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REACTION OF $[(\eta^5\text{-}C_5H_5)_2ZrH(\mu\text{-}H)]_2$ WITH DIPHENYLACETYLENE: MECHANISTIC AND THEORETICAL CONSIDERATIONS

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Summary

The polymeric $(Cp_2ZrH_2)_x$ molecule is shown by ^1H NMR studies to adopt a dimeric structure with bridging and terminal hydride ligands in both benzene-d_6 and toluene-d_8 solution. The reaction of the zirconium dihydride with diphenylacetylene has been re-investigated and produces a zirconacyclopentadiene complex **7**, contrary to literature suggestions of a dimetallic zirconabenzene structure. A qualitative molecular orbital analysis of the $[Cp_2ZrH(\mu\text{-}H)]_2$ dimer lends support to a suggested mechanism involving reaction with diphenylacetylene via a dimeric species.

Introduction

The reactivity of early transition metal hydrides has received considerable attention in recent years. Prominent amongst these studies is the hydrozirconation process involving Cp_2ZrHCl, **1** **, which has proven to be very useful, in organic synthetic methodology [1–3]. Also of significance is the reduction of carbon monoxide with various zirconium hydrides [4,5].

Of the known zirconium hydride complexes **1**–**3**, considerably less information is available for the dihydride derivative **2** than for the hydrochloride (**1**) and hydridoalkyl (**3**) species. Early studies [6] on the preparation of a series of Cp_2ZrHL

$(Cp_2ZrHL)_x$ (**1**, L = Cl; **2**, L = H; **3**, L = alkyl (R))

(L = H, Cl, CH_3) complexes reported extremely poor solubility and infrared absorptions associated with hydride-bridging groups. The dihydride **2** also exhibited terminal ν(Zr–H) bands and polymeric hydride-bridged networks were suggested [6].

Wailes and co-workers originally discovered that **1** and **2** would react with

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[**] $Cp = \eta^5\text{-}C_5H_5$; $CpR = \eta^5\text{-}C_5H_4R$; $CpMe_3 = \eta^5\text{-}1,2,4\text{-}C_5H_2Me_3$; $CpMe_5 = \eta^5\text{-}C_5Me_5$.

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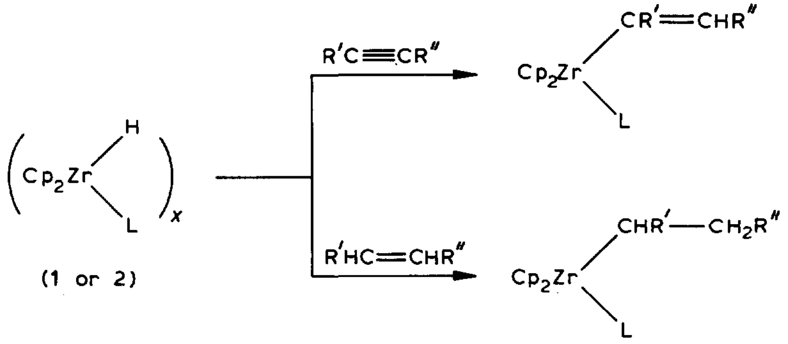
acetylenes [7] and olefins [8] to produce alkenyl- and alkyl-zirconium complexes, respectively, according to equations 1 and 2.

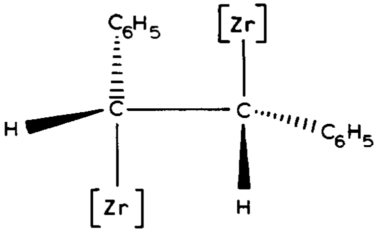


(1)

(2)

More complete studies by Schwartz [1–3] unravelled the details of the addition of **1** to olefins, while hydrozirconation of acetylenes proceeded via stereospecific Zr–H *cis* addition to the carbon–carbon triple bond [9].

The reactions of **1** and **2** with arylacetylenes have proven to be interesting and more complex [7] than their corresponding alkylacetylenes. **1** reacts with one mole of $(C_6H_5)_2C_2$ to produce the expected alkenyl complex according to equation 1, which will react further with **1** to produce the saturated species **4**. Intermediates of this type have been suggested to account for the isomerization of vinylzirconium species formed from the addition of **1** to acetylenes with an excess of the former [9].

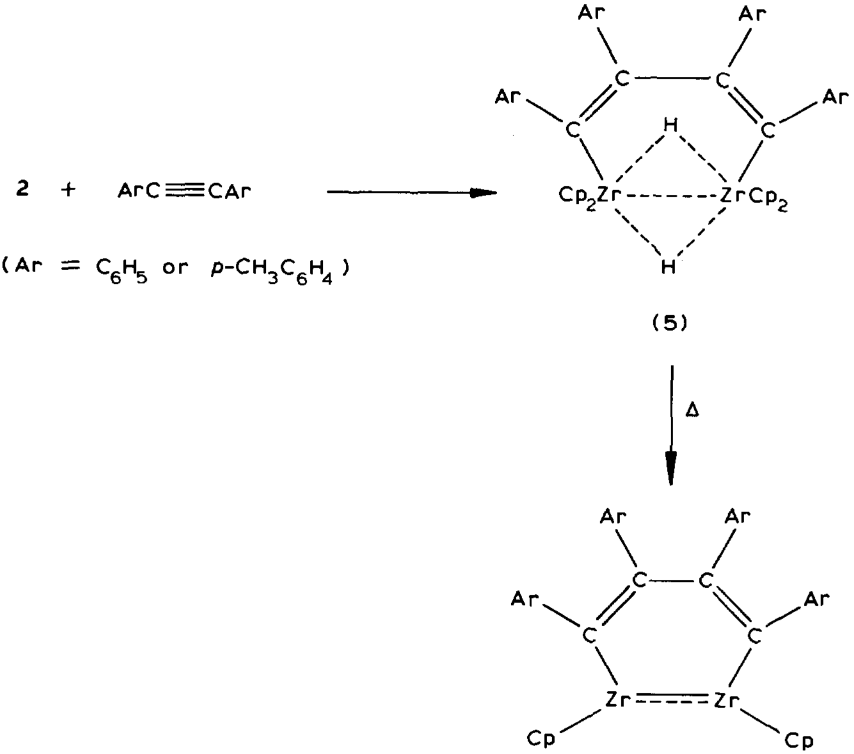


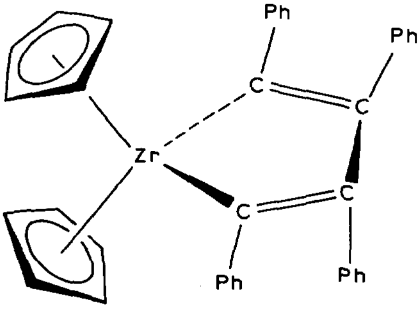
(4 ; [Zr] = Cp_2ZrCl)

In contrast, the dihydride **2** enters into less understood reactions with diarylacetylenes and Scheme 1 has been tentatively proposed for this system by Wailes et al. [7].

As a continuation of our interests in organometallic zirconium systems [10,11], we decided to reinvestigate the reaction of the dihydride **2** with diphenylacetylene, due to the unprecedented nature of the structures suggested for **5** and **6**. We find that the reaction of **2** and diphenylacetylene, under mild conditions, produces the known [12a–e] and structurally characterized [12d] metallocycle **7**. Under more forcing conditions (100°C) using only the hydride present in the system, substantial hydrogenation of the acetylene occurs, producing *trans*-stilbene [13]. Under the influence of several atmospheres of hydrogen, a catalytic hydrogenation process is operative [8,14], from which the zirconium hydride catalyst may be recovered unchanged [14]. Several possible ways in which a formally d^0, Zr^{IV} system can activate hydrogen have been summarized [15].

SCHEME 1





(7)

During the course of our studies, the molecularity of the dihydride species **2** was a matter of concern. Physical data on the insoluble solid indicated a polymeric network. A similar situation is assumed for the hydrochloride **1**. Schwartz's work on the more soluble hydridoalkyl species **3** indicated [16] a dimeric structure with bridging hydride ligands which appear as a broad resonance at $\delta \sim -2$ ppm in the ^1H NMR spectrum.

A related π-indenylzirconium hydride system has been shown to exist as a hydride-bridged dimer in solution from ^1H NMR studies [17] at low temperature, which revealed separate bridging and terminal hydride triplet resonances at δ −1.68 and 4.59 ppm, respectively, both with J 7 Hz.

Attempts to solubilize the dihydride complex by using substituted cyclopentadienyl ligands have been partially successful. Complete substitution using $CpMe_5$ ligands produces an extremely soluble hydride which is monomeric and possesses its own unique chemistry [4,5].

Less complete substitution of the Cp rings leads to other soluble zirconium dihydrides which possess dimeric structures in solution. A number of $[(RCp)_2ZrH_2]_2$ systems have been prepared by Gautheron [14] (R = CH_3, i-Pr, t-Bu) by hydrogenolysis of the corresponding $(RCp)_2Zr(CH_3)_2$ compounds. These hydrides were characterized as dimers by mass spectrometry and ^1H NMR spectroscopy, which revealed two triplets at $\delta \sim -3$ and 3 ppm for bridging and terminal hydride ligands, respectively. This dimeric structure has been confirmed in the solid state with the crystal structure of the $[(C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$ derivative [18a]. The crystal structure of a related zirconium hydride species containing terminal and bridging hydrides has recently been reported [18b].

The subtle nature of these dihydride systems is further exemplified by a recent report [19] on the mixed Cp, $CpMe_3$ and $CpMe_5$ systems. The $(CpMe_5)CpZrH_2$ molecule is dimeric while the $(CpMe_5)(CpMe_3)ZrH_2$ system is monomeric. However, in neither case could any Zr–H resonance in the NMR be detected, at least at room temperature.

In this paper we report the characterization of the unsubstituted cyclopentadienyl Cp_2ZrH_2 complex **2** as a dimer in solution and the reaction of **2** with diphenylacetylene to produce the previously undetected zirconacycle **7**. A mechanistic scheme is proposed for this system, which is amplified using a qualitative molecular orbital analysis of the hydride-bridged dimeric unit. Metallocycle formation in a related hydrozirconation reaction of **2** with a diyne is also reported.

Discussion

Molecularity of $[Cp_2ZrH(\mu\text{-}H)]$ (2)

The preparation [20] of **2** from $Cp_2Zr(BH_4)_2$ and NEt_3 results in the precipitation of a very sparingly soluble white solid, which exhibits both bridging and terminal ν(Zr—H) bands in the solid-state infrared spectrum [6]. Despite the poor solubility of **2**, it is possible to obtain satisfactory ^1H NMR spectra of an extremely dilute solution in C_6D_6 or $CD_3C_6D_5$ if data are collected for a sufficient time (~ 0.5 h). The ^1H NMR spectrum of **2** obtained at ambient temperature in C_6D_6 revealed the expected C_5H_5 resonance at 5.75 ppm and two triplets at δ 3.85 and δ − 3.45 ppm, both with J 7.3 Hz; irradiation of either triplet collapsed the coupling in the other. These data are consistent with a dimeric formulation for **2** with two bridging and two terminal hydrides, and the chemical shift and coupling constant data are similar to those reported for other dimeric zirconium hydride systems [14,16–18]. Almost identical results were obtained in $CD_3C_6D_5$, as shown in Fig. 1. Also shown is the temperature dependence of the two triplets which exhibit evidence of collapse above ~ 60°C and a relative increase in intensity of the terminal hydride signal above ~ 70°C. A similar result has previously been obtained for the related $(\pi\text{-indenyl})_2ZrH_2$ dimer [17], but at relatively lower temperatures. Two triplets were

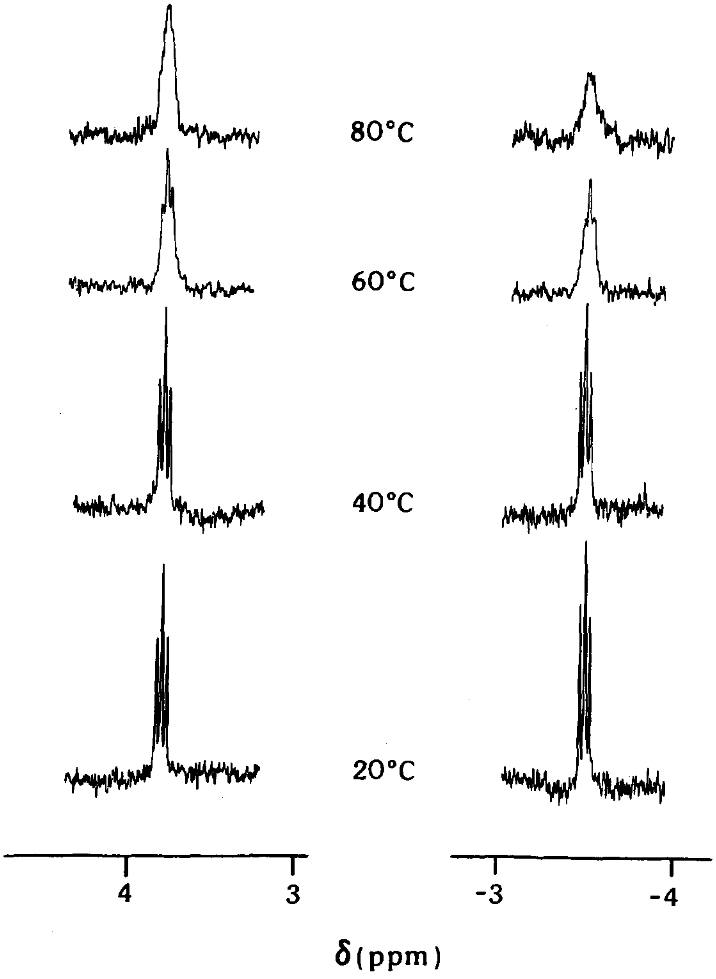


Fig. 1. Variable-temperature ^1H NMR spectra of the two metal hydride signals of **2** in $CD_3C_6D_5$.

observed at −36°C which, on raising the temperature, collapsed at different rates such that at +30°C only two singlets were observed. Spin saturation transfer was also noted, indicating exchange between the two hydride sites. Further heating resulted in the loss of the bridging hydride resonance but not the terminal hydride signal. These results from the work described here and for the indenyl system [17] can only be interpreted in terms of two processes, viz., a rapid bridge-terminal hydride exchange at low temperature and a subsequent dimer-monomer equilibrium at elevated temperatures resulting in the observation of only a terminal hydride resonance. A similar process may explain the failure to detect any Zr–H signals for the mixed $CpMe_5$, $CpMe_3$, and CpZr dihydrides [19]. Of course, such an intermolecular process is inevitably slow in the case of **2** since the concentration is solution is extremely low. Similar arguments have been advanced for the observation of a single hydride resonance, even at −85°C, for the isostructural $[(CpMe_5)_2MH(\mu\text{-}H)]_2$ (M = Th, U) systems [21]. These actinide complexes also undergo rapid intermolecular exchange with dissolved H_2, as demonstrated by magnetization transfer experiments.

We attempted to locate the hydride resonance of the hydrochloride complex **1** using the same techniques as for **2**; however, inconclusive data resulted from complications due to a disproportionation reaction.

Characterization of metallocycle 7

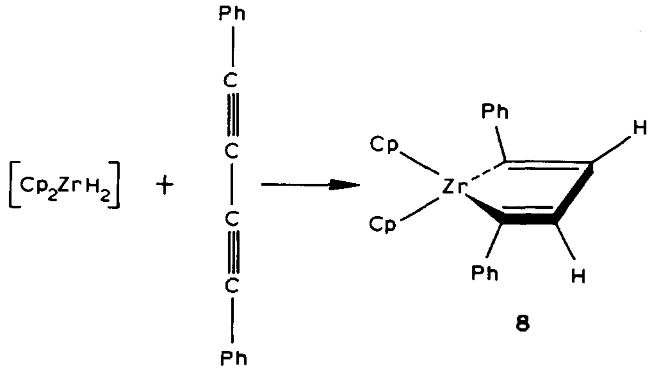
As previously reported [7], gentle warming of a suspension of **2** with a benzene solution of diphenylacetylene led to gradual dissolution of the dihydride, evolution of hydrogen, and the formation of a deep orange solution. Removal of solvent and recrystallization afforded an orange solid whose mass spectrum exhibited a parent peak at m/z 576, complete with a zirconium isotope pattern. This result suggested structure **7** rather than a dizirconium formulation such as **5** or **6**. The reaction was also repeated at room temperature (~ 25°C) and found to be considerably slower with only 45% of the hydrogen being evolved after 3 days. The reaction product was again established as **7**. Traces (~ 5%) of *trans*-stilbene were also observed in each case, but no *cis*-stilbene could be detected.

Confirmation of the product as the zirconacyclopentadiene complex **7** was obtained from ^1H and ^{13}C NMR studies. While the ^1H NMR spectrum is rather uninformative, the correct ratio of the phenyl/Cp protons is observed. ^{13}C NMR spectra of the orange product (with added $Cr(acac)_3$) agreed with the literature data [22] for **7**. We observe the metallocycle ring carbons at 203.1 and 144.7 ppm and the Cp ring carbons at 112.0 ppm in methylene chloride solution.

An authentic sample of **7**, prepared via the literature [12a] reaction of Cp_2ZrCl_2 with dilithio-1,2,3,4-tetraphenylbutadiene, gave mass, ^1H and ^{13}C NMR, and infrared spectra identical with the product of the dihydride reaction.

A completely analogous reaction has been observed by Petersen [13b] between $[(CpMe)_2ZrH_2]_2$, a dimer in the solid state [18a], and diphenylacetylene to produce the zirconacyclopentadiene complex $(CpMe)_2Zr[C_4(Ph)_4]$.

At this point, one must pause to re-evaluate the original data [7] in the light of the current evidence. The tentative identification of the final product as the dizirconabenzene, **6**, rather than **7**, was based on the ^1H NMR spectrum and analytical data. The observed ^1H NMR spectrum is equally assignable in terms of relative intensities to **7**, while the analytical data correspond reasonably well to a contamination of **7** with some dihydride impurity. Furthermore, for the *p*-tolyl derivative analogous to **7**,



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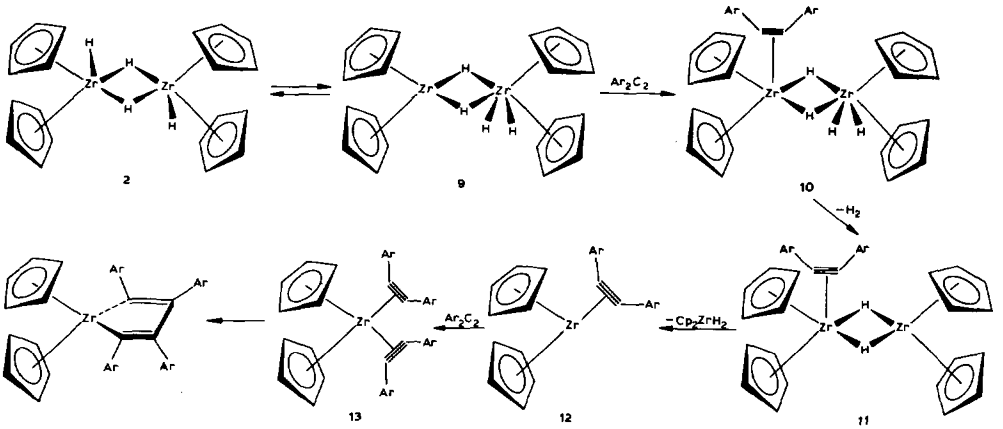
the ebulliometrically obtained molecular weight of 650 corresponds more closely to structure **7** (mol.wt. 634) than **6** (mol.wt. 725).

Another mode of entry into the zirconacyclopentadiene system is also available by hydrozirconation of 1,4-diphenylbuta-1,3-diyne using $[Cp_2ZrH_2]_2$ to give zirconacycle **8**, which was identified by its mass spectrum which gave a parent peak at *m/z* 424. ^{13}C NMR spectral data for **8** were very similar to those of its fully phenylated analogue **7**.

Mechanism

A rational route to **7** probably involves an oxidative cyclization of a bis(alkyne)zirconium(II) species, which in turn requires a formal reductive elimination of H_2 from an initial zirconium hydride species. We propose the sequence of events illustrated in Scheme 2 to account for the unusual reactions of **2** with diphenylacetylene.

SCHEME 2



In Scheme 2 we invoke elimination of dihydrogen from the dimer **10** rather than monomeric $Cp_2ZrH_2(RC{\equiv}CR)$, **14** for several reasons. Firstly, the ^1H NMR data discussed earlier demonstrate that **2** exists in solution as a hydride-bridged dimer and variable-temperature data (Fig. 1) show that this is by far the predominant species in solution. Even at 70°C the ratio of terminal to bridging hydrogens is ~ 2/2 and the monomer only becomes reasonably abundant above 80–90°C. Indeed, it is only at these elevated temperatures that stilbene production is efficient [13] and the reaction path is clearly different from that found at room temperature or under relatively mild conditions. Formation of stilbene at high temperature (> ~ 90°C) is readily envisaged as arising from hydrozirconation of the monomer **14** to give $Cp_2ZrH(PhC{=}CHPh)$; subsequent reductive elimination of stilbene and oxidative addition of dihydrogen to regenerate monomeric Cp_2ZrH_2 can account for the catalytic process observed when the reaction is carried out under an atmosphere of H_2. Now, since the zirconacycle **7** is not observed under the forcing conditions which yield stilbene, and further that monomeric Cp_2ZrH_2 is abundant only at high temperatures, it is not unreasonable to propose that zirconacycle formation requires the intermediacy of the dimer **2**.

Now reductive elimination of dihydrogen is unlikely to occur until a single zirconium atom obtains two terminal hydrides. The transformation step **2** → **9** (in Scheme 2) allows bridge-terminal interchange as observed in the ^{1}H NMR spectra of this and related [17,18b,19,21] systems while the concomitant reconstruction of a dihydride bridge allows for maximum bonding interaction between the two zirconium centers. To help understand how reductive elimination of dihydrogen might proceed via dimeric species such as **2** or **9** we present a qualitative MO scheme based on the frontier orbitals [23] of the bent Cp_2M fragment as analysed by Lauher and Hoffmann [24], and shown in Fig. 2a. Using two sets of these orbitals for two "Cp_2Zr" units together with four hydrogen 1*s* orbitals, a qualitative MO diagram for **2** (under C_{2h} symmetry) may be constructed, as shown in Fig. 2b. The two bridging hydrogens are each involved in three-center, two-electron bonds. Note that both zirconium atoms are coordinatively saturated, although each is only a sixteen electron system. The transformation of a bridging hydride to a terminal hydride in

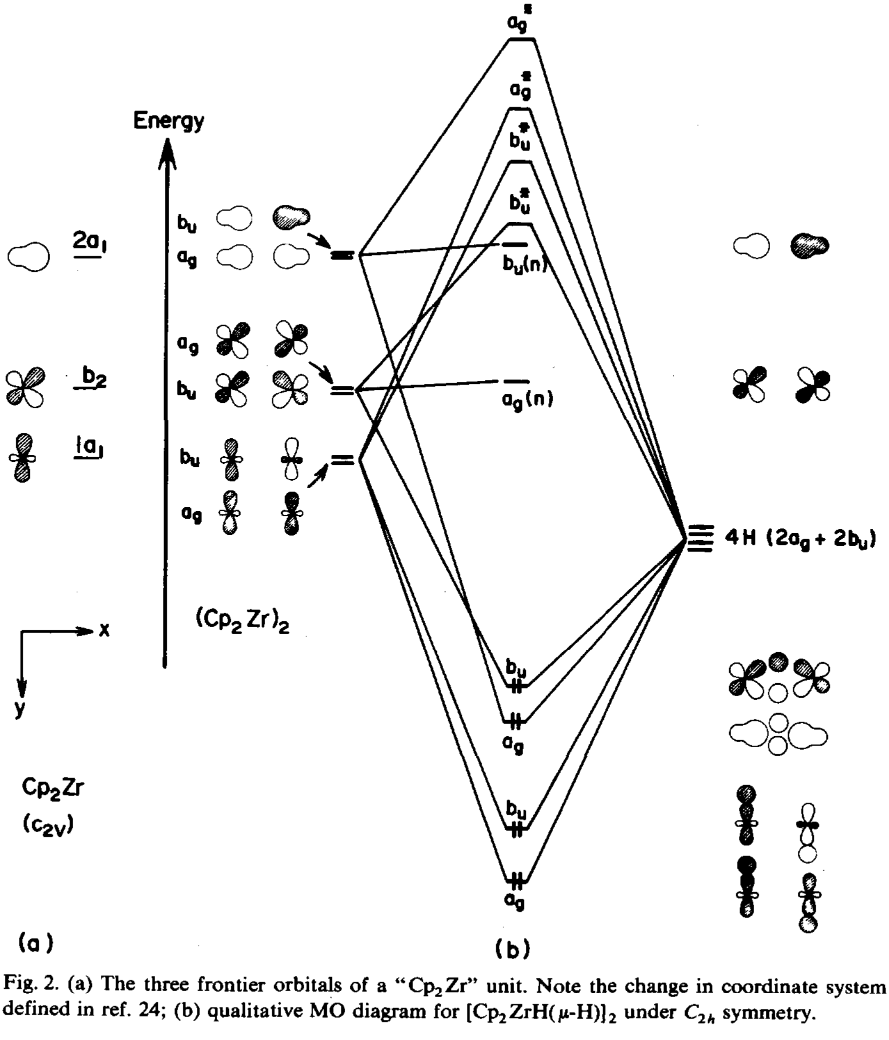


Fig. 2. (a) The three frontier orbitals of a "Cp_2Zr" unit. Note the change in coordinate system to that defined in ref. 24; (b) qualitative MO diagram for $[Cp_2ZrH(\mu\text{-}H)]_2$ under C_{2h} symmetry.

Scheme 2 ($\mathbf{2} \rightarrow \mathbf{9}$) is plausible, especially since the recent crystal structure of the related $[(CpMe)_2ZrH(\mu\text{-}H)]_2$ molecule points out the weaker nature of the bridging hydride bonds. Also, progressive substitution of the hydrogens in the Cp ring by methyl substituents eventually leads to a monomeric $(CpMe_5)_2ZrH_2$ [4,5]. As mentioned earlier, there is ^1H NMR evidence of a facile route for bridge-terminal hydride exchange in related systems. Structure **9** is written with two bridging hydrides and two terminal hydrides on a single Zr atom to maximize electron density in the bridge and to underscore the notion of concertedness in the bridge-terminal hydride exchange.

We note here the resemblance of a structure such as **9** to intermediates proposed by Brintzinger [25] for hydrogen isotope exchange of $(CpR_5)_2ZrH_2$ ($R = H, CH_3$) complexes. Brintzinger proposed a mechanism involving initial formation of an "H_2 adduct", leading to a transition state involving four hydrogen atoms around a "Cp_2Zr" unit, an H^- ligand and a three-center $(H \cdots H \cdots H)^-$ moiety. The energy profile for coordination of the H_2 and migration of one of the H atoms to an H^- ligand via the transition state does not have a significant energy barrier, requiring a maximum * of 11 kcal/mol above the energy of an isolated $(CpR_5)_2ZrH_2$ molecule. Also, throughout the rearrangement coordinate, the Zr atom maintains a charge close to $+1$, while all hydrogen atoms are negatively charged at all times **. In **9**, we not only have a coordinatively unsaturated zirconium center with a low-lying vacant orbital into which the incoming acetylene can donate electrons, but also we have two terminally bonded hydrogen atoms poised for reductive elimination. An organic analogue would be the S_N2' reaction in which nucleophilic attack at an unsaturated center induces elimination of a leaving group positioned two carbons away from the original site of attack. We note (in Fig. 3) that the two MO's associated primarily with the two bridging hydrogens and one σ-type orbital involved in bonding the acetylene remain essentially unchanged on elimination of the hydrogen. We stress that the relative energies and even the ordering shown are only qualitative and indeed change depending on how far the hydrogen is from being bound to a Zr atom. The presumed HOMO in **10** is bonding with respect to the out-of-phase combination of the two terminal hydrogen $1s$ orbitals which only bond to the appropriate orbital on one Zr. The orbital on the other zirconium is of the correct symmetry to overlap with the π^* orbital of the acetylene. Thus, the build up of electron density after elimination of H_2 can be alleviated by delocalization back into this vacant π^* orbital. In essence, the formation of a formally zirconium(II) center is stabilized and facilitated by this π back-donation pathway, however transitory the lifetime of **11**. Effectively, **10** and **11** might be regarded merely as transition states in the ligand-induced monomerisation of **2** to give **12**, H_2 and Cp_2ZrH_2 (which can dimerize and return to the beginning of the reaction cycle). The 16-electron species **12** can then combine with a second acetylene to give the bis(alkyne) unit **13** which in turn can oxidatively couple to generate **7**. Such a process has been discussed by Lauher and Hoffmann [24] for the related coupling of two olefins on a titanium center and is completely symmetry allowed.

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* This energy difference actually depends [25] on the energy of the d orbitals, ranging from almost zero to 16 kcal/mol within the chosen energy limits used in the calculation.

** It appears that the $(H \cdots H \cdots H)^-$ ligand is quite similar to an allyl ligand with regard to its charge distribution and bonding properties [25].

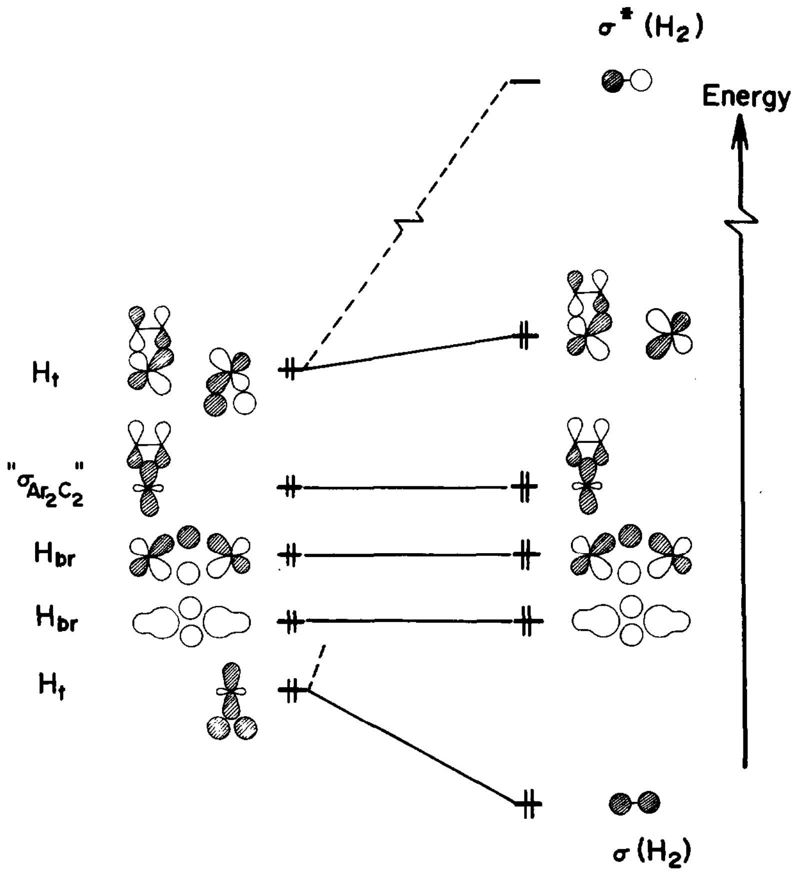

Fig. 3. Qualitative MO diagram for the bonding orbitals of intermediate **10**, and their fate after reductive elimination of hydrogen. See text.

An intermediate analogous to **12** has been suggested by Schwartz for the reaction of alkyl hydride complexes **3** [26] and Cp_2ZrL_2 (L = phosphine) complexes [27] with acetylenes. However, in the case of the alkyl hydride complexes, the breakdown of the dimer structure for **3** into monomeric, coördinatively unsaturated species is postulated to occur before reductive elimination of RH, the eventual coordination of two alkyne units, and finally alkyne coupling to produce zirconacyclopentadiene complexes. No reactions of **3** with diarylacetylenes appear to have been reported and no information is available concerning any stereochemical congestion in such species that might promote monomer formation.

Finally, we note that the hydrochloride **1** differs in its reactivity towards diphenylacetylene from **2**, producing the double hydrozirconation product **4**. Although the molecularity of **1** is not firmly established, solid-state infrared spectra suggest hydride bridging ligands, which might make a mechanism involving reductive elimination of H_2 similar to Scheme 2 inoperative for **1** and perhaps explain the difference in the reactions of **1** and **2** towards diphenylacetylene.

Concluding remarks

In this report we have demonstrated the dimeric nature of the $[Cp_2ZrH(\mu\text{-}H)]_2$ molecule (**2**) in solution and clarified its reaction with diphenylacetylene to produce metallocycle **7**. As such reaction products do not appear at high temperatures when the monomer predominates, we suggest that the dimer is the precursor of **7** whereas hydrozirconation occurs via the monomer. A rational mechanism is proposed based on the dimer structure and a qualitative molecular orbital analysis supports the feasibility of this process. The MO study also points out the ability of π-acids to stabilize a reactive zirconium(II) center in a dimeric unit.

Studies are continuing on the importance of dimer reactivity in the formation of unusual organometallic complexes of boron hydrides and metal carbonyl clusters.

Experimental

General procedures

All reactions were performed under a dry nitrogen atmosphere using conventional benchtop and glovebag techniques. Solvents were dried over sodium metal and degassed before use. Cp_2ZrCl_2 (Alfa), $LiBH_4$ (Aldrich), triethylamine (Baker) and diphenylacetylene (Eastman) were used as received from the indicated commercial source. $[Cp_2ZrH(\mu\text{-}H)]_2$ was prepared by a literature method [20] by treating $Cp_2Zr(BH_4)_2$, prepared in situ from Cp_2ZrCl_2 and $LiBH_4$, with triethylamine.

Instrumentation

^1H NMR spectra were obtained with a Bruker WM-250 spectrometer operating in the FT mode at 250 and 62.86 MHz for ^1H and ^{13}C nuclei, respectively. Chemical shifts are referenced to tetramethylsilane. $Cr(acac)_3$(~ 0.05 *M*) was added for ^{13}C spectra. Mass spectrometry was performed on a VG micromass 7070 spectrometer equipped with a VG 2035 data system. Samples were introduced via the direct insertion probe with the ion source temperature at 100°C.

$Cp_2Zr[C_4(C_6H_5)_4]$ *(7)*

A suspension of 2.35 g (10.52 mmol) of the dihydride in ~ 50 ml of benzene was treated with 3.75 g (21.04 mmol) of diphenylacetylene dissolved in the minimum amount of benzene. The suspension was warmed gently, with stirring, until an orange-red solution was formed. Filtration, followed by solvent removal, gave an orange solid in 75% yield, which was recrystallized from toluene to afford **7**. The product was characterized by infrared, mass spectrometry, and ^1H and ^{13}C NMR data, which were identical with those for an authentic sample prepared from Cp_2ZrCl_2 and $Li_2C_4Ph_4$ according to literature methods [12a]. Mass spectral data: *m/z* 576, $ZrC_{38}H_{30}^+$ (15); 398, $ZrC_{24}H_{20}^+$ (22); 358, $C_{28}H_{22}^+$ (30); 267, $C_{21}H_{15}^+$ (32); 220, $ZrC_{10}H_{10}^+$ (100); 178, $C_{14}H_{10}^+$ (100). The reaction was also repeated at room temperature, again giving the product **7**. However, reaction was considerably slower, with 45% of the H_2 produced after 3 days. The reaction was performed in a closed system and the evolved H_2 collected by Toepler pump and identified mass spectrometrically. *trans*-Stilbene as a product was detected in the crude reaction product, being identified chromatographically and by ^1H NMR.

$Cp_2Zr[C_4(C_6H_5)_2H_2]$ (8)

A suspension of the dihydride (2.18 g; 9.76 mmol) was treated with 1,4-diphenylbuta-1,3-diyne (1.91 g; 9.44 mmol) and was gently warmed, with stirring, until an orange solution was obtained. Filtration, solvent removal and recrystallization from toluene gave the orange solid **8** in 78% yield. Mass spectral data: *m/z* 424, $ZrC_{26}H_{22}^+$ (2); 220, $ZrC_{10}H_{10}^+$ (8); 206, $C_{16}H_{14}^+$ (80); 205, $C_{16}H_{13}^+$ (39); 191, $C_{15}H_{11}^+$ (20); 117, $C_9H_9^+$ (96); 115, $C_9H_7^+$ (40); 91, $C_7H_7^+$ (100); 66, $C_5H_6^+$ (70); 65, $C_5H_5^+$ (50).

Acknowledgement

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