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Synthesis, X-ray Structure, and Electrochemical Study of $[\{\eta^5\text{-}C_5H_4C(CH_3)_3\}_2ZrH(\mu\text{-}H)]_2$. Identification of the $[\{\eta^5\text{-}C_5H_4C(CH_3)_3\}]_2ZrH_2$ Anion Radical by EPR Spectroscopy

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Summary: The synthesis and crystal structure of $[\{\eta^5\text{-}C_5H_4C(CH_3)_3\}_2ZrH(\mu\text{-}H)]_2$ are described. A study by cyclic voltammetry in THF at room temperature shows a pseudoreversible reduction wave at $E_p = -1.9$ V. Electrolysis under reductive current in the cavity of an EPR spectrometer indicates the formation of the dihydride monomer as the radical anion $[\{\eta^5\text{-}C_5H_4C(CH_3)_3\}_2ZrH_2]^{\bullet -}$, characterized by its spectrum (a(H) = 8.4 G, 1:2:1 triplet; $A(^{91}Zr)$ = 16.2 G). Cleavage of the dimeric structure following the reduction is discussed.

Hydrides of zirconocene are among the transition-metal hydrides having found various uses in stoichiometric and catalytic reactions.[1] The first member of this family, $(Cp_2ZrH_2)_2$, which is an insoluble oligomer, was reported in 1970.[2] Since then, soluble hydride dimers with the formula $[(R\text{-}C_5H_4)_2ZrH(\mu\text{-}H)]_2$ have been synthesized[3-5] but only the compound where R = CH_3 has been structurally studied.[6]

Our interest in this area has been recently focused on the study of new hydride systems and especially on Zr(III) compounds potentially active as selective hydrogenation catalysts.[7-10] In this work, we report the X-ray structure of $[\{\eta^5\text{-}C_5H_4C(CH_3)_3\}_2ZrH(\mu\text{-}H)]_2$ (1) and the study of its reduction by chemical and electrochemical methods, with the final purpose of determining the influence of cyclopentadienyl ring substitution on the catalytic activity of the reduced species of the complex.

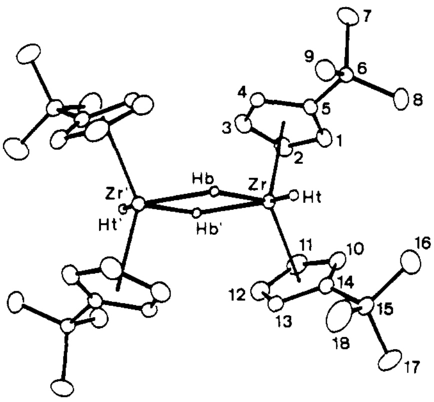

Figure 1. Molecular geometry and atom-labeling scheme for $[\{\eta^5\text{-}C_5H_4C(CH_3)_3\}_2ZrH(\mu\text{-}H)]_2$ (**1**). Selected bond distances (Å) and angles (deg) are as follows: Zr–Cp(1) = 2.219 (4), Zr–Cp(2) = 2.220 (4), Zr–H_b = 1.99 (4), Zr–H_t = 1.82 (7), Zr–$H_{b'}$ = 2.00 (4), Zr···Zr′ = 3.4708 (7); Cp(1)–Zr–Cp(2) = 129.8 (2), Cp(1)–Zr–H_b = 109 (1), Cp(1)–Zr–$H_{b'}$ = 104 (1), Cp(1)–Zr–H_t = 104 (1), Cp(2)–Zr–H_b = 121 (1), Cp(2)–Zr–$H_{b'}$ = 100 (1), Cp(2)–Zr–H_t = 99 (1), H_b–Zr–$H_{b'}$ = 59 (3), H_b–Zr–H_t = 64 (2), $H_{b'}$–Zr–H_t = 121 (2), Zr–H_b–Zr′ = 121 (3) Cp(1) (C1–C5) and Cp(2) (C10–C14) are the centroids of the two C_5H_4 rings, respectively. The prime symbols (′) denote atoms related by centrosymmetry.

Reaction of $[\{\eta^5\text{-}C_5H_4C(CH_3)_3\}_2ZrCl_2]$ with 2 equiv of $AlLiH(OCMe_3)_3$ (or $NaAlH_2(OCH_2CH_2OCH_3)_2$) in THF (or toluene) gives 1, which can be isolated from hexane in the crystalline form. It was characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis.[11] This compound has been previously synthesized[4] by hydrogenolysis of $[\{\eta^5\text{-}C_5H_4C(CH_3)_3\}_2Zr(CH_3)_2]$. In order to ascertain the bimetallic nature of 1, an X-ray crystal structure was undertaken.[12] As shown in Figure 1, this structure is roughly

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[1] See, for example: (a) Schwartz, J.; Labinger, J. A. *Angew. Chem.* **1976**, *88*, 402. (b) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and Hafnium Compounds*; Ellis Horwood: Chichester, U.K., 1986; Chapter 20. (c) Erker, G.; Schlund, R.; Krüger, C. *Organometallics* **1989**, *8*, 2349. (d) Pez, G. P.; Putnik, C. F.; Scrib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6933. (e) Jones, S. B.; Petersen, J. L. *Organometallics* **1985**, *4*, 966.

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[11] ^1H NMR (in toluene-d_8, 250 MHz, 20 °C; δ (ppm)): 6.18, 5.76, 5.38, 5.21 (t, 8 H, C_5H_4); 3.84 (t, 1 H, H_t); 1.59 (s, 18 H, CMe_3); −3.00 (t, 1 H, Hb). ^{13}C (in benzene-d_6, 101.27 MHz, 20 °C; δ (ppm)): 140.5 (substituted C, C_5H_4); 101.66, 101.19, 99.56, 98.0 (C_5H_4); 32.68 ($C(CH_3)_3$); 32.19 ($C(CH_3)_3$). Anal. Calcd for $C_{36}H_{56}Zr_2$: C, 64.44; H, 8.35. Found: C, 64.22; H, 8.10.

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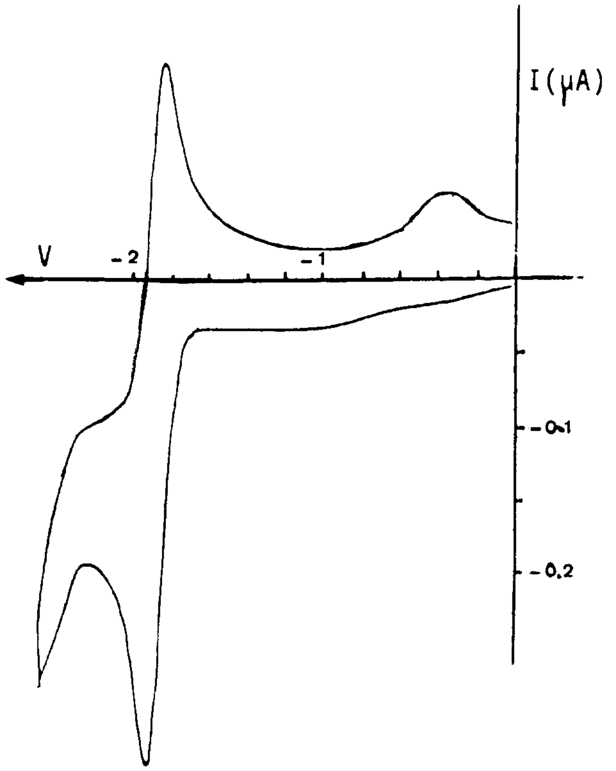

Figure 2. Cyclic voltammogram of 1 (10^{-3} M) in THF at 20 °C (scan speed 200 mV/s, with *iR* compensation).

comparable to that of the previously reported $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$[6] and consists of two $[\{\eta^5\text{-}C_5H_4C(CH_3)_3\}_2ZrH]$ units linked by two bridging hydrogens.

The center of the dimer is a crystallographic center of symmetry, and the dimeric geometry is idealized. The structural parameters of 1 are of the same order of magnitude as those of the Me–Cp derivative with an eclipsed orientation for the *tert*-butyl groups.[13] The core of the dimeric species shows two different hydrides, and because of the limitation of the X-ray diffraction method for the determination of the hydride positions, molecular mechanics calculations provided support for the location of the hydride ligands.[14] The same core $H_tZr(\mu\text{-}H_b)_2ZrH_t$ (H_t = terminal; H_b = bridging) is observed for 1 and $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ except for angles of 64.0 (2) and 70.1 (1°), respectively, for the H_tZrH_b moiety, presumably due to the steric effect of the *tert*-butyl group. The $H_b \cdots H_t$ distance in the Zr_2H_4 core is 2.012 (7) Å, while H_t and $H_{t'}$ are slightly out of the $[Zr(\mu\text{-}H)_2Zr]$ plane. Bond distances and angles are given in Table I.

A study by cyclic voltammetry of compound 1 at room temperature (in 0.2 M NBu_4PF_6/THF) shows the behavior of a pseudoreversible process with E_p(red) = −1.9 V and $\Delta[E_p(\text{red}) - E_p(\text{ox})]$ = 80 mV (Figure 2). This process is temperature-dependent and takes the values $\Delta[E_p(\text{red}) - E_p(\text{ox})]$ = 100 mV at 0 °C and 140 mV at −20 °C, respectively. It is independent of the scan speed at all temperatures.

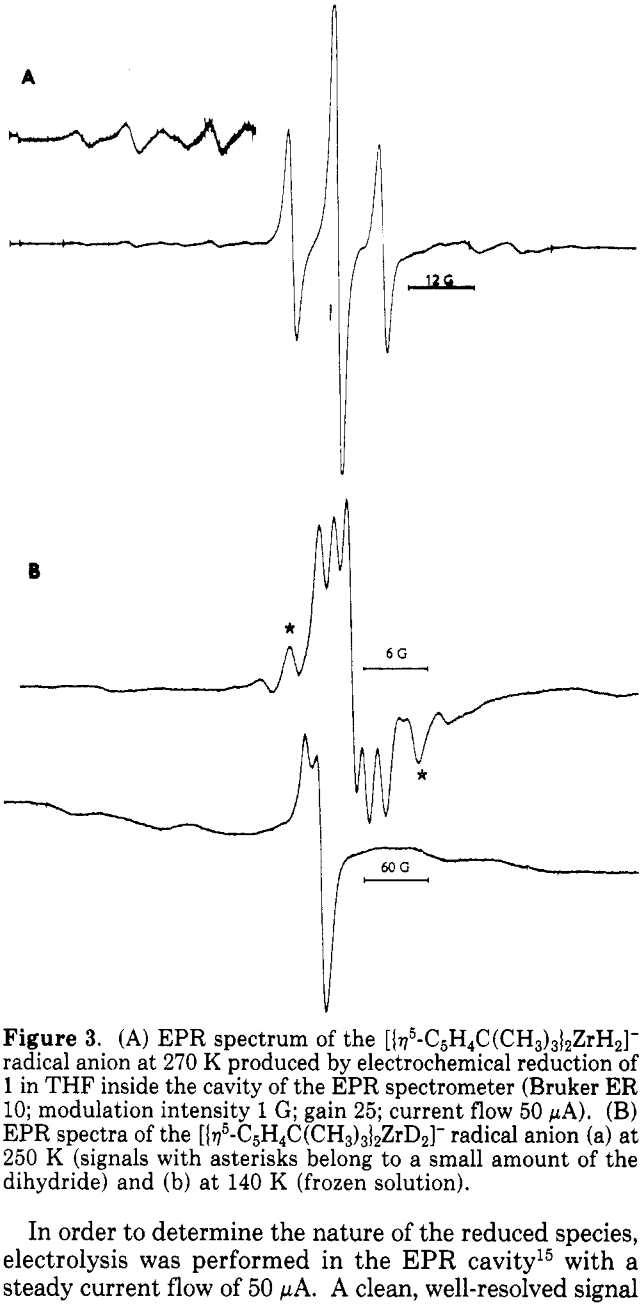

Figure 3. (A) EPR spectrum of the $[\{\eta^5\text{-}C_5H_4C(CH_3)_3\}_2ZrH_2]^-$ radical anion at 270 K produced by electrochemical reduction of 1 in THF inside the cavity of the EPR spectrometer (Bruker ER 10; modulation intensity 1 G; gain 25; current flow 50 μA). (B) EPR spectra of the $[\{\eta^5\text{-}C_5H_4C(CH_3)_3\}_2ZrD_2]^-$ radical anion (a) at 250 K (signals with asterisks belong to a small amount of the dihydride) and (b) at 140 K (frozen solution).

In order to determine the nature of the reduced species, electrolysis was performed in the EPR cavity[15] with a steady current flow of 50 μA. A clean, well-resolved signal (Figure 3A) builds up after a few seconds, and it remains stable for several minutes even if the current flow is stopped. This signal is composed of a central triplet of 1:2:1 intensity (g_{iso} = 1.996) flanked by satellites and is easily attributed to a paramagnetic Zr(III) species with the unpaired electron interacting with the central zirconium atom and with two magnetically equivalent hydrogens bound to it (a(H) = 8.4 G; A(Zr) = 16.2 G; ^{91}Zr, $I = {}^5/_2$, 11.2%; 1 G = 10 mT). The hydrogen hyperfine interaction is comparable in magnitude to that reported for other paramagnetic zirconocene species with terminal hydride ligands,[7-9] whereas the hyperfine interaction with Zr is substantially lower, reflecting important electron delocalization on the hydride ligands in the reduction product of 1. The frozen-solution spectrum exhibits wide features, and the anisotropy of the **g** tensor is not resolved because it is lower than the proton hyperfine interaction tensor.

The assignment of the EPR spectrum was confirmed by the same experiment performed under identical conditions

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[12] Crystal data: $C_{36}H_{56}Zr_2$; a = 10.294 (2) Å, b = 12.658 (2) Å, c = 7.235 (1) Å, α = 106.18 (2)°, β = 108.10 (2)°, γ = 80.31 (2)°, V = 857.1 (6) Å^3, triclinic, space group $P\bar{1}$, Z = 1. A total of 3721 intensity data were recorded in the ω–2θ scan mode on a CAD4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Full-matrix least-squares refinement with 2982 reflections having $F_o^2 > 3\sigma(F_o^2)$ led to a final R value of 0.032.

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Table I. Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses[a]

Zr–Cp(1)	2.219 (4)	Cp(1)–Zr–Cp(2)	129.8 (2)
Zr–H_b	1.99 (4)	Cp(1)–Zr–H_b	109 (1)
Zr–H_t	1.82 (7)	Cp(1)–Zr–$H_{b'}$	104 (1)
Zr–H_b–Zr′	121 (3)	Cp(1)–Zr–H_t	104 (1)
Zr–Cp(2)	2.220 (4)	Cp(2)–Zr–H_b	121 (1)
Zr–$H_{b'}$	2.00 (4)	Cp(2)–Zr–$H_{b'}$	100 (1)
Zr···Zr′	3.4708 (7)	Cp(2)–Zr–H_t	99 (1)
	H_b–Zr–$H_{b'}$	59 (3)	
	H_b–Zr–H_t	64 (2)	
	$H_{b'}$–Zr–H_t	121 (2)	

[a] Cp(1) and Cp(2) are the centroids of the [C(1), C(2), C(3), C(4), C(5)] and [C(10), C(11), C(12), C(13), C(14)] rings, respectively.

in the EPR cavity with the deuterated compound $[\{\eta^5\text{-}C_5H_4C(CH_3)_3\}_2ZrD(\mu\text{-}D)]_2$ (prepared from $AlLiD(OCMe_3)_3$ via $AlLiD_4$, purity checked by NMR spectroscopy). The signal obtained (Figure 3B) is composed of a central quintet with partially overlapping components, and the features are in agreement with what is expected for an unpaired electron interacting with two deuterium nuclei (quintet of relative intensities 1:2:3:2:1). The magnitude of the deuterium hyperfine interaction constant $a(D) = 1.38$ G is one-sixth of the value of the starting compound, as expected. The reduction of the signal bandwidth in the deuterated compound also has a consequence on the frozen-solution spectrum, which now exhibits a well-resolved **g** tensor anisotropy with pseudoaxial symmetry ($g_{\parallel} = 2.003$ and $g_{\perp} = 1.989$). Also detectable, though poorly resolved, are the perpendicular components of the Zr hyperfine tensor on both sides of the central signal, roughly measured to give 80 G. From the $g_{\parallel}$ value it can be deduced that the unpaired electron lies in the d_{z^2} metal orbital.

Reduction of 1 to the Zr(III) hydride species can also be performed by treatment with sodium or potassium naphthalenide in THF. The solution obtained exhibits an intense spectrum consisting of a quartet of triplets due to interaction of the unpaired electron with two hydrogens and with the nuclear spin ($I = {}^3/_2$) of the alkali metal ($g_{iso} = 1.992$; $a(H) = 8.3$ G; $a(^{23}Na) = 10.1$ G; $a(^{39}K) = 2.0$ G; $A(^{91}Zr) = 10.4$ G). This solution can be kept in a sealed tube for at least 2 weeks without change in the signal intensity.

The following steps can be proposed to account for the overall phenomenon observed by cyclic voltammetry combined with electrochemical reduction in the EPR cavity ($Cp' = \eta^5\text{-}C_5H_4C(CH_3)_3$):

$$\underset{\mathbf{1}}{[Cp'_2ZrH(\mu\text{-}H)]_2} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \underset{A}{[Cp'_2ZrH(\mu\text{-}H)]_2} \qquad (1)$$

$$A \rightleftharpoons \underset{B}{[Cp'_2ZrH_2]^-} + \underset{C}{[Cp'_2ZrH_2]} \qquad (2)$$

$$C \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} B \qquad (3)$$

$$2C \rightleftharpoons 1 \qquad (4)$$

Reaction 1 is the primary step that dominates the pseudoreversible process observed by cyclic voltammetry. The capture of one electron is expected to give a mixed-valence Zr(IV)/Zr(III) compound, but this species, which should exhibit a characteristic EPR spectrum, was not detected in the course of electrolysis in the EPR cell even down to −60 °C. The EPR results show therefore that the signal generated under a steady reductive current is due to a chemical process subsequent to the primary electron transfer, such as cleavage of dimer A in reaction 2, to give the neutral monomer C and the radical anion B responsible for the observed spectrum. C may also capture an electron as in (3) to give B or give back the dimer according to (4). However, other mechanisms are also possible and should not be excluded.

In conclusion, the above results show that the zirconium dihydride monomer is the only species detectable by EPR spectroscopy as the radical anion generated by electrochemical reductive cleavage of the corresponding dimer. This behavior appears to be common to the substituted (cyclopentadienyl)zirconium dihydride dimers, since we observed similar electrochemical results with $[Cp^*_2ZrH(\mu\text{-}H)]_2$ ($Cp^* = \eta^5\text{-}C_5H_4Si(CH_3)_3$). It can be reasonably expected therefore that cleavage of the dimer by chemical reductive methods should also lead to the monomer with more interesting reactivity properties. Moreover, these results support previous findings that bis(cyclopentadienyl)zirconium(IV) compounds tend to give stable radical anions by one-electron addition without secondary chemical complications.[16,17]

Supplementary Material Available: Tables of fractional atomic coordinates, hydrogen positional and thermal parameters, final anisotropic thermal parameters, bond lengths and angles, and least-squares planes (6 pages); a listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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Reversible, Stepwise Addition of 1,2-Diester-Substituted Alkenes to $Ru_2[(CH_3)_2PCH_2P(CH_3)_2]_2(CO)_5$. Crystal and Molecular Structure of the Diruthenacyclobutane Complex $Ru_2[(CH_3)_2PCH_2P(CH_3)_2]_2(CO)_4[\mu\text{-}\eta^1{:}\eta^1\text{-}C_2(H)_2(CO_2CH_3)_2]\cdot C_7H_8$

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Summary: cis- and *trans*-Diester-substituted alkenes react with $Ru_2(dmpm)_2(CO)_5$ (dmpm = bis(dimethylphosphino)methane) to form the trans-substituted diruthenacyclobutane. This process was shown to be stepwise and reversible, and a zwitterionic intermediate is proposed.

In 1980, a report by Brady and Pettit stirred widespread interest in dimetallacycloalkanes by providing evidence for the importance of coupling between surface-bound methylene groups in the Fischer–Tropsch reaction.[1] Despite

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[1] Brady, R. C. I.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181.

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