventually raised to 55 °C to determine the effect of raising the temperature on the amount of H_2 evolved. Reaction 2 was run at a temperature above that at which 2 begins to release H_2. To increase the initial concentration of 2 in solution, THF was used as the solvent. Reaction 3 was then conducted on a larger scale with a higher acetylene to 2 ratio (6:1) at 25–35 °C in an effort to isolate the principal organozirconium product(s).

Reaction 1. Phenylacetylene (0.63 mL, 5.74 mmol) was added to a suspension of 2 (0.716 g, 1.42 mmol) in 20 mL of toluene. The reaction was stirred at 25 °C for 15 h and then at 55 °C for 26 h. A total of 0.228 mmol of H_2 was collected. GC analysis of the organic products was conducted by using a 6 ft × 2 mm i.d. glass column packed with 10% SE-30 on 80/100 mesh WHP which had been silanized. The oven was set at 44 °C, and the flow rate was 23 mL/min. GC analysis of the reaction mixture yielded 1.64 mmol of ethylbenzene and 0.192 mmol of styrene. Removal of the volatiles from the reaction mixture left a viscous oily residue. GC analysis of the volatiles yielded 0.73 mmol of ethylbenzene and 0.003 mmol of styrene. Attempts to crystallize the organozirconium product(s) were unsuccessful.

Reaction 2. Phenylacetylene (2.30 mL, 20.94 mmol) was added to a suspension of 2 (2.611 g, 5.19 mmol) in 30 mL of THF. The reaction was stirred between 50 and 55 °C for 17.5 h. A total of 3.08 mmol of H_2 was collected. GC analysis of the volatiles yielded 0.642 mmol of ethylbenzene and 0.369 mmol of styrene.

Table II. Summary of EPR Data from Photolysis of 2 with Substituted Acetylenes

acetylene	g^a	$A(^{91}Zr)$,^{b} G	$A(^1H)$,^{b} G
PhC≡CPh	1.9931	26.0	5.6
PhC≡CMe	1.9857	28.1	5.8 (hydride), 3.8 (methyl protons)
MeC≡CMe	1.9870	not observed	6.5 (hydrides), 4.0 (methyl protons)

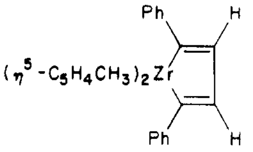
^{a} ±0.0005. ^{b} ±0.2 G.

Reaction 3. Phenylacetylene (3.19 mL, 29.05 mmol) was added to a suspension of 2 (2.435 g, 4.84 mmol) in 30 mL of THF. The reaction temperature was initially 23 °C (41 h) and then raised to 35 °C (54.5 h). During this time the reaction mixture went from colorless to dark red orange with the precipitation of an orange powder. A total of 2.54 mmol of H_2 was collected. The volatiles were removed under vacuum at 45 °C. The residue was dissolved in benzene and filtered to remove an orange precipitate (0.24 g).

The benzene-soluble portion of the product was chromatographed on a 115 × 2 cm column packed with SX-8 Bio-Beads in benzene and gave one orange band. The benzene was removed from this band leaving a viscous orange oil. ^{13}C NMR spectrum of this orange material showed resonances attributable to a zirconacyclopentadiene product as well as several impurity peaks. This crude material was extracted by dissolving it in CH_2Cl_2 and then removing the CH_2Cl_2 until an oil remained. After several days at room temperature a mass of orange crystals was formed. The oil was removed, and the crystals were washed several times with pentane. This orange compound was characterized as the zirconocene metallacycle 1,1-bis(η^5-methylcyclopentadienyl)-2,5-diphenylzirconole, 4, by chemical analysis, ^{1}H and ^{13}C NMR, and hydrolysis. On the basis of this formulation the isolated 2.21 g of 4 corresponds to a yield of 50.3%.

Anal. Calcd for $C_{28}H_{26}Zr$: C, 74.12; H, 5.78. Found: C, 73.89; H, 5.76.

NMR Data. The ^{1}H NMR spectrum (benzene-d_6) exhibits resonances centered at δ 7.11 (complex multiplet, 6 H), 6.05 (t, J_{H-H} = 2.6 Hz, 2 H), 5.48 (t, J_{H-H} = 2.6 Hz, 2 H), 1.86 (s, 3 H). The complex multiplet has been assigned to overlapping phenyl and vinyl protons. The A_2B_2 pattern and the singlet were assigned to the MeCp ring and methyl protons, respectively. The ^{13}C NMR decoupled and gated NOE spectra (CH_2Cl_2, D_2O capillary lock) were measured, and the peak positions are listed in Table I. Of the two symmetrical zirconacyclopentadiene isomers shown below, these spectra are consistent with 4.



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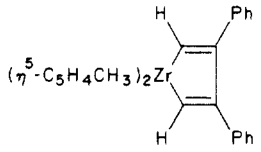

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Hydrolysis. Since hydrolysis of 4 and 5 should yield *trans,trans*-1,4-diphenyl-1,3-butadiene and 2,3-diphenyl-1,3-butadiene, respectively, the identification of the butadiene product will permit the determination of the correct isomer. Hydrolysis of the orange crystalline product with a THF–H_2O solution led to the isolation of a white crystalline solid upon workup. This organic compound melted at 147–148.5 °C compared to 147–149 °C obtained for an authentic sample of *trans,trans*-1,4-diphenyl-1,3-butadiene. A mixed sample melted between 146.5 and 148.5 °C. A ^{1}H NMR spectrum ($CDCl_3$) of the white solid was identical with that of authentic *trans,trans*-1,4-diphenyl-1,3-butadiene.

EPR Measurements. EPR measurements were used to monitor the formation of any paramagnetic intermediates during the photolysis and thermolysis of reaction mixtures of 2 with various acetylenes. In general the thermolysis reactions proceed more slowly than the corresponding photolysis reactions. For each of the acetylenes that were examined, the photolysis and thermolysis experiments led to the formation and observation of analogous paramagnetic species. The corresponding paramagnetic species generated under ambient-temperature photolytic conditions, however, were generally more stable and gave cleaner EPR spectra. For this reason primarily, only the photolysis experiments will be described in detail. The isotropic *g* and hyperfine coupling constants *A* for the principal species generated in each reaction are listed in Table II.

The values of these magnetic parameters were determined either from the measured field positions and the microwave

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[13] Petersen, J. L; Egan, J. W., Jr. *Inorg. Chem.* **1983**, *22*, 3571.

[14] Mattia, J.; Sikora, D. J.; Macomber, D. W.; Rausch, M. D.; Hickey, J. P.; Friesen, G. D.; Todd, L. J. *J. Organomet. Chem.* **1981**, *213*, 441.

frequency, ν_0, or by a computer simulation program supplied with the IBM/Bruker spectrometer. This program is restricted to $S = {}^1/_2$ systems and calculates a spectrum on the basis of the following input data: the isotropic g value, the hyperfine coupling constant for each nucleus, the number of each magnetically nonequivalent nuclei, their corresponding nuclear spin, and an assumed line width.

The EPR samples were prepared as follows: a 3–10-mg sample of **2** was added to a quartz EPR tube equipped with a high vacuum Teflon stopcock. A 4:1 mole ratio of the acetylene to Zr was used. Benzene was vacuum distilled into the EPR tubes. After the samples were freeze–pump–thawed, the EPR tubes were sealed under vacuum. All thermolysis experiments were performed at ca. 75 °C.

Photolysis of 2 with Substituted Acetylenes. Similar photolysis experiments were performed with diphenylacetylene, 1-phenylpropyne, 2-butyne, and phenylacetylene. Photolysis of **2** with diphenylacetylene proceeds cleanly with the generation of a dark red-orange solution. The original hybride doublet[6] observed during the photolysis of **2** is gradually replaced by a new hydride doublet centered at a lower magnetic field. The additional observation of six pairs of equally spaced weaker satellite doublets with the same coupling constant as the primary central doublet is consistent with hyperfine coupling of the unpaired electron with the ^{91}Zr ($I = {}^5/_2$, 11.23% abundance) nucleus. This EPR spectrum persists after several hours of photolysis and is stable for weeks at room temperature.

To assist in the identification of this new hydride species, the photolysis experiments were repeated with 1-phenylpropyne and 2-butyne. For 1-phenylpropyne a red-orange solution is obtained. Each hydride doublet originally observed in the EPR spectrum obtained during the photolysis of **2** and diphenylacetylene is now replaced by a multiplet. This EPR spectrum is not as clean as the corresponding diphenylacetylene spectrum and contains several other smaller resonances. The intensity of the EPR signal in this case gradually dies out after several hours of photolysis. The photolysis of **2** and 2-butyne generates a pale orange solution with a noticeably weaker EPR signal. The major feature of this EPR spectrum is a multiplet, whose intensity dies out completely after less than an hour of photolysis.

Photolysis of **2** with phenylacetylene generates a red-orange solution which exhibits a weak unassignable spectrum.

Discussion of Results

Acetylene Chemistry of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$. The reaction of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$, **2**, with diphenylacetylene below 50 °C proceeds slowly with the formation of the zirconacyclopentadiene compound, $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_4)$, **3**, in high yield. The reaction is accompanied by nearly stoichiometric evolution of H_2 (94% based on (1)) which was frequently removed during the reaction and quantitatively measured. Under these conditions little hydrogenation of diphenylacetylene was observed. The identity of the zirconacyclopentadiene product **3** was determined by hydrolysis, comparison of its ^{13}C NMR spectrum with that of an authentic sample, elemental analysis, and an X-ray structural determination.

$$[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2 + 4PhC{\equiv}CPh \rightarrow 2(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_4) + 2H_2 \quad (1)$$

If this reaction is repeated at higher temperatures (55–58 °C) with less frequent removal of H_2, appreciable hydrogen of the acetylene occurs yielding *trans*-stilbene (20%) and bibenzyl (4%), with the yields based on diphenylacetylene. As a result, only about 50% of the expected H_2 was collected. These results agree with those for the stoichiometric hydrogenation reaction of diphenylacetylene with $[(\eta^5\text{-}C_5H_4\text{-}t\text{-}C_4H_9)_2ZrH_2]_2$[5b] in which the major organic product obtained was *trans*-stilbene, with much smaller amounts of bibenzyl and even less *cis*-stilbene observed. The corresponding *tert*-butyl analogue of **3** was suggested as the major zirconium-containing product.

Phenylacetylene reacts with **2** to yield comparable products to those obtained from diphenylacetylene. Both zirconacyclopentadiene formation and acetylene hydrogenation are observed. If one assumes that the metallacyclic product arises from the coupling of two asymmetric phenylacetylene molecules, then three distinct zirconacyclopentadiene isomers, the corresponding 2,4-, 2,5-, and 3,4-diphenyl-substituted compounds, are possible. The electronic factors that determine the regioselectivity of this metal-assisted reaction for various olefins and acetylenes have been examined theoretically by Hoffmann and Stockis.[16] The outcome of their analysis for unsymmetrically substituted alkenes and alkynes reveals that the stereoselectivity of the coupling reaction is largely controlled by the polarization of the π^* orbital(s). In general, the reaction proceeds with the carbon atom that has the larger coefficient for its 2p orbital in the π^* LUMO winding up in the β-position of the ring. A frontier molecular orbital analysis of phenylacetylene[17] indicates that the larger lobe in its π^* orbitals resides on the unsubstituted carbon. Consequently, one would anticipate the coupling reaction for phenylacetylene to proceed with the formation of a metallacyclopentadiene product with the phenyl groups in the α-positions. Our isolation of the 2,5-diphenyl-substituted zirconacyclopentadiene compound **4** from the reaction of phenylacetylene with **2** is in accord with this prediction. The identity of **4** was established by elemental analysis, hydrolysis, and ^1H and ^{13}C NMR measurements. For the phenylacetylene reaction the principal hydrogenated product, however, is an alkane, ethylbenzene.

In light of these results, the dizirconacyclohexadiene complex **1** that Wailes and co-workers[2a] proposed as the product of the reaction between $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_x$ and diphenylacetylene is unlikely. This remark has been corroborated recently by a reinvestigation of this reaction by McGlinchey and co-workers,[7] who found that the zirconium-containing product was indeed the zirconacyclopentadiene compound $(\eta^5\text{-}C_5H_5)_2Zr(C_4(C_6H_5)_4)$. Additionally, the bis(alkenyl) derivative $(\eta^5\text{-}C_5H_5)_2Zr(CH{=}CHPh)_2$, **6**, formulated as the *major* product in the reaction of $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_x$ with phenylacetylene is also suspect. The supporting data provided by Wailes and co-workers[2a] could not distinguish between **6** and the corresponding zirconacyclopentadiene compound. The presence of a methylcyclopentadienyl analogue of **6** or a bis(alkynyl) compound, $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C{\equiv}CPh)_2$, **7**, as minor products cannot be completely ruled out, however, since the amount of **4** isolated in our studies was never more than 50%.

A closer examination of the corresponding reactions of diphenylacetylene and phenylacetylene with **2** indicates several notable differences. First of all, the reaction conditions needed to initiate these reactions are significantly different. For the former case, no observable reaction occurs until after the solution is heated above 50 °C, which is roughly the temperature at which **2** begins to reductively eliminate H_2. In contrast the reaction of phenylacetylene with **2** is observed to commence at room temperature. This difference suggests that these two acetylene reactions probably involve different initiation steps. A second obvious point of comparison is the amount of H_2 collected from these reactions. For reaction 1 with diphenyl-

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(15) Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Srivastava, R. C.; Frazer, M. J.; Newton, W. E. *J. Chem. Soc. A* **1969**, 2814.

(16) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952 and references cited therein.

(17) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley Interscience: New York, 1976.

acetylene, over 90% of the expected amount of H_2 (based upon the stoichiometry of (1)) was collected, whereas for the corresponding reaction with phenylacetylene, only a small percentage of the expected H_2 was obtained. Despite frequent removal of any evolved H_2 released during the latter reaction, substantial amounts of hydrogenated products, particularly ethylbenzene, were obtained. One might argue that this result simply reflects a substantially faster rate of hydrogenation for phenylacetylene as compared to that for diphenylacetylene. However, considering the negligible amount of H_2 provided by **2** at room temperature, it seems more reasonable to suggest that the mechanisms leading to the corresponding hydrogenated products for these two acetylenes are probably different. Finally, the reaction with phenylacetylene appears to be sensitive to solvent effects. A substantially lower amount of hydrogenated products is obtained when this reaction is run in THF as compared to toluene. This observation is attributed to the ability of THF to occupy available coordination sites in the electron-deficient zirconocene species that are present in solution. Presumably, this interaction inhibits the participation of these zirconocene species in the hydrogenation process and thereby helps to rationalize the correspondingly greater amount of H_2 that is observed. Although the products obtained from the reactions of these acetylenes with **2** are similar, the observed differences (as noted above) suggest that the routes used to arrive at the corresponding products are probably different.

EPR Evidence for Paramagnatic Intermediates. Photolysis and thermolysis studies of **2** have[6,18] revealed that this dinuclear zirconocene hydride readily eliminates hydrogen with the concomitant formation of a paramagnetic Zr hydride species, **8**. Its solution EPR spectrum exhibits a well-resolved doublet centered at $g = 1.9854$ with $A(^1H) = 6.8$ G, which is consistent with the coupling of the unpaired electron of a d^1 metal center with one ^1H nucleus.[19] The relative ease with which this paramagnetic species is generated strongly suggests that it may play an important intermediary role in the acetylene chemistry of **2**. To investigate the possible formation of paramagnetic zirconocene species, parallel photolysis and thermolysis experiments were performed in sealed quartz tubes containing a few milligrams of **2**, benzene, and an appropriately substituted acetylene. The progress of each reaction was monitored periodically by EPR measurements.

For diphenylacetylene, photolysis proceeds cleanly, with the formation of a new paramagnetic zirconium hydride species, **9**, with $g = 1.9931$, $A(^1H) = 5.6$ G, and $A(^{91}Zr) = 26.0$ G (Figure 1, ref. 6). This adduct is stable in solution at room temperature, but upon heating, its concentration in solution slowly diminishes.

To assist in the identification of **9**, the analogous photolysis experiments were repeated in the presence of methyl-substituted acetylenes. For 1-phenylpropyne, the initial hydride doublet of **8** is replaced by a complicated multiplet (Figure 1). Each Zr hyperfine line is split further by hyperfine coupling of the unpaired electron with both a hydride ligand and the methyl protons of the 1-phenylpropyne. Computer simulation of this spectrum was used to determine the isotropic magnetic parameters with $g = 1.9857$, $A(^1H) = 5.8$ G (hydride), $A(^{91}Zr) = 28.1$ G, and $A(^1H) = 3.8$ G (methyl protons). The similarity of $A(^1H)$ for the hydride ligand and $A(^{91}Zr)$ associated with the diphenylacetylene and the 1-phenylpropyne adducts indicates that their structures are analogous. For 2-butyne, the EPR spectrum is further complicated by additional proton coupling from the second methyl group. In this case each hydride doublet is split by the acetylene's six methyl protons. Although the intensity of the EPR signal was insufficient to observe the six corresponding ^{91}Zr satellites, computer simulation of the central multiplet located at $g = 1.9870$ was able to provide approximate values of $A(^1H) = 6.5$ and 4.0 G for the hydride ligand and methyl protons, respectively.

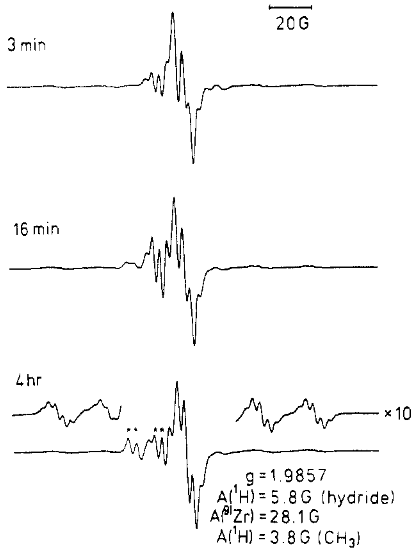

Figure 1. Solution EPR spectra of the photolysis of **2** in the presence of 1-phenylpropyne after 3 min, 16 min, and 4 h (* – unassigned resonances).

These EPR experiments clearly have shown that **8** reacts with these disubstituted acetylenes, RC≡CR (R = Ph or Me), to produce a new paramagnetic hydride species, **9**. The additional hyperfine coupling of the unpaired electron with the methyl protons of these methyl-substituted acetylenes is strong evidence to suggest that **9** is probably the corresponding hydrido–acetylene complex $(\eta^5\text{-}C_5H_4CH_3)_2Zr(H)(RC{\equiv}CR)$. This structure is analogous to that proposed by Labinger and Schwartz[20] for $(\eta^5\text{-}C_5H_5)_2Nb(H)(CH_3C{\equiv}CCH_3)$ on the basis of NMR data. The stability of this zirconium(III) hydrido–acetylene adduct depends on the electronic properties of the acetylene substituents. The inherent stability of $(\eta^5\text{-}C_5H_4CH_3)_2Zr(H)(PhC{\equiv}CPh)$ (as noted earlier) compared to the methyl-substituted acetylene analogues reflects the greater π-acceptor ability of PhC≡CPh to stabilize the Zr(III)–acetylene interaction.

The observation of these paramagnetic zirconocene hydrido–acetylene complexes during these photolysis (and thermolysis) reactions is a good indication that species such as $(\eta^5\text{-}C_5H_4CH_3)_2Zr(H)(RC{\equiv}CR)$ are probably involved in some capacity in the diphenylacetylene reaction with **2**. This zirconocene hydrido–acetylene adduct provides a plausible intermediate in the acetylene hydrogenation process[21] and may be involved to a lesser extent in the stoichiometric formation of **3**. The possible involvement of paramagnetic intermediates in these reactions provides a reasonable alternative explanation to that provided by McGlinchey and co-workers[7] for the observed products.

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(18) Bajgur, C.; Jones, S. B.; Petersen, J. L., manuscript in preparation.

(19) (a) Elson, I. H.; Kochi, J. K.; Klabunde, U.; Manzer, L. E.; Parshall, G.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 7374. (b) Brintzinger, H. H. *J. Am. Chem. Soc.* **1967**, *89*, 6871. (c) Samuel, E.; Maillard, P.; Gianotti, G. *J. Organomet. Chem.* **1977**, *142*, 289. (d) Hudson, A.; Lappert, M. F.; Pichon, R. *J. Chem. Soc., Chem. Commun.* **1983**, 374.

(20) Labinger, J. A.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 1596.

(21) Parshall, G. W. "Homogeneous Catalysis"; Wiley Interscience: New York, 1980.

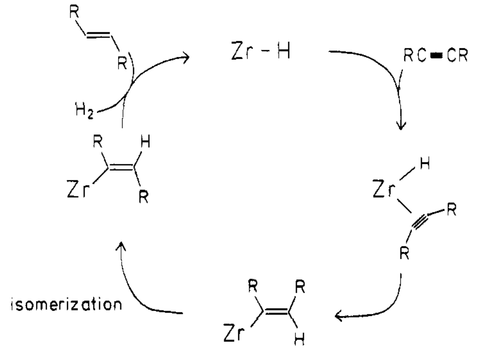
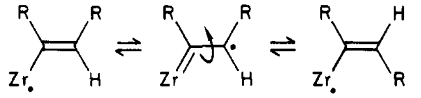


Figure 2. Catalytic cycle for acetylene hydrogenation.

A catalytic cycle (Figure 2) for the hydrogenation of a disubstituted acetylene, RC≡CR, to the corresponding trans olefin RHC=CHR is initiated by the addition of the acetylene to the paramagnetic Zr–H species **8** to produce **9**. Intramolecular hydride migration to the coordinated acetylene leads to the formation of a coordinatively unsaturated *cis*-alkenyl intermediate. Isomerization, according to the radical process[22] shown in (2), followed by hydrogenation produces the trans olefin.[23]



(2)

The corresponding involvement of an analogous paramagnetic species in the hydrogenation of phenylacetylene, however, seems less likely on the basis of two considerations. First, the corresponding EPR spectra measured during the photolysis (or thermolysis) of **2** in the presence of phenylacetylene provide no evidence for any stable paramagnetic zirconocene species in solution. Further, this reaction occurs without having to heat the reaction mixture above the temperature needed to eliminate H_2 and thereby generate **8** from **2**. Consequently, an alternative hydrogenation mechanism that does not require the participation of paramagnetic Zr–H intermediates is needed. One reasonable approach is based upon the results reported by Erker and co-workers[4] for the hydrozirconation of terminal acetylenes with $[(\eta^5\text{-}C_5H_5)_2Zr(H)Cl]_x$. This reaction yields the corresponding substituted vinylzirconocene chlorides. If $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ is now used as the hydrozirconation reagent, then the comparable reaction with phenylacetylene should yield the vinyl hydride species $(\eta^5\text{-}C_5H_4CH_3)_2Zr(H)(CH{=}CHPh)$, which is likely to reductively eliminate styrene. Subsequent hydrozirconation of styrene to the phenylethyl derivative $(\eta^5\text{-}C_5H_4CH_3)_2Zr(H)(CH_2CH_2Ph)$ followed by reductive elimination of ethylbenzene provides an alternative route to the primary hydrogenated product observed for the reaction of phenylacetylene with **2**.

Finally, a reasonable scheme for zirconacyclopentadiene formation based on the availability of paramagnetic Zr hydride intermediates is depicted in Figure 3. Two complementary routes are shown. Both paths are initiated by bimolecular hydride migration and proceed with the formation of a Zr(II) center or a zirconium(II)–acetylene adduct.[25] Comparable Zr(II) centers would also be generated by the reductive elimination of styrene and ethyl benzene from the corresponding phenylvinyl hydride and phenylethyl hydride intermediates suggested for the phenylacetylene reaction. Subsequent addition of either acetylene in each case produces the corresponding bis(acetylene)zirconium complex. Finally, oxidative coupling of the two coordinated acetylenes leads to the observed zirconacyclopentadiene product.

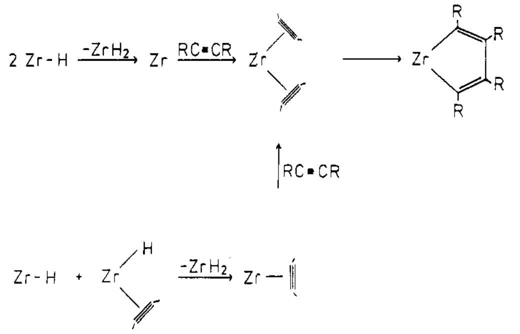


Figure 3. Reaction scheme for the formation of a zirconacyclopentadiene ring.

Although these mechanistic schemes are based upon known chemistry, their viability remains to be tested. The available EPR data clearly has shown that **8** reacts with RC≡CR (R = Me, Ph) to form the corresponding paramagnetic hydrido–acetylene complex, presumably $(\eta^5\text{-}C_5H_4CH_3)_2Zr(H)(RC{\equiv}CR)$. Unfortunately, little more can be said about its actual reactivity until a stable paramagnetic analog has been isolated and characterized. At this point, systematic studies to investigate its reactivity toward H_2 and acetylenes would then be possible. In addition, current efforts are underway to prepare soluble analogs of **2**. Their availability will provide an opportunity to undertake complementary NMR studies of the reactions involving terminal acetylenes.

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Registry No. **2**, 77965-67-4; **3**, 95552-64-0; **3**·C_6H_6, 95552-65-1; **4**, 95552-66-2; **9** (R = Ph), 95552-67-3; **9** (R = Me), 95552-68-4; PhC≡CPh, 501-65-5; PhC≡CMe, 673-32-5; MeC≡CMe, 503-17-3; $(\eta^5\text{-}C_5H_4CH_3)_2Zr(H)(PhC{\equiv}CMe)$, 95552-69-5; *cis,cis*-1,2,3,4-tetraphenyl-1,3-butadiene, 1608-10-2; bibenzyl, 103-29-7; *trans*-stilbene, 103-30-0; ethylbenzene, 100-41-4; styrene, 100-42-5; *trans,trans*-1,4-diphenyl-1,3-butadiene, 538-81-8; phenylacetylene, 536-74-3; bis(methylcyclopentadienyl)zirconium(IV) dichloride, 12109-71-6; dilithio-1,2,3,4-tetraphenyl-1,3-butadiene, 21289-08-7.

Supplementary Material Available: Description of the procedures employed to collect and analyze the X-ray diffraction data, tables of positional parameters and temperature factors, interatomic distances and bond angles, and observed and calculated structure factors, and perspective view and atom labeling scheme for the molecular structure of $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_4)\cdot C_6H_6$ (27 pages). Ordering information is given on any current masthead page.

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(22) Erker, G., personal communication.

(23) Schwartz and co-workers[24] observed cis addition of disubstituted acetylenes to $[(\eta^5\text{-}C_5H_5)_2Zr(H)Cl]_x$. The reaction of the resultant alkenyl species with NBS yielded the corresponding cis olefin.

(24) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679.

(25) Comparable acetylene adducts of V and Mo have been prepared from the oxidative addition of an acetylene to vanadocene[26] and molybdenocene,[27] respectively.

(26) (a) Tsumara, R.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 861. (b) deLiefde Meijer, H. J.; Jellinek, F. *Inorg. Chim. Acta* **1970**, *4*, 651. (c) Fachinetti, G.; Floriani, C.; Chiesa-Villa, A.; Guastini, C. *Inorg. Chem.* **1979**, *18*, 2282. (d) Petersen, J. L.; Griffith, L. *Inorg. Chem.* **1980**, *19*, 1852.

(27) (a) Thomas, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 1838. (b) Thomas, J. L. *Inorg. Chem.* **1978**, *17*, 1507. (c) Petersen, J. L.; Egan, J. W., Jr. *Inorg. Chem.* **1981**, *20*, 2883.