When surfactant I is dissolved in D_2O (0.20 M, pD = 9.58, 34 °C), the acetylenic proton exchanges for deuterium with a half-life of 30 min.

$$HC{\equiv}CCD_2(CH_2)_{10}N(CH_3)_3^+ \xrightarrow[D_2O]{OD^-} [^-C{\equiv}CCD_2(CH_2)_{10}N(CH_3)_3^+] \rightarrow DC{\equiv}CCD_2(CH_2)_{10}N(CH_3)_3^+$$

This compares with 6 h for micellized II and 15 min for monomeric 1-pentyne under similar conditions.[17] Micellization obviously impedes carbanion formation in the basic medium, but the effect is much greater for anionic II than for cationic I. The relatively slow exchange for II can be qualitatively explained by adverse electrostatic effects and by reduced OD^- levels at the Stern region (as have been invoked in classical micellar kinetics).[18] Similarly, one would predict a catalysis with I if the ≡CH termini positioned themselves among the cationic head groups. The small inhibition must then reflect more inwardly directed termini that are, nonetheless, within reach of water molecules.[19]

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Registry No. I, 86436-58-0; II, 86436-59-1; III, 86436-60-4; hydrogen, 1333-74-0.

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[17] The 1-pentyne concentration (0.02 M) was slightly less than its solubility in water. See: McAuliffe, C. *J. Phys. Chem.* **1966**, *70*, 1267.

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[19] Interestingly, the ≡CH chemical shift of vesicles formed from dichain surfactant III below its 36.5 °C phase transition temperature[20] also points to a polar environment (Table I). At least three explanations are possible. (1) The probe may in fact "drag" water into a normally dry bilayer. For the reasons mentioned, we think this unlikely. (2) The NMR data may reflect the presence of relatively wet micelles in equilibrium with the vesicles. (3) Synthetic surfactants like III may be less capable than phospholipids of forming tight water-free bilayers. Perhaps the fast leakage rates of glucose enclosed in didodecyltrimethylammonium bromide vesicles[21] are related to this effect. Clearly, much more work is required to characterize the structure and hydration of vesicles.[22]

[20] We thank Professor T. Kunitake for determining the T_c value.

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[22] Unfortunately, the dichain phosphate in Scheme I was too insoluble to secure reliable NMR spectra with available equipment.

Chemical Reactivity of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$. EPR Evidence for the Formation and Participation of Paramagnetic Zirconocene Complexes

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The chemical reactivity of early transition-metal hydride complexes has attracted considerable attention because of the M^+–H^- polarization associated with the metal–hydride bond. The chemical ramifications of this feature have been extensively explored to evaluate the susceptibility of various metal-coordinated substrates such as CO[1,2] and olefins[3] to nucleophilic attack by H^-. Recently, we have undertaken an effort to investigate the stereochemistry and chemical reactivity of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$. This binuclear complex, I, contains two trans terminal and two bridging hydrides[4] and is stereochemically rigid in solution at 25 °C on a NMR time scale. In contrast to $(\eta^5\text{-}C_5Me_5)_2ZrH_2$, which possesses a vacant metal hybridized orbital, all nine metal valence orbitals of each Zr center in I are involved in chemical bonding. Therefore, unlike the reactivity of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$, which is generally initiated by nucleophilic attack by substrate L (L = CO,[5] PF_3,[5] $C{\equiv}NCH_3$,[6] $(C_5H_5)_2W(CO)$[7]) to produce an intermediate 18-electron species, the chemical reactivity of I presumably follows from the initial degradation of its symmetrical binuclear structure via either a dimer ⇄ monomer equilibrium process involving the formation of an intermediate monohydrido-bridged binuclear species or the reductive elimination of H_2 with the concomitant formation of a reduced zirconocene species. To determine the extent to which these stereochemical features modify the chemical behavior of I, we have begun to examine systematically its reactivity toward acetylenes and its sensitivity toward thermolysis and photolysis.

Diphenylacetylene reacts slowly at 50 °C in a THF slurry of I (acetylene/I ratio of 4:1) to produce $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_4)$ (isolated yield, 80%)[8a] with stoichiometric evolution of H_2, which was periodically collected by means of a Toepler pump. Phenylacetylene reacts more rapidly at 30 °C with I (acetylene/I ratio of 6:1) yielding primarily the 1,4-diphenyl-substituted zirconacyclopentadiene isomer of $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_2H_2)$ (yield, 50%).[8b] If the same reactions are repeated in benzene at 60 °C *without* the removal of H_2, appreciable hydrogenation of the respective acetylene occurs. For diphenylacetylene, the principal hydrogenated product is *trans*-stilbene (20%) and some bibenzyl (4%) is detected by gas chromatography.[9] For phenylacetylene the principal hydrogenated product is ethylbenzene with a trace amount of styrene.[10] From these results the chemistry of I with phenylacetylene and diphenylacetylene involves at least two competing reactions—metallacycle formation and acetylene hydrogenation. These reactions presumably rely on the formation of reduced zirconocene species[10-12] and the availability of H_2.

With this in mind, thermolysis and photolysis studies were undertaken to examine the susceptibility of I to reductive elimination of H_2 in solution and to evaluate the nature and chemical reactivity of any low-valent organozirconium species produced under these conditions. We found that ambient photolysis and prolonged heating at 75 °C of a 20 mL of benzene slurry containing 150 mg of I are similarly accompanied by the evolution of over 2 mol of H_2 per mole of I and proceed with the formation of dark purple solutions.[13] Eventually, after 400 h of heating, the mole ratio of evolved H_2/I levels off at 3. The progress of these degradation reactions was monitored by EPR,[14] which in each case revealed the presence of an intermediate paramagnetic Zr–hydride complex, II. Its solution EPR spectrum exhibits a distinct doublet at $g = 1.9854$ with $A(^1H) = 6.8$ G. The magnitude of $A(^1H)$ is comparable to that reported for $(\eta^5\text{-}C_5H_5)_2NbH_2$,[15] $(\eta^5\text{-}C_5H_5)_2TiH$ (solvate),[16] and the paramagnetic

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[8] (a) The formation of the metallacyclopentadiene complex was verified by hydrolysis, comparison of its ^{13}C NMR spectrum with that of an authentic sample, elemental analysis, and an X-ray structure determination. (b) Hydrolysis of this isomer, which was separated from the product mixture by gel permeation chromatography, yielded *trans,trans*-1,4-diphenyl-1,3-butadiene.

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[14] The solution EPR spectra were measured with an IBM/Bruker ER200D-SRC EPR spectrometer that is controlled by 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 (+0.01 G). Each sample was prepared in a Vacuum Atmospheres inert atmosphere drybox, and the solvent was introduced by vacuum distillation. The samples were degassed by freeze–pump–thaw methods and sealed under vacuum.

0002-7863/83/1505-5502$01.50/0

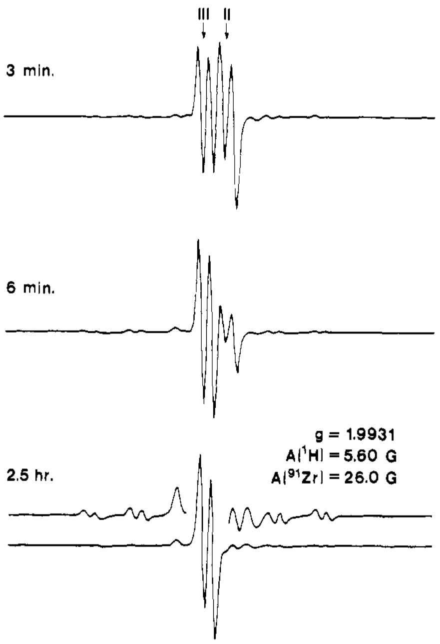

Figure 1. Solution EPR spectra of the photolysis of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ in the presence of $PhC{\equiv}CPh$ after 3 min, 6 min, and 2.5 h.

Zr hydrides produced during the photolysis of $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$[17] and $(\eta^5\text{-}C_5H_5)_2Zr(C_6H_5)_2$.[18]

To investigate the chemical reactivity of II, we have photolyzed I in benzene containing either diphenylacetylene, D_2, or PPh_3 and followed the reactions by EPR. For diphenylacetylene, the hydride doublet of II diminishes with the formation of a new paramagnetic Zr-hydride species, III, with $g = 1.9931$, $A(^1H) = 5.6$ G, and $A(^{91}Zr) = 26.0$ G (Figure 1). The EPR spectrum of III may be that of the hydridoacetylene complex, $(\eta^5\text{-}C_5H_4CH_3)_2Zr(H)(PhC{\equiv}CPh)$,[19] which represents a plausible intermediate in the acetylene hydrogenation process.[21] When photolysis of I is performed under a D_2 atomosphere, the hydride doublet is replaced by an "apparent" singlet due to H/D exchange of the Zr–H bond in II. The magnitude of $A(^2D)$, *ca.* $^1/_6$ of $A(^1H)$, is sufficiently small to prevent resolution of the ^2D hyperfine coupling. Further EPR experiments have shown that the H/D exchange process for II is reversible.[22] Finally, for PPh_3 the hydride doublet slowly fades with the appearance of another doublet centered at $g = 1.9977$. The larger hyperfine splitting of the latter is consistent with the formation of a paramagnetic Zr(III)–monophosphine species with $A(^{31}P) = 24.3$ G and $A(^{91}Zr) = 11.3$ G.[23] Analogous spectra are obtained in each case for the corresponding thermal reactions performed at 75 °C. Their spectral features, however, deteriorate upon prolonged heating. Although these EPR studies represent preliminary measurements, they suggest that paramagnetic zirconocene hydride complexes may participate in the chemical reactivity of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$. Work is in progress to determine the stereochemistry of these paramagnetic complexes and to examine further their chemical behavior.

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Registry No. I, 77965-67-4; $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_4)$, 86508-08-9; $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_2H_2)$, 86508-09-0; D_2, 7782-39-0; PPh_3, 603-35-0; phenylacetylene, 536-74-3; diphenylacetylene, 501-65-5.

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Synthesis and Properties of Macrobicyclic Amine Complexes of Rhodium(III) and Iridium(III)

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The macrobicyclic amine complexes $[M(sep)]^{3+}$, $[M(diNOsar)]^{3+}$, $[M(diAMsar)]^{3+}$, and $[M(diAMsarH_2)]^{5+}$ (Scheme I), M = Rh(III) and Ir(III), have been synthesized in moderate (~40%, Ir(III)) to high (90–100%, Rh(III)) yields from $[M(en)_3]^{3+}$ precursors,[1] demonstrating a remarkable degree of regiospecificity for formation of the cage structure. It was anticipated that the rare,[2-4] mononuclear octahedral d^7 Rh(II) and Ir(II) ions might be stabilized, since Co(III) analogues undergo reversible one-electron reductions to substitution inert Co(II) complexes,[5-10] and the d^7 Pt(III) cage complexes are stabilized in the solid state.[11] This expectation has been realized for Rh(II).

The cage complexes were prepared from $[M(en)_3]^{3+}$ ions[12-14] in a similar manner to the cobalt analogues[5-7,10] (Scheme I), except

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[1] sar = sarcophagine = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane; sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane; diNOsar = 1,8-dinitrosarcophagine; diAMsar = 1,8-diaminosarcophagine; diAMsarH$_2$ = 1,8-diammonium sarcophagine; en = 1,2-ethanediamine.

[2] The M(II) oxidation state is normally only observed as a transient intermediate or in spin-paired dimers.[3,4]

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