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The *Ansa*-Effect in Zirconocene Chemistry: The Syntheses and Interconversions of the Hydride Complexes $\{[Me_2Si(C_5Me_4)_2]Zr(H)(\mu\text{-}H)\}_2$, $[Me_2Si(C_5Me_4)_2]ZrH_2(PMe_3)$, and $[Me_2Si(C_5Me_4)_2]Zr(Ph)H$

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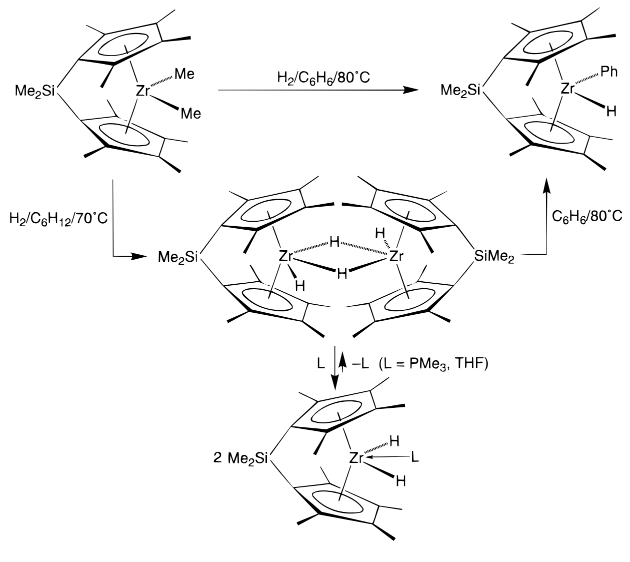
Zirconocene complexes, $(\eta^5\text{-}C_5R_5)_2ZrX_2$, have long been the subjects of considerable attention. Such interest stems not only from their participation in the discovery of novel structures and reactivity in organometallic chemistry, but also from their applications in organic synthesis[1] and their use as catalysts in olefin polymerization.[2] More recently, a large variety of *ansa*-zirconocene complexes $[ACp^R{}_2]ZrX_2$[3] have been investigated. These studies have chiefly been driven by efforts to improve polymer stereoregularity as a result of the configurational stability imparted by the *ansa* bridge.[2] Despite numerous studies on *ansa*-metallocene complexes, however, there has been relatively little attention given to delineating the *ansa*-effect in well-defined systems.[4,5] In this paper, a detailed comparison of the chemistry of $[Cp^*{}_2Zr]$ and $\{[Me_2Si(C_5Me_4)_2]Zr\}$ derivatives[6] allows interesting consequences of the $[Me_2Si]$ *ansa* bridge to be elucidated.

The formation of hydride complexes by hydrogenation of Zr−alkyl bonds is a common reaction of zirconocene derivatives. For example, Bercaw has reported the synthesis of the dihydride $[Cp^*][Cp^{Me}]ZrH_2$ by reaction of $[Cp^*][Cp^{Me}]ZrMe_2$ with H_2 in toluene,[7] while Marks has described the formation of $Cp^*{}_2ZrH_2$ upon treatment of $Cp^*{}_2ZrMe_2$ with H_2 in benzene.[8] It is, therefore, particularly striking that we have discovered that the corresponding reaction of the *ansa*-complex $[Me_2Si(C_5Me_4)_2]ZrMe_2$[9] does *not* yield a dihydride; rather, the reaction results in C−H bond activation of benzene and the formation of the phenyl−hydride complex $[Me_2Si(C_5Me_4)_2]Zr(Ph)H$ (Scheme 1).[10] The molecular structure of $[Me_2Si(C_5Me_4)_2]Zr(Ph)H$ has been determined by X-ray diffraction,[11] and the location of the phenyl group is indicative of a β-agostic interaction.[12]

Scheme 1



Despite the inability to isolate a dihydride complex for the *ansa*-zirconocene system under the conditions used to synthesize $Cp^*{}_2ZrH_2$, a related species may be obtained by reaction of $[Me_2Si(C_5Me_4)_2]ZrMe_2$ with H_2 in cyclohexane. Interestingly, the bridging dihydride so obtained, $\{[Me_2Si(C_5Me_4)_2]Zr(H)(\mu\text{-}H)\}_2$,[11] reacts readily with benzene to give $[Me_2Si(C_5Me_4)_2]Zr(Ph)H$ (Scheme 1). Together with additional observations,[13] this result suggests that the formation of the phenyl−hydride complex upon hydrogenation of $[Me_2Si(C_5Me_4)_2]ZrMe_2$ in benzene, as compared to the dihydride for the corresponding permethylzirconocene system, is a consequence of the different equilibrium positions for the reactions of the dihydrides with benzene, i.e. $K_{ansa} > K_{Cp^*}$.[14]

The dimeric structure of $\{[Me_2Si(C_5Me_4)_2]Zr(H)(\mu\text{-}H)\}_2$ is also of interest since it provides a contrast with the monomeric nature of the permethylzirconocene analogue, $Cp^*{}_2ZrH_2$.[15−17] Dissocia-

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(3) The term *ansa* (meaning bent handle, attached at both ends) was first introduced with respect to metallocene chemistry by Brintzinger. See: Smith, J. A.; von Seyerl, J.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *173*, 175−185.

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(6) Marks has applied the $[Me_2Si(C_5Me_4)_2]$ *ansa* ligand to lanthanide chemistry, with the intention that the *ansa* bridge would create a more "open" coordination sphere. See: Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828−1838 and references therein.

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(9) $[Me_2Si(C_5Me_4)_2]ZrMe_2$ and $[Me_2Si(C_5Me_4)_2]Zr(CO)_2$ are prepared from $[Me_2Si(C_5Me_4)_2]ZrCl_2$[9a] by standard methods. See Supporting Information. (a) Jutzi, P.; Dickbreder, R. *Chem. Ber.* **1986**, *119*, 1750−1754.

(10) Another illustration of an *ansa*-effect in hydrogenation is the observation that hydrogenation of the ethylene-bridged complex $[(C_2H_4)Si(C_5Me_4)_2]Zr(X)CH_2Bu^t$ (X = F, Cl, Br) is more facile than that for $Cp^*{}_2Zr(X)CH_2Bu^t$. See: Wochner, F.; Brintzinger, H. H. *J. Organomet. Chem.* **1986**, *309*, 65−75.

(11) Crystal data: $[Me_2Si(C_5Me_4)_2]Zr(Ph)H$ is orthorhombic, *Pnma* (No. 62), $a = 15.219(2)$ Å, $b = 11.201(4)$ Å, $c = 13.942(2)$ Å, $V = 2377(1)$ Å^3, $Z = 4$, $R_1 = 0.0423$ $[I < 2\sigma(I)]$; $\{[Me_2Si(C_5Me_4)_2]Zr(H)(\mu{-}H)\}_2$ is orthorhombic, *Pbcn* (No. 60), $a = 19.0228(2)$ Å, $b = 10.3503(1)$ Å, $c = 19.2320(1)$ Å, $V = 3787(1)$ Å^3, $Z = 4$, $R_1 = 0.0311$ $[I < 2\sigma(I)]$; $[Me_2Si(C_5Me_4)_2]ZrH_2(PMe_3)$ is orthorhombic, *Cmca* (No. 64), $a = 14.338(3)$ Å, $b = 11.787(2)$ Å, $c = 28.686(4)$ Å, $V = 4848(2)$ Å^3, $Z = 8$, $R_1 = 0.0473$ $[I < 2\sigma(I)]$.

(12) For example, the Zr−C−C bond angles [98.5(4)° and 146.0(5)°] deviate considerably from 120°.

(13) For example, $Cp^*{}_2Zr(Ph)H$ reacts with H_2 in benzene to give $Cp^*{}_2ZrH_2$.

(14) K_{ansa} and K_{Cp^*} are defined as $[\{Zr\}(Ph)H][H_2]/[\{Zr\}H_2][PhH]$.

(15) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716−2724.

(16) Other dimeric $\{[Cp^R]_2Zr(H)(\mu\text{-}H)\}_2$ complexes have, nevertheless, been reported, but these are normally associated with less heavily substituted cyclopentadienyl derivatives, *e.g.* $[(Cp^{Me})_2Zr(H)(\mu\text{-}H)]_2$,[16a] $[(Cp^{t-Bu})_2Zr(H)(\mu\text{-}H)]_2$,[16b] and $[(Cp^{TMS})_2Zr(H)(\mu\text{-}H)]_2$.[16c] (a) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889−2894. (b) Choukroun, R.; Dahan, F.; Larsonneur, A.-M.; Samuel, E.; Petersen, J.; Meunier, P.; Sornay, C. *Organometallics* **1991**, *10*, 374−376. (c) Larsonneur, A.-M.; Choukroun, R.; Jaud, J. *Organometallics* **1993**, *12*, 3216−3224.

(17) Dimeric hydride bridged complexes supported by the *ansa* ligand $[Me_2Si(C_5Me_4)_2]$ have also been reported for the larger elements, Y and Th: $\{[Me_2Si(C_5Me_4)_2]Y(\mu\text{-}H)\}_2$,[17a] and $\{[Me_2Si(C_5Me_4)_2]Th(\mu\text{-}H)_2\}_2$.[6] However, it should be noted that for these elements the non-*ansa* derivatives, $[Cp^*{}_2Y(\mu\text{-}H)]_2$[17b]

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tion is, nevertheless, facile in solution, as evidenced by a single, highly concentration and temperature dependent, resonance for the bridging and terminal Zr−H ligands.[18] Further evidence that the monomer−dimer equilibrium is facile is provided by the observation that addition of PMe_3 instantaneously traps the monomer as the adduct $[Me_2Si(C_5Me_4)_2]ZrH_2(PMe_3)$ (Scheme 1), which has been characterized by X-ray diffraction.[11,19] The permethylzirconocene complex $Cp^*_2ZrH_2$ also binds PMe_3, but much less strongly than does the *ansa* analogue.[20] For example, ^{31}P dynamic NMR studies demonstrate that the barrier to PMe_3 dissociation is much greater for the *ansa* complex, with $k_{Cp^*} > 500k_{ansa}$ at 25 °C.[21] Such an observation is of particular interest since it provides a clear indication that the zirconium center of the *ansa* system, $\{[Me_2Si(C_5Me_4)_2]Zr\}$, is significantly more Lewis acidic than that of the *non-ansa* system, $[Cp^*_2Zr]$.

Support for this notion is provided by ^1H NMR spectroscopic studies on the dihydride complexes in d^8-THF. Specifically, the hydride signal of $Cp^*_2ZrH_2$ in d^8-THF is highly temperature dependent, whereas that of the *ansa* analogue is almost insensitive to temperature.[22] This difference is interpreted in terms of THF dissociation from the adducts $[Me_2Si(C_5Me_4)_2]ZrH_2(THF)$ and $Cp^*_2ZrH_2(THF)$ being more favored for the permethylzirconocene system.[23] As such, the *ansa* ligand may be viewed as engendering a more electrophilic metal center.

A similar conclusion regarding the relative electrophilicity of the zirconium centers may also be derived by comparison of the ν(CO) stretching frequencies of the dicarbonyl complexes, $[Me_2Si(C_5Me_4)_2]Zr(CO)_2$ (1947 and 1861 cm^{-1}) and $Cp^*_2Zr(CO)_2$ (1942 and 1850 cm^{-1}).[24] Furthermore, electrochemical, XPS, and gas-phase electron-transfer studies also suggest that the $[Me_2Si]$ *ansa* bridge,[25] in contrast to the $[Me_3Si]$ group,[26] has an electron-withdrawing effect.[27] Since the $[Me_2Si]$ *ansa* bridge does *not* perturb the zirconocene geometry significantly in terms of the $Cp_{cent}-Zr-Cp_{cent}$ angle,[28] the origin of this effect is presumably a result of a subtle shift toward η^3,η^3-coordination of the *ansa* ligand,[25a] which serves to reduce the overall electron-donating ability of the two cyclopentadienyl fragments. In addition to this electronic effect, another consequence of the $[Me_2Si]$ *ansa* bridge is that the central equatorial site is more spacious for the *ansa* system, since this position is never eclipsed by a cyclopentadienyl methyl substituent. As such, the less sterically demanding *ansa* ligand promotes the binding of additional ligands to the central equatorial site and consequently enhances the electrophilicity of the zirconium center. Consistent with this notion, the dihydride $[Me_2Si(C_5Me_4)_2]ZrH_2$ exists as a dimer in the solid state.

Brintzinger was the first to discuss the "*ansa*-effect" (i.e. the influence of an *ansa* bridge on the reactivity of a system)[29] with respect to a comparison of Cp_2TiX_2 and $[(CH_2CH_2)(C_5H_4)_2]TiX_2$.[4a,30] More recently, Green has described the *ansa*-effect with respect to a comparison of Cp_2MX_2 and $[Me_2C(C_5H_4)_2]MX_2$ (M = Mo, W).[5] In each case, the *ansa*-effect in these systems has been attributed to the inability of the *ansa* ligand to adopt parallel ring structures. For the zirconium system described herein, however, the *ansa*-effect is best ascribed to the creation of a more electrophilic metal center.

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Supporting Information Available: Tables of analytical, spectroscopic, and crystallographic data (plus ORTEP drawings), and preparative details for all new complexes (38 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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and $[Cp^*_2Th(H)(\mu\text{-}H)]_2$,[17c] are also dimeric. (a) Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *Inorg. Chim. Acta* **1996**, *242*, 205−210. (b) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053−2060. (c) Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science* (*Washington, D.C.*) **1979**, *203*, 172−174.

(18) Despite fluxionality, studies on the partially deuterated species $\{[Me_2Si(C_5Me_4)_2]Zr\}_2(H_{4-x}D_x)$ provide decisive evidence that the major species present at low temperature (−70 °C) is a dimer. Specifically, the ^1H NMR spectrum of $\{[Me_2Si(C_5Me_4)_2]Zr\}_2(H_{4-x}D_x)$ ($x = 0-3$) exhibits *four* hydride signals attributable to four isotopomers (δ 3.39, 3.44, 3.48, and 3.53 at 200 K), a result that is only consistent with a dimeric structure persisting under these conditions.

(19) In solution, $[Me_2Si(C_5Me_4)_2]ZrH_2(PMe_3)$ is characterized by a triplet (δ −21.7, $^2J_{P-H} = 67$ Hz) in the selectively decoupled $^{31}P\{^1H-Me\}$ NMR spectrum at room temperature, thereby confirming the presence of two hydride ligands.

(20) $Cp^*_2ZrH_2(PMe_3)$ is characterized by a triplet (δ −13.4, $^2J_{P-H} = 64$ Hz) in the selectively decoupled $^{31}P\{^1H-Me\}$ NMR spectrum at −70 °C.

(21) $Cp^*_2ZrH_2(PMe_3)$: $\Delta H^\ddagger = 14.8(6)$ kcal mol^{-1}, $\Delta S^\ddagger = 10(2)$ eu. $[Me_2Si(C_5Me_4)_2]ZrH_2(PMe_3)$: $\Delta H^\ddagger = 18.5(3)$ kcal mol^{-1}, $\Delta S^\ddagger = 10(1)$ eu.

(22) For example, over the temperature range −82 to 25 °C, the hydride ^1H NMR signal of $Cp^*_2ZrH_2$ in d^8-THF varies from δ 4.31 to 5.96 ppm, approaching that of base-free $Cp^*_2ZrH_2$ in C_6D_6 (δ 7.46).[15] In contrast, the hydride signal for the *ansa* analogue only varies from δ 4.02 to 4.17 ppm over the same temperature range.

(23) Evidence that the *ansa* dihydride is monomeric in THF is provided by T_1 relaxation studies. See Supporting Information.

(24) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733−6735.

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(27) For theoretical calculations which support the notion of increased electrophilicity for the $[Me_2Si]$ *ansa* system, see: Woo, T. K.; Fan, L.; Ziegler, T. *Organometallics* **1994**, *13*, 2252−2261.

(28) For example, the $Cp_{cent}-Zr-Cp_{cent}$ angles in $Cp^*_2ZrCl_2$ and $[Me_2Si(C_5Me_4)_2]ZrCl_2$ are 130° and 129°, respectively. An η^3,η^3-coordination of the *ansa* ligand is, nevertheless, suggested by the range of Zr−C bond lengths, *i.e.* 2.48, 2.51, and 2.62 Å for the C_α, C_β, and C_γ ring carbon atoms, respectively. For $Cp^*_2ZrCl_2$, the Zr−C bond lengths range from 2.52 to 2.54 Å. Lee, H.; Parkin, G. Unpublished results.

(29) Bailey, N. J.; Green, M. L. H.; Leech, M. A.; Saunders: J. F.; Tidswell, H. M. *J. Organomet. Chem.* **1997**, *538*, 111−118.

(30) Brintzinger has also compared the chemistry of the vanadium complexes Cp_2VCl_x with $[(CMe_2CMe_2)(C_5H_4)_2]VCl_x$ (x = 1, 2). See ref 4b.