Synthesis of Singly and Doubly Bridged *ansa*-Zirconocene Hydrides. Formation of an Unusual Mixed Valence Trimeric Hydride by Reaction of H_2 with $\{(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2\}Zr(CH_3)_2$ and Generation of a Dinitrogen Complex by Reaction of N_2 with a Zirconocene Dihydride

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A series of singly and doubly bridged *ansa*-zirconocene dihydride complexes has been prepared from hydrogenation of the corresponding dimethyl complexes. For the singly [$SiMe_2$]-bridged species, the hydrogenation reaction is facile at 25 °C, whereas for the doubly [$SiMe_2$]-bridged complexes hydrogenation occurs over the course of days at 87 °C. Hydrogenation of {*meso*-$Me_2Si(\eta^5\text{-}C_5H_3\text{-}3\text{-}CMe_3)_2$}$ZrMe_2$ affords the isomeric dimeric dihydrides [{*meso*-$Me_2Si(\eta^5\text{-}C_5H_3\text{-}3\text{-}CMe_3)_2$}$ZrH]_2(\mu_2\text{-}H)_2$, one of which has been characterized by X-ray diffraction. The *racemo* isomer of $Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}CMe_3)_2ZrMe_2$ ($BpZrMe_2$) reacts with dihydrogen, affording the first example of a monomeric *ansa*-zirconocene dihydride, {*rac*-$Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}CMe_3)_2$}$ZrH_2$ (*rac*-$BpZrH_2$). In the presence of dinitrogen, *rac*-$BpZrH_2$ undergoes thermal reductive elimination of H_2 and reaction with N_2, yielding the dinitrogen complex $BpZr(\mu_2,\eta^2,\eta^2\text{-}N_2)ZrBp$, for which the dinitrogen ligand is coordinated in a side-on fashion to both zirconiums with a N−N bond distance of 1.241(3) Å. The doubly [$SiMe_2$]-bridged zirconium dimethyl complex $\{(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2\}ZrMe_2$ ($RpZrMe_2$) undergoes hydrogenation under forcing conditions, affording the mixed valent (Zr(IV)/Zr(IV)/Zr(III)) hydride trimer $[RpZr]_3(\mu_3\text{-}H)_2(\mu_2\text{-}H)_3$, which has been characterized by X-ray diffraction. More substituted doubly [$SiMe_2$]-bridged zirconocene dihydrides such as $[\{(Me_2Si)_2(\eta^5\text{-}C_5H\text{-}3,5\text{-}(CHMe_2)_2)(\eta^5\text{-}C_5H_2\text{-}4\text{-}CHMeEt\}ZrH]_2(\mu_2\text{-}H)_2$ ([*sec*-$BuThpZrH]_2(\mu_2\text{-}H)_2$) and $[(Me_2Si)_2(\eta^5\text{-}C_5H\text{-}2,4\text{-}(CHMe_2)_2)(\eta^5\text{-}C_5H_2\text{-}4\text{-}CHMe_2)ZrH]_2(\mu_2\text{-}H)_2$ ($[^iPrThpZrH]_2(\mu_2\text{-}H)_2$) have been prepared and shown to be robust dimers in solution.

Introduction

Group 4 *ansa*-metallocene complexes have received considerable attention due to their utility in olefin polymerization[1] and use as catalysts for a host of other enantioselective bond-forming processes.[2] For many of these transformations, a metallocene hydride is believed to be the active species during the catalytic cycle. In the asymmetric hydrogenation of 1,1-disubstituted and trisubstituted alkenes with chiral *ansa*-zirconocene[3] and titanocene catalysts,[4] olefin insertion into metallocene hydride bonds is believed to be the enantioselective step. Although group 4 *ansa*-metallocene hydrides are often implicated in a variety of catalytic cycles, the synthesis and characterization for many of these complexes has not been fully documented.

The synthesis of *rac*-$[(EBTHI)ZrH_2]_2$ (EBTHI = ethylene-1,2-bis(η^5-tetrahydroindenyl)) by reduction of the dichloride complex has been reported by Buchwald and co-workers.[5] The dimeric structure of the dihydride has been proposed on the basis of the observation of distinct terminal and bridging zirconium hydride resonances in the ^1H NMR spectrum. Royo[6] has used similar synthetic methodology to prepare the doubly [$SiMe_2$]-bridged $[\{(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2\}ZrH_2]_2$, which has also been reported to be dimeric in solution on the basis of its ^1H NMR spectrum. Parkin has prepared $[\{Me_2Si(\eta^5\text{-}C_5Me_4)_2\}ZrH_2]_2$ ($[OpZrH_2]_2$) by hydrogenation of the dimethyl complex at elevated temperatures in cyclohexane solution.[7] Characterization of the hydride dimer has been accomplished by NMR spectroscopy and X-ray crystallography.

As part of our investigations of ancillary ligand effects in group 4 metallocene chemistry, we describe the

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[1] (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Reiger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255.

[2] Hoveyda, A. H.; Morken, J. P. In *The Metallocenes*; Togni, A., Haltermann, L., Eds.; Wiley-VCH Publishers: Weinheim, 1988; Vol. 2, Chapter 10.

[3] (a) Waymouth, R. M.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911. (b) Troutman, M. V.; Appella, D. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 4916.

[4] Broene, R. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 11688.

[5] Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501.

[6] Cuenca, T.; Galakhov, M.; Royo, B.; Royo, P. *J. Organomet. Chem.* **1996**, *515*, 33.

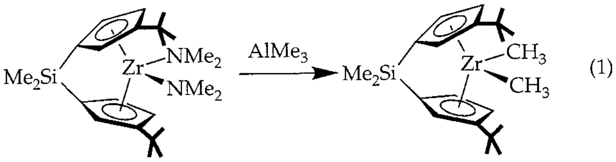
[7] Lee, H.; Desrosiers, P. J.; Guzei, I.; Rheingold, A. L.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 3255.

10.1021/om000739h CCC: $20.00

preparation and characterization of both singly and doubly [$SiMe_2$]-bridged zirconocene dihydrides using the hydrogenation of the corresponding dimethyl complexes. During the course of our investigations, we have been able to prepare the first example of a monomeric *ansa*-zirconocene dihydride. This monomer is unique among the zirconocene dihydrides examined in that it undergoes thermal reductive elimination of dihydrogen, and in the presence of dinitrogen it cleanly results in the coordination of dinitrogen between two zirconium(II) centers. The zirconocene dinitrogen complex has been characterized by X-ray diffraction and displays side-on [$Zr(\mu_2,\eta^2,\eta^2\text{-}N_2)Zr$] coordination geometry. We also report that a doubly [$SiMe_2$]-bridged zirconocene dimethyl complex undergoes hydrogenation to afford a mixed valent (Zr(IV)/Zr(IV)/Zr(III)) hydride trimer, which has been characterized by X-ray diffraction.

Results and Discussion

Preparation of Singly Silylene-Bridged Zirconocene Dihydride Complexes. The first synthetic target in our study was [{*meso*-$Me_2Si(C_5H_4\text{-}3\text{-}CMe_3)_2$}-$ZrH_2$]$_n$ ([*meso*-$DpZrH_2$]$_n$), since the preparation of the corresponding zirconocene dichloride as the pure *meso* isomer had been previously reported.[8] Methylation of *meso*-$DpZrCl_2$ in diethyl ether affords a 2:1 mixture of *meso* and *rac* isomers of $DpZr(CH_3)_2$, arising from competitive epimerization. Similar *racemo* ⇄ *meso* interconversions promoted by various salts and Grignard reagents have been observed previously with both group 3 and group 4 metallocenes.[9] Preparation of pure *meso*-$DpZr(CH_3)_2$ (**1**) may be accomplished by addition of $AlMe_3$ to *meso*-$DpZr(NMe_2)_2$ (eq 1).[10] Slow cooling of a petroleum ether solution of **1** affords large yellow crystals suitable for X-ray diffraction. The solid-state structure of **1** is shown in Figure 1 and confirms its identity as the *meso* isomer.



(1)

1

Compound **1** crystallizes with two molecules in the asymmetric unit. There are no significant differences in the conformations of these two molecules. Compound **1** displays a normal coordination environment for an *ansa*-metallocene with the two zirconium methyl groups contained in the metallocene wedge, displaying typical zirconium methyl bond lengths of 2.272(4) and 2.273(4) Å for molecule A and 2.264(4) and 2.274(4) Å for molecule B.

Hydrogenation of **1** in benzene-d_6 proceeds over the course of hours at 25 °C, affording the dihydride dimer, [*meso*-$DpZrH]_2(\mu_2\text{-}H)_2$ (**2**) (eq 2).

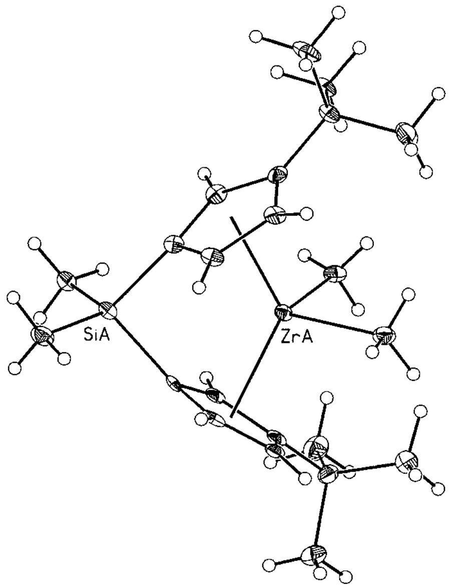
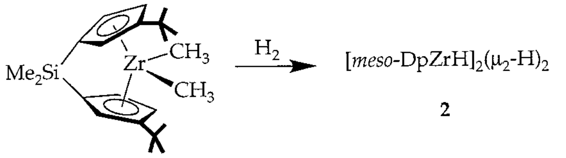


Figure 1. Molecular structure of **1** with 50% probability ellipsoids (hydrogen atoms shown at arbitrary scale).



(2)

2

1

The ^1H NMR spectrum (500 MHZ) of **2** in toluene-d_8 ([Zr] = ca. 0.02 M) displays two resonances for *tert*-butyl substituents in an approximately 1.1:1 ratio, together with two sets of three cyclopentadienyl resonances and two sets of two dimethylsilyl resonances, all in approximately the same 1.1:1 ratio. Broad, overlapping zirconium hydride resonances are centered at δ 4.01, the region associated with terminal hydride resonances. Upfield of $SiMe_4$ in the region associated with bridging hydrides are a triplet at δ −2.39 ppm and a broad unresolved multiplet at δ −5.32 ppm in approximately this same 1.1:1 ratio. These data suggest that hydrogenation of **1** yields a mixture of two symmetric isomeric dimers.

Upon standing in benzene-d_6, clear, colorless crystals of **2a** are deposited over the course of several days at 25 °C. Complex **2a** crystallizes in space group $P\bar{1}$ with two dimers in the unit cell; each sits on an inversion center (Figure 2). As result, the dihedral angle between the planes formed by the two metallocene wedges is zero, and the terminal hydrides must thus be in a *trans* relationship. Unfortunately, neither the bridging nor terminal hydride atoms were found in the difference map. However, the zirconium−zirconium distances of 3.492(2) and 3.450(2) Å for **2a** are consistent with other crystallographically characterized zirconocene dihydride dimers which display metal−metal distances between 3.4 and 3.5 Å.[11]

A dihedral angle of zero degrees between the two zirconocene equatorial planes contrasts with previous

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[8] Diamond, G. M.; Jordan, R. F.; Peterson, J. L. *Organometallics* **1996**, *15*, 4045.

[9] Yoder, J. C.; Day, M. W.; Bercaw, J. E. *Organometallics* **1998**, *17*, 4946.

[10] Kim, I.; Jordan, R. F. *Macromolecules* **1996**, *29*, 489.

[11] (a) [$(\eta^5\text{-}C_5H_4CH_3)_2ZrH]_2(\mu_2\text{-}H)_2$ (3.460 Å): Jones, S. B.; Peterson, J. L. *Inorg. Chem.* **1981**, *20*, 2889. (b) [$(\eta^5\text{-}C_5H_4Me_3)_2ZrH]_2(\mu_2\text{-}H)_2$ (3.471 Å): Choukroun, R.; Dahan, F.; Larsonneur, A. M.; Samuel, E.; Peterson, J.; Meunier, P.; Sornay, C. *Organometallics* **1991**, *10*, 374. (c) [$(\eta^5\text{-}C_5H_4SiMe_3)_2ZrH]_2(\mu_2\text{-}H)_2$ (3.437 Å): Larsonneur, A. M.; Choukroun, R.; Jaud, J. *Organometallics* **1993**, *12*, 3216. (d) [$Me_2Si(\eta^5\text{-}C_5Me_4)_2ZrH]_2(\mu_2\text{-}H)_2$ (3.549 Å): Lee, H.; Desrosiers, P. J.; Guzei, I.; Rheingold, A. L.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 3255.

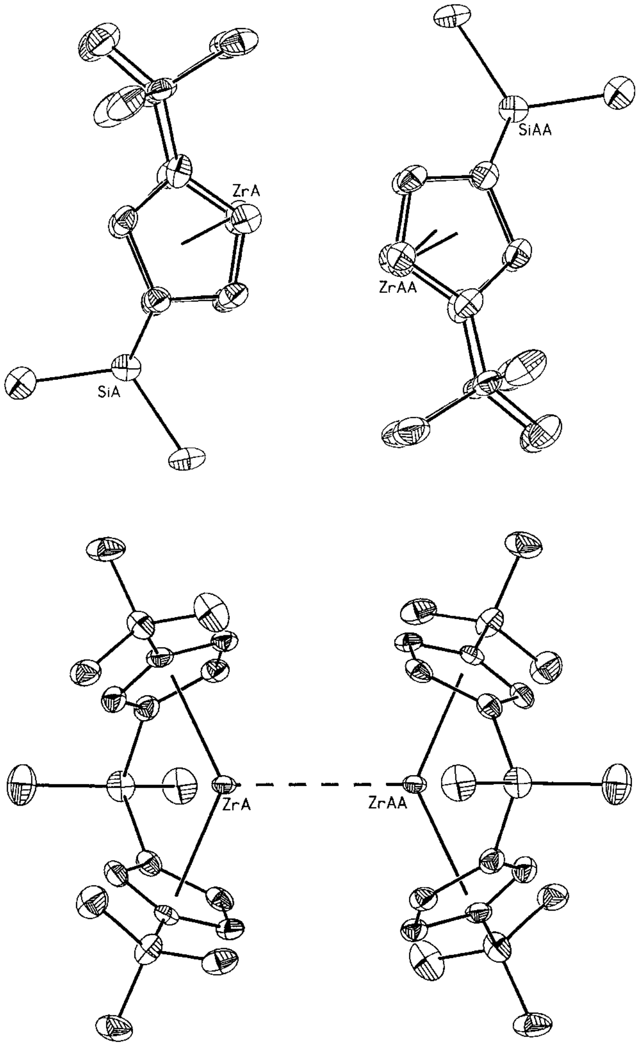
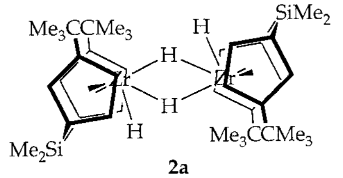


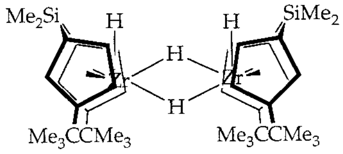
Figure 2. Molecular structure of one zirconium center of **2a** with 30% probability ellipsoids, as viewed from above and in the equatorial plane. Hydrogen atoms omitted for clarity.

results for *ansa*-metallocene hydride complexes. The *ansa*-zirconocene dihydride $[\mathrm{OpZrH}]_2(\mu_2\text{-H})_2$[7] and the *ansa*-titanocene $[rac\text{-(EBTHI)TiH}]_2$[12] display substantial (53° in the latter case) twisting of the metallocene equatorial planes in order to alleviate unfavorable steric interactions between substituents of opposing cyclopentadienyl groups. A dihedral angle of 40° has been measured for the *ansa*-yttrocene hydride $[rac\text{-}\{(\mathrm{OC_{10}H_6C_{10}H_6O})\mathrm{Si}(\eta^5\text{-}\mathrm{C_5H_2}\text{-2-}\mathrm{SiMe_3}\text{-4-}\mathrm{CMe_3})_2\}\mathrm{Y}]_2(\mu_2\text{-H})_2$ ($[rac\text{-BnBpY}]_2(\mu_2\text{-H})_2$).[13] For **2a**, the unfavorable steric interactions between the *tert*-butyl groups are reduced by a rotation about the Zr–Cp bonds which moves the $[\mathrm{SiMe_2}]$ linking groups from the rear to the side of the zirconocene wedge, thus placing these substituents in a *trans*-like arrangement in the dihydride dimer.

The solid-state structure for one of the two isomeric forms (**2a**) allows assignment of the structure of the other component of the mixture. On the basis of the ^{1}H NMR integrations, the major isomeric dimer in solution is thus **2a**. Of the several possible dimeric arrangements, the ^{1}H NMR data for the minor isomeric dimer appear to be consistent only with structure **2b** (below), one with equivalent terminal hydrides in a *cis* arrangement and inequivalent bridging hydrides.



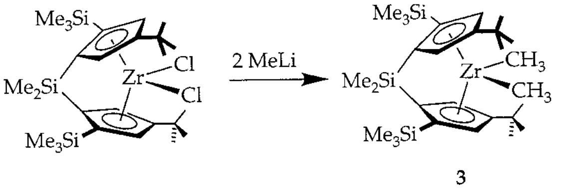
2a



2b

Toluene-d_8 solutions of **2a** and **2b** display ^{1}H NMR spectra at high temperatures (>60 °C) that suggest exchange between these two dimers. In particular, a single resonance for Zr-*H* is observed, and ligand resonances that are separated by small chemical shift differences for the two different isomers at low temperatures give rise to single averaged resonances.

The structures of **2a** and **2b** illustrate two ways that the bulky *tert*-butyl substituents on opposing *meso*-zirconocene units can avoid unfavorable steric crowding for dimeric arrangements. For a *racemo* isomer with bulky substituents at both the 2- and 4-positions relative to the linking $[\mathrm{SiMe_2}]$ group, it is difficult to envision a structure that would allow for a sterically unencumbered dimer, unless the metallocene units undergo twisting of their equatorial planes to a dihedral plane angle other than 0°. We therefore examined synthetic routes to the dihydride derivative $rac\text{-}\{\mathrm{Me_2Si(C_5H_2\text{-2-}SiMe_3\text{-4-}CMe_3)_2}\}\mathrm{ZrH_2}$ ($rac\text{-BpZrH}_2$). At the outset, we anticipated a possible limitation of working with this zirconcene system: the synthetic difficulty associated with the preparation of $rac\text{-BpZrCl}_2$.[14] The optimized procedure requires heating $\mathrm{ZrCl_4}$ with the dipotassio salt of the ligand for one month and produces only a 15% yield of the desired zirconocene dichloride. Once prepared, $rac\text{-BpZrCl}_2$ may be cleanly converted to $rac\text{-BpZrMe}_2$ by addition of methyllithium in diethyl ether (eq 3).



(3)

3

Unlike **1**, $rac\text{-BpZrMe}_2$ does not undergo epimerization in the presence of alkyllithium reagents or salts such as LiCl. This difference is undoubtedly attributable to the instability of the *meso* isomer, which would necessarily eclipse the bulky $[\mathrm{SiMe_3}]$ groups in the narrow portion of the zirconocene wedge.

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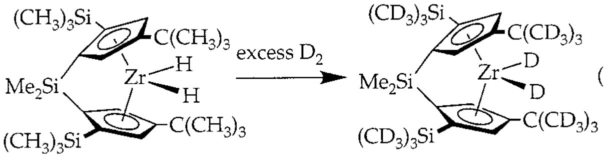
(12) Xin, S.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1994**, *116*, 11562.

(13) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045.

(14) Chacon, S. T.; Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *497*, 171.

Hydrogenation of **3** in toluene affords over the course of hours at 25 °C the desired *rac*-BpZrH$_2$ (**4**), a reaction that is considerably more rapid than observed for the unlinked systems which hydrogenate only slowly over the course of days under the same conditions.[15] The ^{1}H NMR spectrum for **4** displays a singlet at 7.20 ppm for ZrH_2, indicative of a monomeric structure in solution,[15] and in agreement with the experimentally determined solution molecular weight of 625 (569 calculated for monomer).

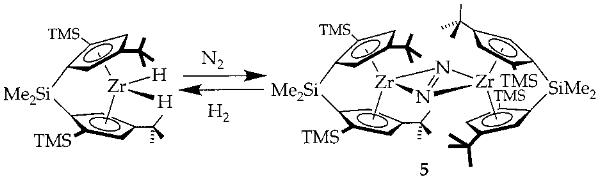
Under dihydrogen pressure, no Zr-H resonance is observed in the ^{1}H NMR spectrum of **4** (nor for dissolved H_2), suggesting rapid exchange between dihydrogen and the zirconium hydrides on the ^{1}H NMR time scale. Confirmation of this rapid exchange process has been obtained from addition of dideuterium gas to **4**. Exchange of the zirconium hydrides with deuterium is observed before the spectrum can be recorded at −78 °C. Interestingly, deuteration of the CMe$_3$ and SiMe$_3$ groups on the ligand array is also observed over the course of 12 h at 25 °C (eq 4). Deuteration of the cyclopentadienyl substituents likely arises from reversible formation of "tuck-in" intermediates, in which a C−H bond of *tert*-butyl and [SiMe$_3$] groups undergoes reversible σ-bond metathesis with [Zr−H] with loss of H$_2$.[15]



4

(4)

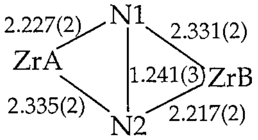
Allowing a pale yellow toluene solution of **4** to stand in the drybox under an atmosphere of dinitrogen results in formation of a forest green solution. Cooling the solution to −30 °C precipitates pleochroic crystals over the course of several days (eq 5).



5

(5)

X-ray diffraction reveals that the crystals are the dinitrogen complex $[rac\text{-BpZr}]_2(\mu_2,\eta^2,\eta^2\text{-N}_2)$ (**5**), i.e. a dimeric structure with a bridging, side-on dinitrogen fragment (Figure 3). The Zr$_2$N$_2$ core is planar within ±0.02 Å.



A crystallographic 2-fold axis passes through both nitrogen atoms. Consequently, the zirconium atoms are disordered over two sites 0.415(2) Å apart. No neighboring atoms are appreciably affected by this disorder.

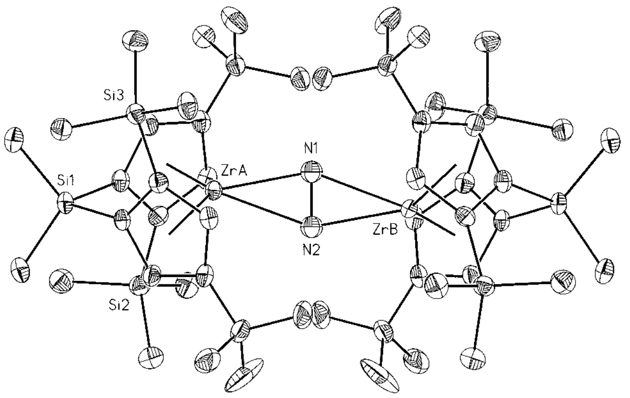
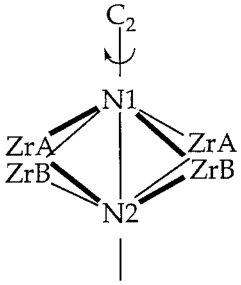


Figure 3. Molecular structure of **5** with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.



Side-on coordination of dinitrogen in a metallocene complex, although no longer rare, is unusual. Sodium reduction of metallocene dichloride complexes such as (η^5-C$_5$Me$_5$)$_2$MCl$_2$ (M = Ti,[16] Zr,[17] Hf [18]) provides end-on bridging (M(μ_2,η^1,η^1-N$_2$)M) dinitrogen coordination with relatively short (<1.2 Å) N−N bond distances. Fryzuk has prepared a series of macrocyclic amido−phosphine zirconium complexes with side-on Zr(μ_2,η^2,η^2-N$_2$)Zr dinitrogen ligands.[19] In these molecules, very long N−N bond distances (~1.4−1.5 Å) are observed. Other examples of a metallocene with a side-on dinitrogen fragment are (η^5-C$_5$Me$_5$)$_2$Sm(μ_2,η^2,η^2-N$_2$)Sm(η^5-C$_5$Me$_5$)$_2$, which has an anomalously short N−N distance of 1.088 Å[20] and a tris(amido)uranium(III) dimer with a [U(μ_2,η^2,η^2-N$_2$)U] core and N−N distance of 1.109(7) Å.[21] Side-on bonding for complexes having more than two metal atoms has also been reported for a samarium/sodium cluster[22] and a niobium/sodium cluster.[23]

The N−N bond distance of 1.241(3) Å for the dinitrogen ligand in **5** is intermediate between these classes of structures. Although the two Zr−N distances are different, they are not very much so (vide supra). Comparison of d(N1−N2) to the d(NN) for C$_6$H$_5$N=NC$_6$H$_5$ (1.255 Å)[24] suggests that the dinitrogen fragment in **5** possesses double bond character as, for example in

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(15) Chirik, P. J.; Day, M. D.; Bercaw, J. E. *Organometallics* **1999**, *18*, 1873.

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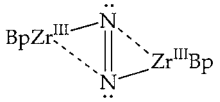
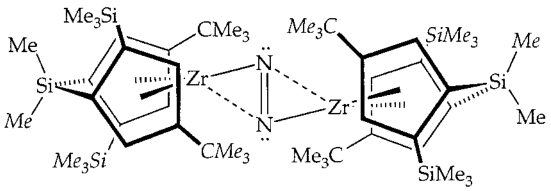
the structure shown below, although the Zr−N1−N2 bond angle of approximately 74° is much more acute than the corresponding C−N−N bond angles of 112−115° for azohydrocarbons.[25] If this representation is correct, antiferromagnetic coupling of the d^1, Zr(III) centers must be invoked to account for the apparent diamagnetism for **5** (NMR).



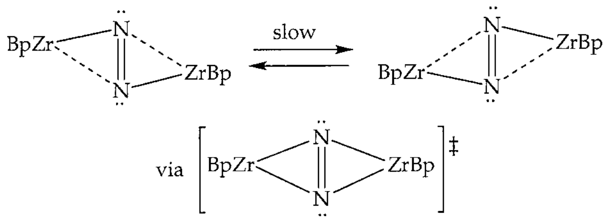
Unlike the solid-state structure for **2a**, **5** displays a dihedral angle of 46.4° between equatorial planes of the zirconocene wedges. The origin of this twist likely arises from the need for the bulky *tert*-butyl substituents to avoid the opposing cyclopentadienyl rings. This twist angle observed in **5** is larger than the value of 32° observed with $[rac\text{-BnBpY}]_2(\mu_2\text{-H})_2$.[13] Not surprisingly the distance between the two nitrogen-bridged zirconium atoms in **5** of 4.383(1) Å is significantly greater than the hydride-bridged Zr−Zr distances of 3.492(2) and 3.450(2) Å observed in **2a**.

With the zirconium atoms off the C_2 axis of the Bp ligand (in the Zr_2N_2 plane perpendicular to N1−N2), then the NMR spectra for **5** (two signals each for $\{CMe_3\}$, $\{SiMe_3\}$, $\{SiMe_2\}$, and cyclopentadienyl hydrogens) are readily explained: the two sides of the Bp ligand are inequivalent and are expected to give rise to twice the number of Bp ligand signals as compared with, for example, $BpZrH_2$ (**4**).



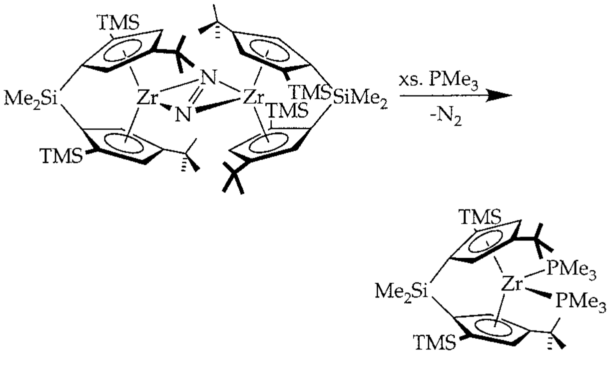
This explanation for the observed NMR behavior for **5** requires that movement of the zirconium atoms through the Bp ligand 2-fold axis to the other side of the wedge is slow.[26] Given the small differences in Zr−N1 and Zr−N2 distances (ca. 0.11 Å average), we admit that this situation is rather surprising.

Conversion of an early transition metal hydride to a dinitrogen complex is rather rare. Typically, coordinated dinitrogen undergoes rapid and irreversible displacement by dihydrogen, forming a dihydride complex; competitive recoordination of N_2 is generally not observed. For example, treatment of $[(\eta^5\text{-}C_5Me_5)_2ZrN_2]_2N_2$ with dihydrogen at 0 °C affords $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ in quantitative yield.[27] Late transition metal (e.g., Co, Ni) hydrides have been shown to eliminate dihydrogen and coordinate dinitrogen.[28] On the other hand, the only previous examples of such a transformation with early metal systems are the conversion of $\{[PhP(CH_2SiMe_2NPh)_2]TaH_2\}_2$ ($\{[NPN]TaH_2\}_2$) to $([NPN]TaH)_2(\mu_2,\eta^1,\eta^2\text{-}N_2)$[29] and reaction of $(\eta^5\text{-}C_5Me_4H)_2TiH$ with N_2 to yield $[(\eta^5\text{-}C_5Me_4H)_2Ti]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$.[30]



Toluene solutions of **5** are forest green and display two absorption bands at 392 and 612 nm. The FT-Raman spectrum, measured in benzene solution, displays three resonances at 1182.6, 1001.5, and 984 cm^{-1} assignable to the Zr_2N_2 core. Attempts to obtain resonance Raman spectra have been unsuccessful due to sample decomposition upon irradiation.

Exposure of **5** to 1 atm of dihydrogen bleaches the green solution and regenerates the starting dihydride, **4** (eq 5). Although quantities of **5** are rather limited (vide supra), some preliminary survey reactions have been examined. Addition of a slight excess of PMe_3 to **5** results in an immediate reaction, liberating dinitrogen and forming the bis-phosphine complex $rac\text{-BpZr}(PMe_3)_2$ (eq 6). Reactions of **4** with either carbon monoxide or ethylene are not clean and appear to result in decomposition.



(6)

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The mechanism of formation of **5** from **4**, whereby dihydrogen is displaced by dinitrogen, has been addressed briefly. One possibility is a photoinduced reduc-

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[24] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

[25] (a) *trans*-PhN=NPh (114.706°): Bouwstra, J. A.; Schouten, A.; Kroon, J. *Acta Crystallogr. C* **1983,** *39*, 1121. (b) *trans*-$Me_3CN{=}NCMe_3$ (112.210°): Argay, G.; Sasvari, K. *Acta Crystallogr. B* **1971**, *27*, 1851.

[26] Rapid interconversions through the symmetric structure would effect time-averaged D_2 molecular symmetry. Hence, the ^1H and ^{13}C NMR spectra would be expected to display equivalent *tert*-butyl, trimethylsilyl, $[Me_2Si]$, and cyclopentadienyl resonances. The number of the peaks observed is twice that expected for D_2 symmetry. The possibility that **5** coordinates additional dinitrogen in solution is eliminated by the observation that samples of **5** prepared both under vacuum and under an atmosphere of argon display the same NMR spectra as samples prepared under N_2. Another possibility is the presence of two sets of diastereomeric dimers, homochiral dimers (the (*R*, *R*) and (*S*, *S*) enantiomeric pair) and heterochiral dimer (the (*R*, *S*) pair). Similar behavior has been observed in the preparation of $[rac\text{-BpY}]2(\mu_2\text{-H})_2$ and $[rac\text{-AbpY}]2(\mu_2\text{-H})_2$, where both homochiral and heterochiral dimers are observed. Although we have not confirmed this possibility by preparing enantiomerically pure **4** and consequently enantiopure **5**, this explanation would also account for the observed solution NMR behavior for **5**.

[27] Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716.

[28] (a) Bianchini, C.; Meli, A.; Perruzzini, M.; Vizza, F.; Zanobini, F. *Organometallics* **1989**, *8*, 2080. (b) Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1985**, *4*, 1727.

[29] Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 11024.

[30] de Wolf, J. M.; Blaauw, R.; Meetsma, A.; Teuben, J. H.; Gyepes, R.; Varga, V.; Mach, K.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 4977.

tive elimination of H_2 from **5** followed by coordination of dinitrogen to the intermediate Zr(II) species. However, parallel experiments have been conducted in the presence and absence of light, and the rates of conversion are qualitatively the same. Another likely pathway is coordination of dinitrogen to **4** to induce reductive elimination of dihydrogen.[31] Stirring a toluene solution of **4** under argon open to a mercury bubbler results in decomposition of the dihydride at a rate comparable to conversion to **5** in the presence of dinitrogen. The products of this decomposition pathway do not react cleanly with either N_2 or H_2. These experiments thus suggest that formation of the dinitrogen complex, **5**, proceeds via slow, thermal reductive elimination of dihydrogen followed by rapid trapping by dinitrogen.

The spontaneous thermal reductive elimination of dihydrogen from **4** is quite unusual, considering monomeric zirconocene dihydrides with unlinked cyclopentadienyl ligands such as $Cp^*_2ZrH_2$ and $Cp^*\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}ZrH_2$ display no propensity to eliminate H_2 even after months in solution.[15] It would therefore appear that the *ansa*-bridge of **4** promotes reductive elimination. This *ansa* effect thus contrasts to *ansa* effects noted for molybdocene dihydride complexes, where an *ansa*-bridge inhibits reductive elimination by disfavoring the preferred parallel ring structure for the molybdenocene product.[32] Reductive elimination promoted by an *ansa* bridge has been observed in a d^0, Ta(V) trihydride complex. The *ansa*-tantalocene, $\{Me_2Si(\eta^5\text{-}C_5Me_4)_2\}TaH_3$, undergoes reductive elimination over 100 times faster than $(\eta^5\text{-}C_5Me_5)_2TaH_3$.[33] The observed rate enhancement has been attributed to the reduced electron-donating ability and hence destabilization of the Ta(V) complex in the *ansa* system. Similar electronic effects may be invoked to explain the increased rate of reductive elimination of **4** relative to unlinked zirconocene dihydrides.

Since the *ansa* bridge and the monomeric nature of **4** are believed to be responsible for the observed reactivity with dinitrogen, we sought to prepare other monomeric *ansa*-group 4 zirconocene dihydrides. These complexes not only would be useful in determining the generality of this unusual transformation but also may allow preparation of multigram quantities of a dinitrogen complex which has not been possible with **5** due to the difficulties of preparing convenient quantities of *rac*-$BpZrCl_2$.

Preparation of $Li_2[Me_2Si(C_5Me_4)(C_5H_2\text{-}2,4\text{-}(CHMe_2)_2]$ $(Li_2[^iPr_2Tp])$ has been accomplished via standard procedures.[34] The design of this ligand was inspired by the observation that $[\{Me_2Si(\eta^5\text{-}C_5Me_4)_2\}ZrH]_2(\mu_2\text{-}H)_2$ can be prepared in multigram quantities and is a mixture of monomer and dimer in solution.[7] Reaction of $Li_2[^iPr_2Tp]$ with $ZrCl_4$ in refluxing toluene for 24 h affords $(^iPr_2Tp)ZrCl_2$ in 50% yield. Methylation affords $(^iPr_2Tp)ZrMe_2$ (**8**), which undergoes hydrogenation, affording what we assume is a robust dimer $[(^iPr_2Tp)ZrH_2]_2$ (**9**). Unexpectedly, the dihydride is completely insoluble in aromatic hydrocarbon solvents and, as a result, has been characterized only in THF-d_8 as the solvento complex, $(^iPr_2Tp)ZrH_2(THF\text{-}d_8)$. Neither PMe_3 (5 equiv) nor dinitrogen reacts with benzene-d_6 slurries of **9**. Our attempts to increase the steric bulk of the ligand by introducing *tert*-butyl substituents in place of isopropyls have not been successful.

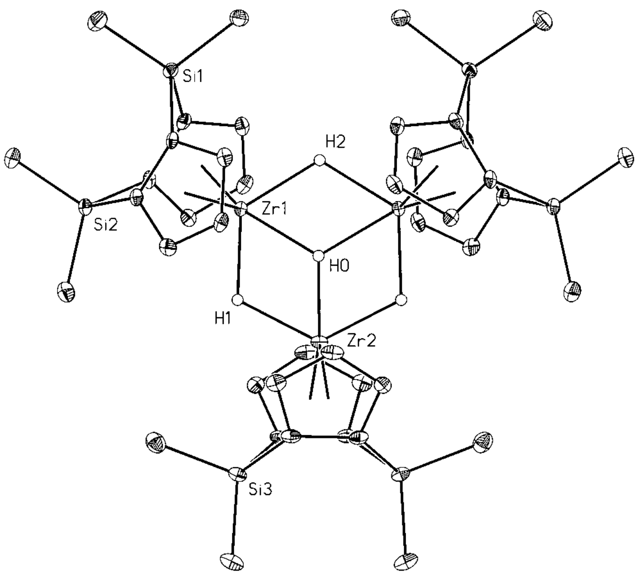

Figure 4. Molecular structure for **11** with 50% probability ellipsoids. Hydrogen atoms other than the five hydrides have been omitted for clarity.

Preparation of Doubly Silylene-Bridged Zirconocene Dihydride Complexes. In addition to singly $[SiMe_2]$-bridged metallocenes, we also targeted doubly silylene-bridged *ansa*-zirconocene dihydrides. Initially we focused on the preparation of complexes derived from the $\{(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2\}$ ligand, which has been previously reported by Royo.[35] Preparation of $[\{(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2\}ZrH]_2(\mu_2\text{-}H)_2$ has been achieved by reduction of the zirconocene dichloride with $NaBHEt_3$.[36] Curiously, all attempts to hydrogenate $\{(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2\}ZrMe_2$ (**10**) at 25 °C produce no reaction, contrary to previous results with unlinked and singly $[SiMe_2]$-bridged zirconocenes. Heating the reaction mixture to 100 °C in benzene-d_6 results in formation of methane (^1H NMR) and precipitation of dichroic crystals of a zirconocene hydride (**11**) that is distinct from $[\{(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2\}ZrH]_2(\mu_2\text{-}H)_2$. Hydride **11** is completely insoluble in common organic solvents such as benzene, THF, toluene, and methylene chloride, and hence no solution spectroscopic data have been obtained.

The structure of **11** has been determined by X-ray diffraction, revealing a trimeric zirconocene cluster, $[\{(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2\}Zr]_3(\mu_3\text{-}H)_2(\mu_2\text{-}H)_3$ (Figure 4). The molecule lies on a 2-fold axis through Zr2 and μ_2-hydride H2. All five hydride ligands (2.5 independent atoms) have been found in the difference map and freely refined. The three zirconium centers and the three μ_2-hydride ligands are all approximately coplanar and are capped above and below the plane with two μ_3-hydride

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(31) Ligand-promoted reductive elimination has been observed in zirconocene alkyl hydride complexes. See: McAlister, D. R.; Erwin, D. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966.

(32) Chernaga, A.; Cook, J.; Green, M. L. H.; Labella, L.; Simpson, S. J.; Souter, J.; Stephens, A. H. H. *J. Chem. Soc., Dalton Trans.* **1997**, 3225.

(33) Shin, J.; Parkin, G. *Chem. Commun.* **1999**, 187.

(34) Herzog, T. A. Ph.D. Thesis, California Institute of Technology, 1997.

(35) Cano, A.; Cuenca, T.; Gómez-Sal, P.; Royo, B.; Royo, P. *Organometallics* **1994**, *13*, 1688.

(36) Cuenca, T.; Galakhov, M.; Royo, B.; Royo, P. *J. Organomet. Chem.* **1996**, *515*, 33.

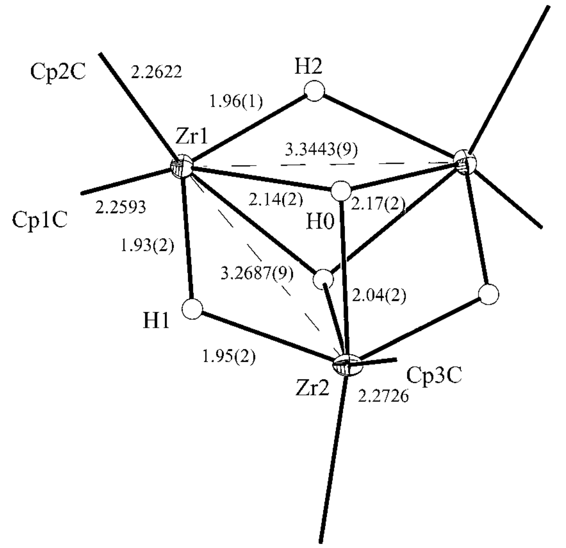
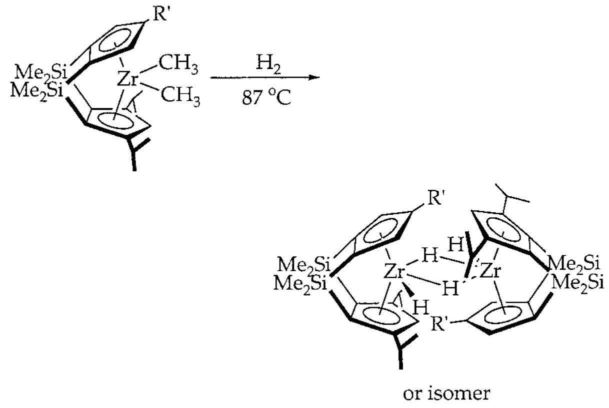


Figure 5. View of the zirconium hydride core of **11**. Distances are reported in angstroms.

ligands. As shown in Figure 5, the metallocene wedge defined by Zr2 is tilted with respect to the plane formed by the three zirconium centers. The zirconium$-\mu_2$-hydride distances are shorter (1.93(2) and 1.96(1) Å) than the zirconium$-\mu_3$-hydride ligand distances (2.04(2) and 2.17(2) Å).

The zirconium$-$zirconium distances in **11** of 3.2687(9) and 3.443(9) Å are slightly shorter than the 3.492(2) and 3.450(2) Å observed for **2** and related dihydride dimers.[11] Moreover, this distance is significantly longer than observed in the triple hydride-bridged dimer, $[Zr_2H_3(BH_4)_5(PMe_3)_2]$ (3.124 Å),[37] and the tetrahydride-bridged dimer, $[Zr_2H_4(BH_4)_4(PMe_3)_4]$.[38] In these structures, only μ_2-hydride bridges are observed. Moreover, these hydride dimers are formally Zr(IV)/Zr(IV) diamagnetic, whereas **11** is formally Zr(IV)/Zr(IV)/Zr(III) mixed valent, paramagnetic, and therefore some Zr$-$Zr bonding is likely.

Increasing the substitution on the cyclopentadienyl ligand array has a dramatic impact on the hydrogenation reaction. Hydrogenation of $\{(Me_2Si)_2(\eta^5\text{-}C_5H\text{-}3,5\text{-}(CHMe_2)_2)(\eta^5\text{-}C_5H_2\text{-}4\text{-}CHMeEt\}Zr(CH_3)_2$ (*sec*-BuThp)ZrMe$_2$ (**12**)) in benzene-d_6 solution at 87 °C results in clean and quantitative formation of [(*sec*-BuThp)ZrH]$_2$(μ_2-H)$_2$ (**13**) (eq 7).



(7)

R' = CHMeEt: **13**
R' = CHMe$_2$: **15**

The ^{1}H NMR spectrum displays two triplets, one at 4.25 ppm and the other at 0.13 ppm for the terminal and bridging hydrides, respectively. Although each zirconocene unit is rigorously C_1 symmetric, the zirconium hydride resonances nonetheless give rise to a rather simple spectrum. Apparently, the stereogenic methine carbon of the *sec*-butyl substituent does not result in resolvable diastereotopic hydride signals. The solution molecular weight for **13** has been determined and found to be 914 (monomer = 477).

Similar experiments have been conducted with $\{(Me_2Si)_2(\eta^5\text{-}C_5H\text{-}3,5\text{-}(CHMe_2)_2)(\eta^5\text{-}C_5H_2\text{-}4\text{-}CHMe_2\}Zr(CH_3)_2$ (^{i}PrThpZrMe$_2$ (**14**)). Hydrogenation of the dimethyl complex proceeds smoothly at 87 °C, producing methane and one isomer of [(^{i}PrThp)ZrH$_2$]$_2$ (**15**). As with **13**, **15** displays a triplet at 4.25 ppm for the terminal zirconium hydrides and a triplet at 0.20 ppm for the bridging hydrides. Both **13** and **15** undergo exchange with D_2 gas over the course of several days at room temperature, whereas the unlinked metallocene hydride dimers, [Cp*(CpR$_n$)ZrH}$_2$(μ_2-H)$_2$, undergo rapid exchange with deuterium at 25 °C.[15] These results suggest that **13** and **15** form more robust dimers than the corresponding unlinked zirconocene dihydride dimers.

In an attempt to prepare a monomeric, doubly silylene-bridged zirconocene dihydride, a tertiary center was incorporated into the 4-position of the (upper) cyclopentadienyl ring. Preparation of (TMSThp)ZrMe$_2$ (**16**) has been accomplished via methylation of the dichloride complex. Unfortunately, hydrogenation of **16** at 87 °C results in liberation of methane and decomposition of the organozirconium complex.

Changing the overall symmetry of the zirconocene was also attempted with the goal of preparing a monomeric, doubly silylene-bridged zirconocene dihydride. Methylation of C_2-symmetric $\{(Me_2Si)_2(\eta^5\text{-}C_5H\text{-}3,5\text{-}(CHMe_2)_2)_2\}ZrCl_2$[39] ((Tip)ZrCl$_2$) (**17**) affords the dimethyl complex (Tip)ZrMe$_2$ (**18**) in high yield. Hydrogenation at 87 °C over the course of 24 h results in formation of [(Tip)ZrH]$_2$(μ_2-H)$_2$ (**19**). At 22 °C, the ^{1}H NMR spectrum of **19** in benzene-d_6 displays resonances at -5.65 and 2.10 for the terminal and bridging hydride ligands. Preliminary evidence suggests that the dimer may be in equilibrium with some amount of monomer, since warming of the sample to 67 °C results in a shift of the 2.10 δ resonance to 3.10 δ.

Although the increased substitution of **19** compared to **13** and **15** resulted in some destabilization of the dihydride dimer, a predominantly monomeric dihydride was still not obtained. Another approach is to prepare doubly silylene-bridged C_{2v} symmetric metallocenes with bulky substituents in front of the metallocene wedge. Reaction of $\{(Me_2Si)_2(\eta^5\text{-}C_5H_2\text{-}4\text{-}CMe_3)_2\}ZrCl_2$ (BsZrCl$_2$ (**20**))[43] with 2 equiv of methyllithium results in formation of BsZrMe$_2$ (**21**). Addition of dihydrogen

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[37] Gozum, J. E.; Girolami, G. S. *J. Am. Chem. Soc.* **1991**, *113*, 3829.

[38] Bown, M. *Acta Crystallogr. C* **1994**, *50*, 367.

[39] Miyake, S.; Bercaw, J. E. *J. Mol. Catal. A* **1998**, *128*, 29.

[40] Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; ACS Symposium Series 357; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 4.

[41] Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046.

[42] Veghini, D.; Day, M. D.; Bercaw, J. E. *Inorg. Chem. Acta* **1998**, *280*, 226.

to a benzene-d_6 solution of **21** at 87 °C results in formation of methane, although no tractable zirconocene dihydride product has been identified. Monitoring the reaction by ^{1}H NMR spectroscopy reveals that the benzene-d_6 is hydrogenated to isotopomers of cyclohexane, thus implicating the presence of a zirconocene dihydride.[15] Performing the reaction in cyclohexane-d_{12} produces methane and results in H/D exchange in the alkane solvent, but no zirconocene dihydride could be observed. It appears that the zirconocene dihydride is formed in the above reactions, but that it may be too unstable for its clean isolation.

In all of the doubly silylene-linked zirconocene dimethyl complexes studied, elevated temperatures are required for hydrogenation of the zirconium methyl groups, contrasting with previous results for unlinked and singly bridged dimethyl zirconocene systems where hydrogenation occurs readily at room temperature. Although one might be tempted to attribute the apparently higher barrier for σ-bond metathesis to steric blocking of H_2 approach to the empty $1a_1$ orbital of the zirconocene dimethyl complex by the linking dimethylsilylene methyl groups that extend into the zirconocene wedge, we hesitate to invoke steric effects as significantly influencing approach of the smallest molecule. Moreover, there is some likelihood that the reaction of these dimethylzirconocene complexes with H_2 is not a simple bimolecular σ-bond metathesis process, but rather some sort of chain reaction, at least for some cases.

Conclusions

A series of *ansa*-zirconocene dihydride complexes have been prepared from hydrogenation of the corresponding dimethyl complexes. The *tert*-butyl-substituted metallocene **2** exists as isomeric $[\mathrm{Zr{-}H}]_2(\mu_2\text{-H})_2$ dimers in solution, due to the ability of the *tert*-butyl groups on opposing cyclopentadienyl ligands to orient themselves in dispositions to avoid unfavorable steric interactions. The first example of a monomeric *ansa*-zirconocene dihydride has been prepared via hydrogenation of **3**, yielding **4**. Exposure of **4** to dinitrogen results in thermal reductive elimination of dihydrogen and coordination of dinitrogen, forming the unusual $[\mathrm{Zr}(\mu_2,\eta^2,\eta^2\text{-N}_2)\mathrm{Zr}]$, side-on bridging dinitrogen complex, **5**. Doubly silylene-bridged zirconocene dihydrides have also been prepared via hydrogenation of the dimethyl complexes, but elevated temperatures are required. The doubly [SiMe$_2$]-bridged zirconium dimethyl complex $\{(\mathrm{Me_2Si})_2(\eta^5\text{-C}_5\mathrm{H}_3)_2\}\mathrm{ZrMe}_2$ (RpZrMe$_2$) undergoes hydrogenation under forcing conditions to afford the mixed valent (Zr(IV)/Zr(IV)/Zr(III)) hydride trimer $[\mathrm{RpZr}]_3(\mu_3\text{-H})_2(\mu_2\text{-H})_3$. In the cases of these more crowded, doubly silylene-bridged systems, very robust dimeric dihydride complexes are unexpectedly obtained, and in no case examined has a stable, monomeric zirconocene dihydride been observed.

Experimental Section

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques or in a drybox under a nitrogen atmosphere as described previously.[40] Molecular weights were determined by ebulliometry as described previously.[36] Argon, dinitrogen, dihydrogen, and dideuterium gases were purified by passage over columns of MnO on vermiculite and activated molecular sieves. Solvents for air- and moisture-sensitive reactions were dried over titanocene[41] or sodium benzophenone ketyl. Toluene-d_8 and cyclohexane-d_{12} were distilled from sodium benzophenone ketyl and stored over titanocene. Tetahydrofuran-d_8 was distilled from benzophenone ketyl and stored over 4 Å molecular sieves. Preparations of *meso*-$\mathrm{Me_2Si}(\eta^5\text{-C}_5\mathrm{H}_3\text{-3-CMe}_3)_2\mathrm{Zr(NMe_2)_2}$,[8] **12**, **14**,[42] **17**,[39] **20**, **21**,[43] and **10**[35] were carried out as described previously.

{*meso*-Me$_2$Si(C$_5$H$_3$-3-CMe$_3$)$_2$}ZrMe$_2$ (1). In the drybox, a 50 mL round-bottom flask was charged with 0.500 g (1.04 mmol) of *meso*-DpZr(NMe$_2$)$_2$. Approximately 25 mL of toluene was added, forming an orange solution. Via pipet, 0.500 g (6.94 mmol) of trimethylaluminum was added. With time, a darker orange solution forms. The reaction was stirred for 16 h, after which time a 180° needle valve was attached to the flask and the toluene was removed in vacuo, leaving a dark, oily solid. Petroleum ether was added, forming an orange solid, and recrystallization at −30 °C over the course of 3 days afforded 0.257 g (58.3%) of **1**. ^{1}H (benzene-d_6): δ 0.026 (s, 6H, ZrMe_2); 0.158 (s, 3H, SiMe_2); 0.258 (s, 3H, SiMe_2); 1.39 (s, 18H, CMe_3); 5.39 (s, 1H, Cp); 5.73 (s, 1H, Cp); 6.71 (s, 1H, Cp). ^{13}C (benzene-d_6): −5.682 (SiMe_2); −3.237 (SiMe_2); 31.39 (ZrMe_2); 33.81 (ZrMe_2); 31.99 (CMe_3) 144.76 (CMe$_3$); 98.08, 111.75, 112.15, 120.45, *1 not located* (Cp). Anal. Calcd for $C_{22}H_{36}Zr_1Si_1$: C, 62.94; H, 8.64. Found: C, 62.76; H, 8.42.

[{*meso*-Me$_2$Si(C$_5$H$_3$-3-CMe$_3$)$_2$}ZrH]$_2$(μ_2-H)$_2$ (2). In the drybox, a thick-walled glass bomb was charged with 0.150 g (0.354 mmol) of **1**. On the vacuum line, approximately 15 mL of toluene was added by vacuum transfer. At room temperature, 1 atm of dihydrogen was added. The reaction mixture was stirred for 16 h, and the toluene was removed in vacuo and replaced with petroleum ether, affording a white solid. The solid was collected by filtration and dried in vacuo, yielding 0.087 g (62.1%) of **2**. Major isomer: ^{1}H (benzene-d_6, 25 °C, 0.02 M): δ 0.202 (s, 3H, SiMe_2); 0.370 (s, 3H, SiMe_2); 3.94 (m, 1H, ZrH_{term}); −2.39 (t, 6.0 Hz, 1H, ZrH_{br}); 1.40 (s, 18 H, CMe_3); 5.06, 6.06, 6.23 (m, 1H, Cp). Minor isomer: ^{1}H (benzene-d_6, 25 °C, 0.02 M): δ 0.239 (s, 3H, SiMe_2); 0.386 (s, 3H, SiMe_2); 4.03 (m, 1H, ZrH_{term}); −5.32 (m, 1H, ZrH_{br}); 1.34 (s, 18 H, CMe_3); 4.99, 5.90, 6.16, (m, 1H, Cp). ^{13}C (benzene-d_6): −6.60 (SiMe_2); −6.40 (SiMe_2); −1.93 (SiMe_2); −1.79 (SiMe_2); 33.30 (CMe_3); 33.40 (CMe_3); 152.49 (CMe$_3$); 152.88 (CMe$_3$); 91.25, 101.92, 102.66, 104.72, 106.90, 110.25, 110.51, 118.74, *2 not located* (Cp). Anal. Calcd for $C_{20}H_{32}Zr_1Si_1$: C, 61.32; H, 8.23. Found: C, 61.76; H, 8.56.

{*rac*-Me$_2$Si(C$_5$H$_2$-2-SiMe$_3$-4-CMe$_3$)$_2$}ZrMe$_2$ (3). In the drybox, a medium swivel frit assembly was charged with 1.10 g (1.82 mmol) of *rac*-BpZrCl$_2$. On the vacuum line, approximately 30 mL of diethyl ether was added by vacuum transfer. At −80 °C against an argon counterflow, 2.90 mL (4.1 mmol) of 1.4 M MeLi solution in ether was added. The reaction was warmed to room temperature and stirred. Upon reaching room temperature, a yellow solution and white precipitate formed. After 24 h, the ether was removed in vacuo and was replaced with toluene. The white precipitate was removed by filtration and was washed with recycled toluene. The toluene was removed in vacuo, and the yellow solid was recrystallized from cold petroleum ether, affording 0.980 g (91%) of **3**. ^{1}H (benzene-d_6): δ 0.23 (s, 6H, ZrMe_2); 0.31 (s, 18 H, SiMe_3); 1.38 (s, 18 H, CMe_3); 6.05 (s, 2H, Cp); 7.21 (s, 2H, Cp). ^{13}C (benzene-d_6): δ −0.810 (SiMe_2); 2.16 (SiMe_3); 30.94 (CMe_3); 34.09 (ZrMe_2); 106.65, 116.14, 125.60, 129.47, *1 not located* (Cp), 148.92 (CMe$_3$). Anal. Calcd for $C_{28}H_{52}Zr_1Si_3$: C, 59.61; H, 9.29. Found: C, 59.27; H, 9.01.

***rac*-[Me$_2$Si(C$_5$H$_2$-2-SiMe$_3$-4-CMe$_3$)$_2$]ZrH$_2$ (4).** **4** was prepared in an analogous manner to **2** with 0.940 g (1.58 mmol) of **3**, yielding 0.750 g (84%) of a green solid identified as **4**. ^{1}H

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(43) Bulls, A. R. Ph.D. Thesis, California Institute of Technology, 1988.

(benzene-d_6): δ 0.35 (s, 18H, SiMe_3); 0.49 (s, 6H, SiMe_2); 1.49 (s, 18H, CMe_3); 5.96 (s, 2H, Cp); 7.83 (s, 2H, Cp); 7.25 (bs, 2H, ZrH); ^{13}C (benzene-d_6): δ 2.23 (SiMe_3); 2.82 (SiMe_2); 32.17 (CMe_3); 152.9 (CMe$_3$); 98.63, 11.34, 118.27, 119.49, 123.22 (Cp). Anal. Calcd for $C_{26}H_{48}Zr_1Si_3$: C, 58.25; H, 9.02. Found: C, 57.98; H, 8.67.

[{*rac*-Me$_2$Si(C$_5$H$_2$-2-SiMe$_3$-4-CMe$_3$)$_2$}Zr]$_2$(μ_2-, η^2-,η^2-N$_2$) (5). In the drybox, a Teflon-capped scintillation vial was charged with 57.0 mg (0.100 mmol) of **4** and approximately 2.0 mL of toluene. The solid was dissolved, forming a green solution, which was allowed to stand at room temperature for 1 week, after which time a red solid had deposited on the bottom of the vial. The solid was collected by filtration, washed with petroleum ether, transferred into a flask, and dried in vacuo, affording 21.0 mg (35.7%) of **5**. ^{1}H NMR (toluene-d_8): δ 0.441 (s, 18H, SiMe_3); 0.454 (s, 18H, SiMe_3); 0.651 (s, 6H, SiMe_2); 0.923 (s, 6H, SiMe_2); 1.47 (s, 18 H, CMe_3); 1.67 (s, 18H, CMe_3); 4.77 (s, 2H, Cp); 5.11 (s, 2H, Cp); 6.14 (s, 2H, Cp); 6.66 (s, 2H, Cp). ^{13}C NMR (toluene-d_8): δ −0.940 (SiMe_2); −0.108 (SiMe_2); 32.51 (CMe_3); 33.50 (CMe_3); 2 CMe$_3$ not located; 104.0, 104.20, 105.4, 107.91, 110.18, 112.24, 115.67, 117.21, 117.34 (Cp). UV−vis (toluene): 392.0 nm; 612.0 nm. FT-Raman (benzene-d_6): 1182.6 cm^{-1}; 1001.5 cm^{-1}; 984 cm^{-1}. Anal. Calcd for $C_{52}H_{92}Si_6Zr_2N_2$: C, 56.97; H, 8.46; N, 2.56. Found: C, 56.69; H, 8.76; N, 2.68

{*rac*-Me$_2$Si(C$_5$H$_2$-2-SiMe$_3$-4-CMe$_3$)$_2$}Zr(PMe$_3$)$_2$ (6). In the drybox, a J. Young NMR tube was charged with 5.0 mg (4.30 × 10^{-3} mmol) of **5**. On the vacuum line, the tube was degassed with three freeze−pump−thaw cycles. Via calibrated gas volume, 3 equiv of PMe$_3$ was added at −196 °C. The tube was thawed and shaken and the progress of the reaction monitored by NMR spectroscopy. ^{1}H (benzene-d_6): δ −0.15 (s, 18H, SiMe_3); 0.19 (s, 6H, SiMe_2); 0.85 (d, 36 Hz, 18H, PMe_3); 1.22 (s, 18H, CMe_3); 6.44, 6.70 (m, 2H, Cp). ^{31}P (benzene-d_6): δ 34.04.

{Me$_2$ Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_2$-2,4-(CHMe$_2$)$_2$}ZrCl$_2$ (7). In the drybox, a round-bottom flask was charged with 3.66 g (11.23 mmol) of Li$_2$[^{i}Pr$_2$Tp] and 2.61 g (11.23 mmol) of ZrCl$_4$. A reflux condenser and 180° needle valve were attached. On the vacuum line, approximately 50 mL of toluene was added along with 5 mL of THF. The reaction mixture was heated to reflux for 24 h, after which time the toluene was removed in vacuo, leaving a yellow paste. Approximately 100 mL of CH$_2$Cl$_2$ and 25 mL of 4 M HCl were added. The organic layer was collected and the aqueous layer washed with three small portions of CH$_2$Cl$_2$. The organic layers were combined and dried over MgSO$_4$ for 1 h. After filtration, the solvent was removed by rotary evaporation, leaving a yellow tar. Pentane was added, and a white solid precipitated. The solid was washed with small portions of diethyl ether and pentane and dried in vacuo. Analytically pure material may be obtained via vacuum sublimation (10^{-4} Torr) at 160 °C. ^{1}H (benzene-d_6): δ 0.816 (s, 3H, SiMe_2); 0.945 (s, 3H, SiMe_2); 1.10 (d, 6.6 Hz, 3H); 1.21 (d, 6.5 Hz, 3H); 1.24 (d, 6.5 Hz, 3H); 1.26 (d, 6.5 Hz, 3H); 1.87 (s, 3H, C$_5$$Me_4$); 1.90 (s, 3H, C$_5$$Me_4$); 1.98 (s, 3H, C$_5$$Me_4$); 2.01 (s, 3H, C$_5$$Me_4$); 2.71 (sept, 7.0 Hz, 1H, CHMe$_2$); 3.06 (sept, 7.0 Hz, 1H, CHMe$_2$); 5.25 (s, 1H, Cp); 6.50 (s, 1H, Cp). ^{13}C (benzene-d_6): δ 1.22 (SiMe_3); 1.25 (SiMe_3); 11.90, 12.61, 14.63, 14.93 (C$_5$$Me_4$); 20.30, 22.25, 22.75, 29.39 (CHMe_2); 29.24, 29.89 (CHMe$_2$); 96.28, 99.50, 110.79, 117.79, 112.90, 113.99, 137.07, 143.49, 149.63 (Cp). Anal. Calcd for $C_{22}H_{34}Zr_1Cl_2$: C, 57.36; H, 7.44. Found: C, 57.57; H, 7.14.

{Me$_2$ Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_2$-2,4-(CHMe$_2$)$_2$}ZrMe$_2$ (8). This compound was prepared in a manner analogous to that for **3** employing 0.760 g (1.56 mmol) of **7** and 2.5 mL of 1.4 M MeLi solution in diethyl ether, yielding 0.560 g (80.4%) of a white solid identified as **8**. ^{1}H (benzene-d_6): δ 0.440 (s, 3H, SiMe_2); 0.575 (s, 3H, SiMe_2); −0.352 (s, 3H, ZrMe_2); −0.258 (s, 3H, ZrMe_2); 1.14 (d, 7.0 Hz, 3H); 1.23 (d, 6.8 Hz, 3H); 1.29 (d, 6.9 Hz, 3H); 1.33 (d, 7.0 Hz, 3H); 1.63 (s, 3H, C$_5$$Me_4$); 1.79 (s, 3H, C$_5$$Me_4$); 1.95 (s, 3H, C$_5$$Me_4$); 1.98 (s, 3H, C$_5$$Me_4$); 2.54 (sept, 7.0 Hz, 1H, CHMe$_2$); 3.03 (sept, 7.0 Hz, 1H, CHMe$_2$); 5.04 (s, 1H, Cp), 6.65 (s, 1H, Cp). ^{13}C (benzene-d_6): δ 1.54 (SiMe_3); 1.65 (SiMe_3); 11.36, 11.64, 14.37, 14.53 (C$_5$$Me_4$); 20.56, 23.39, 23.89, 29.54 (CHMe_2); 28.37, 29.72 (CHMe$_2$); 32.88 (ZrCH$_3$); 35.93 (ZrCH$_3$) 91.02, 93.77, 109.76, 113.04, 120.94, 123.22, 140.18, 140.49 (Cp).

{Me$_2$ Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_2$-2,4-(CHMe$_2$)$_2$}ZrH]$_2$(μ_2-H)$_2$ (9). This compound was prepared in a manner analogous to that for **2** employing 0.320 g (0.716 mmol) of **8** and 1 atm of H$_2$. After stirring for 2 days, the product was collected by filtration and dried in vacuo, yielding 0.170 g (56.7%) of **9**. ^{1}H (THF-d_8): δ 0.421 (s, 3H, SiMe_2); 0.620 (s, 3H, SiMe_2); 3.87 (d, 20 Hz, 1H, Zr-H_2); 4.13 (d, 20 Hz, 1H, Zr-H_2); 1.10 (d, 7.0 Hz, 3H); 1.15 (d, 7.0 Hz, 3H); 1.20 (d, 7.0 Hz, 3H); 1.60 (d, 7.0 Hz, 3H); 1.92 (s, 3H, C$_5$$Me_4$); 2.02 (s, 3H, C$_5$$Me_4$); 2.23 (s, 3H, C$_5$$Me_4$); 2.32 (s, 3H, C$_5$$Me_4$); 2.83 (sept, 7.0 Hz, 1H, CHMe$_2$); 3.08 (sept, 7.0 Hz, 1H, CHMe$_2$); 4.86 (s, 1H, Cp), 5.69 (s, 1H, Cp). Anal. Calcd for $C_{22}H_{34}Zr_1Cl_2$: C, 62.94; H, 8.64. Found: C, 62.07; H, 8.63.

[{(Me$_2$Si)$_2$(C$_5$H$_3$)$_2$}Zr]$_3$(μ_3-H)$_2$(μ_2-H)$_3$ (11). In the drybox, a J. Young NMR tube was charged with 10.5 mg of **10** and the sample dissolved in benzene-d_6. On the vacuum line, the tube was degassed with three freeze−pump−thaw cycles and 1 atm of dihydrogen was admitted at −196 °C. The tube was thawed, shaken, and placed into a 100 °C oil bath. Heating the tube for 24 h produced a few crystals that were collected for X-ray diffraction.

{(Me$_2$Si)$_2$(η^5-C$_5$H-3,5-(CHMe$_2$)$_2$)(η^5-C$_5$H$_2$-4-CHMeEt)}-ZrH]$_2$(μ_2-H)$_2$ (13). In the drybox, a thick walled glass bomb was charged with 0.560 g (1.10 mmol) of **12**. On the vacuum line, cyclohexane was added by vacuum transfer. Upon warming to room temperature, the bomb was then charged with 1 atm of dihydrogen. The bomb was then placed in an 80 °C oil bath and stirred. The reaction was continued for 2 days, after which time the contents of the bomb were transferred into a swivel frit assembly. The cyclohexane was removed in vacuo and replaced with petroleum ether. Cooling the solution to −80 °C afforded a white solid that was collected by filtration and dried in vacuo, yielding 0.325 g (61.6%) of **3**. ^{1}H (benzene-d_6): δ 0.13 ppm (t, 5 Hz, 2H, ZrH, bridging); 0.583 (s, 3H, SiMe_2); 0.604 (s, 3H, SiMe_2); 0.614 (s, 3H, SiMe_2); 0.638 (s, 3H, SiMe_2); 1.02 (t, 7 Hz, 3H, CH(CH$_3$)(CH$_2$$CH_3$)); 1.78(d, 6.5 Hz, 3H, CH-(CH_3)(CH$_2$CH$_3$)); 1.19 (d, 6.5 Hz, 3H, CHMe_2); 1.40 (d, 6.5 Hz, 3H, CHMe_2); 1.61 (d, 6.5 Hz, 3H, CHMe_2); 1.72 (d, 6.5 Hz, 3H, CHMe_2); 1.80 (m, 2H, CH(CH$_3$)(CH_2CH$_3$)); 3.53 (m, 1H, CH(CH$_3$)(CH$_2$CH$_3$); 3.14 (sept, 6.5 Hz, 1H, CHMe$_2$); 3.66 (sept, 6.5 Hz, 1H, CHMe$_2$); 4.25 (t, 5 Hz, 2H, ZrH, terminal); 5.86 (s, 1H, Cp); 6.56 (s, 1H, Cp); 7.14 (s, 1H, Cp). ^{13}C (benzene-d_6): δ −0.475 (SiMe_2); −0.071 (SiMe_2); 4.16 (SiMe_2); 4.21 (SiMe_2); 11.30, 19.34, 22.68, 23.22, 29.79, 30.13, 20.40, 33.79, 34.65 (CHMe$_2$ and CH(CH$_3$)(CH$_2$CH$_3$); 97.88, 99.08, 102.60, 104.20, 109.28, 117.32, 119.09, 139.09, 155.91, 159.62 (Cp). Anal. Calcd for $C_{24}H_{40}Zr_1Si_2$: C, 60.56; H, 8.47. Found: C, 59.54; H, 8.32.

[{(Me$_2$Si)$_2$(η^5-C$_5$H-3,5-(CHMe$_2$)$_2$)(η^5-C$_5$H$_2$-4-CHMe$_2$}ZrH]$_2$-(μ_2-H)$_2$ (15). In the drybox, a J. Young NMR tube was charged with 10.0 mg (0.0189 mmol) of **14**, and the sample was dissolved in benzene-d_6, forming a clear solution. On the vacuum line, the tube was degassed with three freeze−pump−thaw cycles. The tube was then cooled to −196 °C and 1 atm of dihydrogen added. The tube was then heated in an 87 °C oil bath and the reaction monitored by NMR spectroscopy. ^{1}H NMR (benzene-d_6): δ 0.20 ppm (t, 5 Hz, 2H, ZrH, bridging); 0.561 (s, 3H, SiMe_2); 0.601(s, 3H, SiMe_2); 0.635 (s, 3H, SiMe_2); 0.681 (s, 3H, SiMe_2); 0.891 (d, 6.5 Hz, 3H, CHMe_2); 0.954 (d, 6.5 Hz, 3H, CHMe_2); 1.12 (d, 6.5 Hz, 3H, CHMe_2); 1.18 (d, 6.5 Hz, 3H, CHMe_2); 1.21 (d, 6.5 Hz, 3H, CHMe_2); 1.51 (d, 6.5 Hz, 3H, CHMe_2); 2.45 (sept, 6.5 Hz, 1H, CHMe$_2$); 2.94 (sept, 6.5 Hz, 1H, CHMe$_2$); 3.43 (sept, 6.5 Hz, 1H, CHMe$_2$); 4.25 (t, 5 Hz, 2H, ZrH, terminal); 5.73 (s, 1H, Cp); 6.27 (s, 1H, Cp); 7.09 (s, 1H, Cp).

Table 1. X-ray Experimental Data

	1	**2a**	**5**	**11**
formula	$C_{22}H_{36}SiZr$	$C_{40}H_{62}Si_2Zr_2$	$C_{52}H_{92}N_2Si_6Zr_2 \cdot C_7H_8$	$C_{42}H_{59}Si_6Zr_3$
fw	419.82	781.52	1096.25 · 92.14	1006.11
cryst syst	monoclinic	triclinic	monoclinic	tetragonal
space group	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P2/n$ (#13)	$P4_32_12$ (#96)
a [Å]	19.899(4)	10.0511(11)	16.7641(9)	15.804(4)
b [Å]	16.667(6)	14.2131(16)	10.7439(6)	15.804(4)
c [Å]	13.417(5)	15.3334(17)	18.3696(10)	17.018(3)
α [deg]	90	82.573(2)	90	90
β [deg]	94.16(2)	79.502(2)	100.758(1)	90
γ [deg]	90	70.609(2)	90	90
V [Å^3]	4438(2)	2026.1(4)	3250.4(3)	4250.5(17)
Z	8	2	2	4
ρ_{calc} [g·cm^{-3}]	1.257	1.281	1.214	1.572
μ [mm^{-1}]	0.551	0.598	0.466	0.921
cryst shape	tapered block	plate	wedge	prism
cryst color	pale yellow	colorless	trichroic, pale yellow/rose/ dark brown	dichroic, dark brown-green/ colorless
cryst size [mm]	0.07 × 0.19 × 0.33	0.04 × 0.07 × 0.08	0.19 × 0.26 × 0.33	0.10 × 0.26 × 0.52
T [K]	85	98	98	85
diffractometer	Nonius CAD4	Bruker SMART 1000	Bruker SMART 1000	Nonius CAD4
$2\theta_{max}$ [deg]	50	50	56.8	50
h,k,l limits	0, 22; −16, 18; −14, 14	−11, 11; −16, 16; −18, 18	−21, 22; −14, 14; −24, 23	0, 18; −18, 18; 0, 20
data measured	13 928	20 564	31 707	13 292
unique data	6332	7112	7795	3746
data, $F_o > 4\sigma(F_o)$	4992	4312	6406	3688
R1, wR2; all data	0.054, 0.064	0.122, 0.127	0.051, 0.076	0.017, 0.041
R1, wR2; $F_o > 4\sigma(F_o)$	0.034, 0.059	0.061, 0.116	0.040, 0.074	0.016, 0.040
GOF on F^2	1.30	1.73	2.03	1.63
$\Delta\rho_{max}$ [e·Å^{-3}]	0.43, −0.34	1.75, −0.67	0.60, −0.36	0.25, −0.31

$\{(Me_2Si)_2(\eta^5\text{-}C_5H\text{-}3,5\text{-}(CHMe_2)_2)(\eta^5\text{-}C_5H_2\text{-}4\text{-}SiMe_3)\}ZrMe_2$ (16). This compound was prepared in an analogous manner as those published for **12** and **14**. ^{1}H NMR (benzene-d_6): δ −0.142 (s, 6H, Zr*Me₂*); 0.392 (s, 9H, Si*Me₃*); 0.387 (s, 6H, Si*Me₂*); 0.555 (s, 6H, SiMe₂); 1.05 (d, 7 Hz, 6H, CH*Me₂*); 1.27 (d, 7 Hz, 6H, CH*Me₂*); 2.69 (sept, 7 Hz, 2H, C*H*Me₂); 6.86 (m, 2H, Cp); 6.44 (m, 1H, Cp). ^{13}C NMR (benzene-d_6): δ 0.94 (Si*Me₃*); −1.12 (Si*Me₂*); 3.85 (Si*Me₂*); 21.39, 29.18 (CH*Me₂*); 29.32 (*C*HMe₂); 105.34, 111.40, 115.45, 124.68, 134.78, 154.22 (Cp). Anal. Calcd for $Zr_1Si_3C_{25}H_{44}$ C, 57.73, H, 8.53. Found: C, 57.90; H, 8.82.

$\{(Me_2Si)_2(\eta^5\text{-}C_5H\text{-}3,5\text{-}(CHMe_2)_2)_2\}ZrMe_2$ (18). In the drybox, a 25 mL round-bottom flask was charged with 2.00 g (2.72 mmol) of **17**. On the vacuum line, approximately 15 mL of ether was added by vacuum transfer. At −80 °C against an Ar counterflow, 4.3 mL (6.00 mmol) of 1.4 M MeLi was added via syringe. The reaction was warmed to room temperature and stirred. With time a white slurry formed. The reaction was stirred for 5 h, and the solvent was removed in vacuo. Toluene was added, and the white precipitate was removed by filtration. The toluene was removed in vacuo, leaving 1.20 g (65%) of a yellow solid identified as **18**. ^{1}H NMR (benzene-d_6): δ −0.207 (s, 6H, Zr*CH₃*); 0.498 (s, 6H, Si*Me₂*); 0.616 (s, 6H, Si*Me₂*); 1.14 (d, 6 Hz, 12H, CH*Me₂*); 1.38 (d, 6 Hz, 12H, CH*Me₂*); 2.97 (sept, 6.5 Hz, 4H, C*H*Me₂), 6.61 (s, 2H, Cp). ^{13}C NMR (benzene-d_6): δ 1.61 (Si*Me₂*); 6.14 (Si*Me₂*); 21.53 (CH*Me₂*); 29.30 (CH*Me₂*); 29.92 (*C*HMe₂); 30.25 (Zr*CH₃*); 106.14, 111.53, 153.08 (Cp).

$[\{(Me_2Si)_2(\eta^5\text{-}C_5H\text{-}3,5\text{-}(CHMe_2)_2)_2\}ZrH]_2(\mu_2\text{-}H)_2$ (19). This compound was prepared in an analogous manner to **2** employing 0.950 g (1.69 mmol) of **18** and 4 atm of dihydrogen. The reaction was heated to 87 °C for 1 week and afforded 0.650 g (72.3%) of **19**. ^{1}H NMR (benzene-d_6): δ −5.649 (m, 2H, Zr*H* (bridging)); −5.205 (m, 1H, Zr*H* (bridging); 0.161 (s, 6H, Si*Me₂*); 0.783 (s, 6H, Si*Me₂*); 1.18 (d, 7 Hz, 12H, CH*Me₂*); 1.22 (d, 7 Hz, 12H, CH*Me₂*); 3.16 (sept, 6,5 Hz, 4H, C*H*Me₂); 6.23 (s, 2H, Cp). ^{13}C NMR (benzene-d_6): δ 3.99 (Si*Me₂*); 6.73 (Si*Me₃*); 23.15 (CH*Me₂*); 28.83 (CH*Me₂*); 29.64 (*C*HMe₂); 116.44, 118.00, 152.78 (Cp). Anal. Calcd for $C_{26}H_{44}Zr_1Si_2$: C, 61.96; H, 8.80. Found: C, 61.43; H, 8.43.

$\{(Me_2Si)_2(\eta^5\text{-}C_5H_2\text{-}4\text{-}(CMe_3))_2\}ZrMe_2$ (21). In the drybox, a 25 mL round-bottom flask was charged with 1.70 g (3.28 mmol) of **20**. On the vacuum line, approximately 25 mL of diethyl ether was added by vacuum transfer. At −80 °C against an Ar counterflow, 5.2 mL (7.28 mmol) of 1.4 M MeLi was added via syringe. The reaction was warmed to room temperature and stirred. With time a blackish slurry formed. The reaction was stirred for 16 h, and the solvent was removed in vacuo. Petroleum ether was added, and the black precipitate was removed by filtration. The petroleum ether was removed in vacuo, leaving 0.75 g of a white solid identified as $\{(Me_2Si)_2(\eta^5\text{-}C_5H_2\text{-}4\text{-}(CMe_3))_2\}ZrCl(CH_3)$. Subsequent redissolving in diethyl ether and treatment with a second 1.5 mL of 1.4 M MeLi, with workup as before, yielded a white sample of clean (^{1}H NMR) **21**.

Crystallography. Crystal, intensity collection, and refinement details are presented in Table 1 for compounds **1**, **2a**, **5**, and **11**.

Data Collection and Processing. Data for crystals of **1** and **11** were collected on a Nonius CAD 4 serial diffractometer; data for crystals of **2a** and **5** were collected on a Bruker SMART 1000 area detector running SMART v5.054.[44] Both diffractometers were equipped with Crystal Logic CL24 low-temperature devices, and all datasets were collected at low temperature. Both diffractometers used graphite-monochromated Mo Kα radiation with $\lambda = 0.71073$ Å.

CAD 4 Samples (1, 11). The crystals were mounted on glass fibers with Paratone-N oil. The unit cell was calculated from 25 centered reflections. Two sets of data were collected with ω-scans. CRYM[45] programs were used to apply Lorentz and polarization factors to the Nonius datasets and to merge the multiples in the appropriate point group, *2/m* for **1** and 422 for **11**. The individual backgrounds were replaced by a background function of 2θ derived from weak reflections. Weights w were calculated as $1/\sigma^2(F_o^2)$; variances ($\sigma^2(F_o^2)$) were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014\langle I\rangle)^2$.

CCD Samples (2a, 5). The crystals were mounted on glass fibers with Paratone-N oil. For **2a**, four runs of data were

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[44] Bruker. *SMART*, *SAINT*, and *SHELXTL*; Bruker AXS Inc.: Madison, WI, 1999.

[45] Duchamp, D. J. American Crystallographic Association Meeting, Bozeman, MT, Paper B14, 1964; pp 29−30.

collected with 90 s long, −0.20° wide ω-scans at four values of φ (0°, 120°, 240°, and 300°). For **5**, three runs of data were collected with 20 s long, −0.2° wide ω-scans at three values of φ (0°, 120°, and 240°). For both crystals, the detector was 5 cm (nominal) distant at a θ of −28°. The initial cell for data reduction was calculated from just under 1000 reflections chosen from throughout the data frames. For data processing with SAINT v6.02,[44] all defaults were used, except the following: box size optimization was enabled, periodic orientation matrix updating was disabled, the instrument error was set to zero, no Laue class integration restraints were used, the model profiles from all nine areas were blended, and for the post-integration global least-squares refinement, no constraints were applied. The data were corrected with SADABS v. 2.0 (beta) using default parameters except that the scale factor esd was set to the mininum value of 0.002.

Structure Analysis and Refinement. SHELXTL v5.1[44] was used to solve, via direct methods or by the Patterson method, and to refine all structures using full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. For **1**, there are two molecules in the asymmetric unit, with essentially identical conformations. Hydrogen atoms were placed at calculated positions with U_{iso} values of 120% of U_{eq} of the attached atom. As the data for **2a** were weak, the dataset was cut off at a 2θ of 50°. There are two molecules in the asymmetric unit, as the structurally similar dimers lie on centers of symmetry. The hydrogen atoms were placed at calculated positions with U_{iso} values of 120% of U_{eq} of the attached atom except for the hydride atoms, which could not be located in difference maps and were omitted from the calculations. For **5**, there is half of the Zr complex in the asymmetric unit; the dimer lies on a 2-fold axis that passes through both atoms of the bridging dinitrogen. There is also half of a toluene in the asymmetric unit; this also lies on a 2-fold axis that passes through the methyl carbon and bisects the phenyl ring. All parameters were refined on all hydrogen atoms including the half hydrogen atoms of the solvent. For **11**, there is half a molecule in the asymmetric unit, as the trimer lies on a 2-fold axis which passes through one Zr atom and the opposite μ_2-bridging hydride. All hydrogen atom parameters were freely refined.

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Supporting Information Available: Drawings showing the complete atom labeling schemes, tables of atomic coordinates, complete bond distances and angles, and anisotropic displacement parameters for all structurally characterized complexes. This material is available free of charge via the Internet at http://pubs.acs.org.[46]

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(46) Crystallographic data for the structures of **1** (CCDC 114738), **2** (CCDC 147896), **5** (CCDC 147897), and **11** (CCDC 110868) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications. Copies of the data can be obtained on request, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk). Structure factors are available electronically: e-mail: xray@caltech.edu.