

**Table IV.** Packing Efficiencies of Several Hexafluorophosphate Salts with Spherical Cations

salt	packing efficiency, %	$V_a/V_c$	coordn no.
[NMe <sub>4</sub> ][PF <sub>6</sub> ]	66.9	1.7	8
[Fe( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>3</sub> ][PF <sub>6</sub> ]	64.6	2.6	6
[Fe(CO) <sub>3</sub> (C <sub>6</sub> Me <sub>7</sub> )][PF <sub>6</sub> ]	65.4	5.0	6
[Co( $\eta$ -C <sub>6</sub> Me <sub>6</sub> ) <sub>2</sub> ][PF <sub>6</sub> ]	68.9	6.7	6
[Ni <sub>6</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>6</sub> ][PF <sub>6</sub> ]	71.5	8.7	6
[Co(NO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ][PF <sub>6</sub> ]	67.8	10.2	6
[Mn(CO) <sub>2</sub> [P(OMe) <sub>2</sub> Ph] <sub>4</sub> ][PF <sub>6</sub> ]	68.0	12.2	4
[Au(PMePh <sub>2</sub> ) <sub>4</sub> ][PF <sub>6</sub> ]	69.9	14.7	4

isolated in a trigonal-bipyramidal form with [Ni(phen)<sub>3</sub>]<sup>2+</sup> as the counterion. The large counterion PPN<sup>+</sup>, i.e. [(Ph<sub>3</sub>P)<sub>2</sub>N]<sup>+</sup>, has also been widely used to crystallize organometallic and carbonyl anionic complexes, e.g. [PPN][HFe(CO)<sub>4</sub>].

The volumes of many of the cations and anions that form the basis of Basolo's generalizations have been calculated and used to compute the volume ratios  $V_a/V_c$  (a = anion, c = cation) summarized in Table III. It appears from the calculated anion to cation volume ratios given in Table III that the stabilization of unusual anionic coordination compounds may be achieved if the volume of the cation is greater than or equal to that of the anion. For example, in the series [NMe<sub>4</sub>]<sub>2</sub>[NiCl<sub>4</sub>], [NEt<sub>4</sub>]<sub>2</sub>[NiCl<sub>4</sub>], and [Ph<sub>3</sub>AsMe]<sub>2</sub>[NiCl<sub>4</sub>] the volume of the cation increases by a factor of 3 relative to that of the anion. The largest anion/cation volume ratio for the salts isolated as solids and listed in Table III is 1.10, and the smallest is 0.16. Therefore, contrary to previous suggestions, it is not necessary to match the cation and anion sizes with any great precision in order to stabilize unusual coordination environments and the cation volume may exceed that of the anion by up to a factor of 6. However, an anion with an unusual coordination environment is not likely to be isolated if  $V_a/V_c$  greatly exceeds 1.0. For example, the calculated  $V_a/V_c$  ratios for Li<sub>2</sub>NiCl<sub>4</sub> and K<sub>2</sub>NiCl<sub>4</sub>, which cannot be isolated, are 50 and 10, respectively. Therefore, optimum conditions for crystallization are achieved when the cation is approximately equal to or larger in volume than the anion. The analysis is thus consistent with McDaniel's concept of a lower critical cation volume, with the lower limit corresponding approximately to Basolo's size matching criterion.

The precise matching of the sizes of the cations and anions in molecular salts is not a dominating consideration in crystallization, since ions with quite different volumes can pack efficiently within a crystal by varying their coordination numbers. This effect may be illustrated by reference to the series of [PF<sub>6</sub>]<sup>-</sup> salts with spherical cations, whose packing coefficients have been summarized in Table IV. Although the volume ratio ( $V_a/V_c$ ) varies from 1.7 to 14.7, the packing efficiency within the unit cell calculated from the volumes given in Tables I and II and the literature unit cell volumes lies within the narrow range of 64.6-71.5%. It is apparent from Table IV that this is achieved by varying the coordination numbers of the cations and anions. Although the ions chosen in the table have relatively spherical geometries, similar considerations apply to ions with less symmetrical geometries. These results have encouraged us to develop a set of "radius ratio rules" for interpreting the structures of molecular salts, and these results will be described in subsequent publications.<sup>11,12</sup>

It is apparent from the results presented in this paper that the crystallization of salts using large counterions may be successful even when the  $V_a/V_c$  ratio falls to ca. 0.20, because the structure in the solid state can achieve a close-packed arrangement by varying the coordination number. The size effect may play an important role in the isolation process, however, if the cation is highly polarizing and is capable of forming a binary compound with a high lattice energy. For example, Li<sup>+</sup> salts of [MX<sub>n</sub>]<sup>n-</sup> anions are thermodynamically unstable<sup>6</sup> because of the high lattice

energy associated with LiX. For molecular cations M<sup>+</sup> with a volume greater than or equal to that of the anion, there is a significant contribution to the lattice energy from van der Waals forces and the thermodynamic driving force for forming M<sup>+</sup>X<sup>-</sup> is less critical.

The variation in coordination number may not be important for characterizational purposes but could influence the magnetic, conductivity, and nonlinear optical properties of the compound significantly.

The moments of inertia calculated for cations and anions provide objective criteria for evaluating their shape characteristics. For example, it is apparent from Table III that [dienH<sub>3</sub>]<sup>3+</sup> is rather cylindrical in shape, whereas [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> is effectively spherical. Therefore, although these counterions have similar volumes ([dienH<sub>3</sub>]<sup>3+</sup>, 108 Å<sup>3</sup>, [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, 126 Å<sup>3</sup>), only the chromium complex stabilizes the [CuCl<sub>5</sub>]<sup>3-</sup> ion.

The complex [Pt(NH<sub>3</sub>)<sub>4</sub>][CuCl<sub>4</sub>] provides a particularly interesting example of size and shape matching. The volumes of the cation and anion are equal to within 1 Å<sup>3</sup>, and their shape parameters are both indicative of discoidal geometries if the [CuCl<sub>4</sub>]<sup>2-</sup> ion adopts a square-planar geometry. In general, the packing efficiencies of discoidal molecules are greater than that of spherical molecules, which encourages the adoption of this geometry by [CuCl<sub>4</sub>]<sup>2-</sup>.

The availability of the size and shape factors in Tables I and II should encourage the study of more systems where the coordination geometry is influenced by the shape of the cation. The complementary problem of stabilizing unusual cation geometries by selecting the appropriate counteranions could also be addressed using the data provided. It is noteworthy that currently there are few well-documented examples of this phenomenon.

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### Chemistry of (Silica)zirconium Dihydride

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To most organometallic chemists, especially to those who use metals in "fine" synthesis, the notion of organozirconium chemistry is intimately tied to that of a "soft" ligand environment which usually involves "Cp" (or Cp\*) or phosphine ligation.<sup>1</sup> In contrast, well-known processes for ethylene or propylene polymerization<sup>2</sup> or olefin isomerization<sup>3</sup> involve "hard", oxide-bound organozirconium compounds,<sup>2,4</sup> including hydrides<sup>4</sup> formed by hydrolysis<sup>4-6</sup> of oxide-bound alkyls; apart from catalyzed olefin isomerization, the chemistry of these oxide-bound hydrides is

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otherwise unexplored, and no soluble analogues have been reported. It was therefore of interest to us to compare the chemistry of zirconium hydrides in a hard (oxide) vs a soft ligation environment<sup>7</sup> in order to delineate the fundamental chemistry of oxide-bound zirconium hydrides and to learn if new reagent procedures based on them could be developed.

### Experimental Section

**General Procedures.** All operations were performed in a Vacuum Atmospheres glovebox. Octane, THF, and ether were distilled from Na/benzophenone ketyl and stored in the glovebox. Pentane was dried over molecular sieves. Silica gel, Degussa Aerosil 300, was dried at 225 °C (<0.1 Torr) for 24 h. Infrared spectra were recorded on a Perkin-Elmer 1710 spectrometer. Pellets were made by pressing about 30 mg of sample to 8 tons on a hydraulic press. Gas chromatography was done on a Hewlett-Packard 5840 and 5970 chromatograph; GC-MS analysis was performed with a Hewlett-Packard 5971A mass-sensitive detector. Proton NMR spectra were recorded on a General Electric QE-300 spectrometer operating at 300 MHz.

**Tetranepentylzirconium.**<sup>8</sup> Neopentylmagnesium bromide in ether (20 mL, 1.12 M, prepared from neopentyl bromide and magnesium turnings and titrated<sup>9</sup>) was added to a stirred suspension of ZrCl<sub>4</sub> (1.35 g, 5.80 mmol) in a 4:1 mixture of ether and pentane (100 mL) at -40 °C. The mixture was stirred overnight at 0 °C, allowed to warm to room temperature, and filtered. The filtrate was evaporated and extracted thoroughly with pentane. After filtration, the pentane solution was evaporated to give the title compound as a light tan solid (1.85 g, 85%). This material was pure by NMR analysis and was used without sublimation. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.38 (s, 2 H), 1.09 (s, 9 H).

**(SiO<sub>2</sub>)Zr(neopentyl)<sub>2</sub>.**<sup>3</sup> Tetranepentylzirconium (200 mg, 0.56 mmol) was added to a suspension of Degussa Aerosil 300 SiO<sub>2</sub> (1.00 g) in pentane (25 mL). The mixture was stirred overnight and filtered, and the solid was washed with pentane. Evaporation of the filtrate yielded no residue. The product was evacuated for 24 h with intermittent crushing to powder the material. IR (neat pellet): 3600 (br), 2960, 2904, 2870, 1858, 1630, 1469, 1362 cm<sup>-1</sup>. Anal. Found: Zr, 4.06.

**(SiO<sub>2</sub>)ZrH<sub>2</sub> (1).** A 100-mL flask containing (SiO<sub>2</sub>)Zr(neopentyl)<sub>2</sub> (200–500 mg) was evacuated and filled with hydrogen at 1 atm. The material was heated to 120 °C overnight. IR (neat pellet): 3500 (br), 2960, 2930, 2872, 1858, 1623 cm<sup>-1</sup>; ν<sub>Zr-H</sub> = 2254, 2190 cm<sup>-1</sup>.

**(SiO<sub>2</sub>)ZrH<sub>2</sub>-OC(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>.** (SiO<sub>2</sub>)ZrH<sub>2</sub> (200 mg, 0.1 mmol of Zr) was suspended in 4 mL of pentane, and 3-pentanone (20 μL, 18 mg, 0.2 mmol) was added. The solvent and excess ketone were removed in vacuo. IR (neat pellet): 3620 (br), 2970, 2944, 2884, 1858, 1675 (vs), 1572, 1464 cm<sup>-1</sup>; ν<sub>Zr-H</sub> = 2255 (sh), 2219 cm<sup>-1</sup>.

**(SiO<sub>2</sub>)ZrH[OC(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>].** (SiO<sub>2</sub>)ZrH<sub>2</sub>-OC(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> was heated to 120 °C overnight. IR (neat pellet): 3500 (br), 2972, 2940, 2880, 1858, 1660, 1559, 1462 cm<sup>-1</sup>; ν<sub>Zr-H</sub> = 2258 cm<sup>-1</sup>.

**(SiO<sub>2</sub>)ZrH<sub>2</sub>-O(H)CH<sub>2</sub>CH<sub>3</sub>.** (SiO<sub>2</sub>)ZrH<sub>2</sub> (200 mg, 0.1 mmol of Zr) was suspended in 4 mL of pentane, and ethanol (10 μL, 9 mg, 0.2 mmol) was added. The solvent and excess alcohol were removed in vacuo. IR (neat pellet): 3400 (br), 2981, 2875, 1858, 1640 cm<sup>-1</sup>; ν<sub>Zr-H</sub> = 2256, 2200 cm<sup>-1</sup>.

**(SiO<sub>2</sub>)ZrH(OCH<sub>2</sub>CH<sub>3</sub>).** (SiO<sub>2</sub>)ZrH<sub>2</sub>-O(H)CH<sub>2</sub>CH<sub>3</sub> was heated to 120 °C overnight. IR (neat pellet): 3500 (br), 2980, 1858, 1640, 1448, 1392 cm<sup>-1</sup>; ν<sub>Zr-H</sub> = 2262 cm<sup>-1</sup>.

**(SiO<sub>2</sub>)ZrHCl.** HCl gas (10 mL, 5 mmol) was injected via a gastight syringe into an evacuated flask containing (SiO<sub>2</sub>)ZrH<sub>2</sub>. The flask was heated to 120 °C overnight. IR (neat pellet): 3600 (br), 2970, 1858, 1620 cm<sup>-1</sup>; ν<sub>Zr-H</sub> = 2268 cm<sup>-1</sup>.

**General Procedure for the Reactions of (SiO<sub>2</sub>)ZrH<sub>2</sub> with Olefins and Acetylenes.** The olefin or acetylene (1.0–2.0 mmol) was added to a stirred suspension of (SiO<sub>2</sub>)ZrH<sub>2</sub> (50–80 mg) in 2–4 mL of pentane (for room-temperature reactions) or octane (for those at 80 °C). Decane was commonly used as an internal standard. The mixture was stirred for 24 h, and the solvent mixture was examined by gas chromatography. Infrared spectra of the catalyst were obtained by filtering off the solid, washing and drying it, and pressing a pellet.

**Cyclization of 1,5-Hexadiene.** 1,5-Hexadiene (100 μL, 68.8 mg, 838 μmol) was added to a suspension of **1** (80 mg, 35.7 μmol) in octane (2 mL) and decane (25 μL). The mixture was heated to 80 °C for 24 h. GC analysis and comparison with an authentic sample showed that 1-methylcyclopentene had been formed in 64% yield (536 μmol; 15 turnovers).

**Trimerization of 1-Hexyne.** 1-Hexyne (100 μL, 71.6 mg, 872 μmol) was added to a suspension of **1** (80 mg, 35.7 μmol) in octane (2 mL) and decane (25 μL). The mixture was heated to 80 °C for 24 h. 1,2,4-Tributylbenzene and 1,3,5-tributylbenzene were formed in a 2:1 ratio in 16% yield (130 μmol of product; consumes 417 μmol of 1-hexyne; 12 turnovers).

**Deposition of HSi(OMe)<sub>3</sub> onto SiO<sub>2</sub>.** Silica gel (500 mg) was added to a solution of HSi(OMe)<sub>3</sub> (104 mg, 1.0 mmol) in pentane (25 mL). After being stirred overnight, the mixture was filtered, and the solid was washed with pentane. The product was dried in vacuo. IR (neat pellet): 3420, 2958, 2856, 1858, 1630, 1460 cm<sup>-1</sup>; ν<sub>Si-H</sub> = 2238 cm<sup>-1</sup>. The compound is air stable and undergoes none of the reactions of (SiO<sub>2</sub>)Zr-H species.

### Results

Mechanistic studies on soluble Cp<sub>2</sub>ZrXY ("16e") species show that both halogen atom transfer (to Zr<sup>II</sup><sup>10,11</sup>) and electrophilic attack (on Zr<sup>IV</sup><sup>12</sup>) occur via a coordinative mechanism. Various reactions of (SiO<sub>2</sub>)ZrH<sub>2</sub> illustrate both adduct formation and the need for adduct formation prior to reaction of the Zr-H bond with a substrate, modeling what is inferred, but not directly observed, for Cp<sub>2</sub>ZrXY systems. Cp<sub>2</sub>ZrXY complexes do not readily add exogenous ligands, but (SiO<sub>2</sub>)ZrH<sub>2</sub> (ν<sub>Zr-H</sub> = 2254, 2190 cm<sup>-1</sup>) forms stable adducts,<sup>13</sup> as does 16e (triox)<sub>2</sub>ZrCl<sub>2</sub>,<sup>14</sup> even with THF (for (SiO<sub>2</sub>)ZrH<sub>2</sub>-THF, ν<sub>Zr-H</sub> = 2256, 2227 cm<sup>-1</sup>). The Zr-H bands in the adduct showed inverted intensities compared to those of the starting dihydride, presumably due to closing of the H-Zr-H angle by coordination of THF. In contrast with Cp<sub>2</sub>ZrH<sub>2</sub>, which reacts rapidly with methylene chloride to give Cp<sub>2</sub>ZrHCl,<sup>15</sup> (SiO<sub>2</sub>)ZrH<sub>2</sub> was unreactive; only when it was stirred in neat methylene chloride for several days was decomposition observed. Excess methyl iodide in pentane also failed to react with **1**. Stepwise reaction was noted when (SiO<sub>2</sub>)ZrH<sub>2</sub> was treated with protonic reagents.<sup>13</sup> Treatment with 1 equiv of ethanol at room temperature gave an adduct (ν<sub>Zr-H</sub> = 2258, 2230 cm<sup>-1</sup>) and, on heating (120 °C), a monohydride species ((SiO<sub>2</sub>)ZrH(OEt); ν<sub>Zr-H</sub> = 2262 cm<sup>-1</sup>). Even when (SiO<sub>2</sub>)ZrH<sub>2</sub> was allowed to react with 5–25 equiv of ethanol in the gas phase at 120 °C or in pentane solution, only this monohydride product was formed. Gaseous HCl (1 equiv) failed to react rapidly with (SiO<sub>2</sub>)ZrH<sub>2</sub>. Instead, IR analysis showed attack on the surface of silica (ν<sub>Zr-H</sub> = 2258, 2190 cm<sup>-1</sup>; ν<sub>O-H</sub> = 3650 (br), 3730 (sh) cm<sup>-1</sup>). On being heated (120 °C), the dihydride converted to the monohydride species (SiO<sub>2</sub>)ZrHCl (ν<sub>Zr-H</sub> = 2266 cm<sup>-1</sup>). Treating (SiO<sub>2</sub>)ZrH<sub>2</sub> with 2 equiv of 3-pentanone gave an adduct (ν<sub>Zr-H</sub> = 2219, 2254 [sh]); ν<sub>CO</sub> = 1675 cm<sup>-1</sup> which, on being heated to 120 °C, yielded the alkoxide (ν<sub>Zr-H</sub> = 2258 cm<sup>-1</sup>). One equivalent of the ketone was recovered, and further treatment of the alkoxide with the ketone gave neither adduct nor dialkoxide. In contrast, both Cp<sub>2</sub>ZrH<sub>2</sub> and Cp<sub>2</sub>ZrHCl react rapidly with ketones or alcohols to give the dialkoxide and alkoxide chloride, respectively.<sup>16</sup> Even excess HCl failed to react with (SiO<sub>2</sub>)ZrHCl, at temperature as high as 180 °C. From an "electronic" point of view, the high electronegativity of O vs Cp<sup>-</sup> might make (oxide)Zr<sup>IV</sup> a more Lewis acidic, polarizing species and, hence, a better π-acceptor from other ligands than is Cp<sub>2</sub>Zr<sup>IV</sup>. Thus, the surprisingly low reactivity of (SiO<sub>2</sub>)ZrHX (X = π-donor group) in comparison with Cp<sub>2</sub>Zr<sup>IV</sup> analogues may be in part attributable to greater functional saturation of the zirconium center in the oxide-bound metal hydride. (See Scheme I.)

The standard hydrozirconation reagent Cp<sub>2</sub>ZrHCl reacts with simple olefins<sup>1,13</sup> to form stable alkyls, and [Cp<sub>2</sub>Zr(alkyl)]<sup>+</sup> de-

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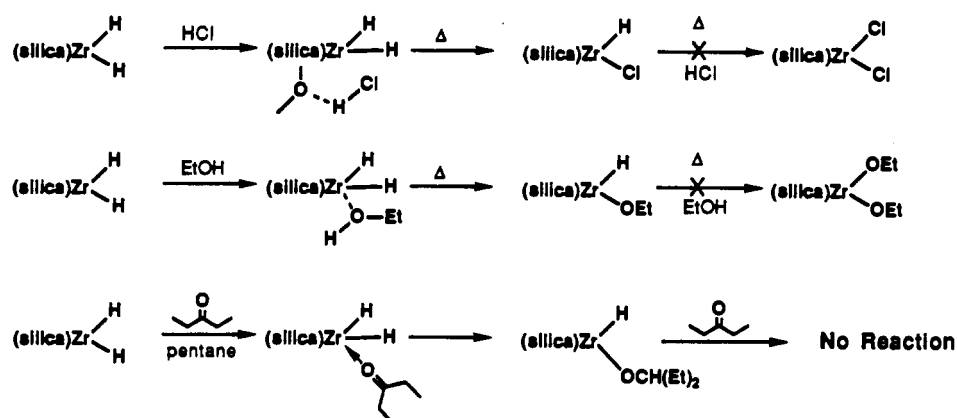
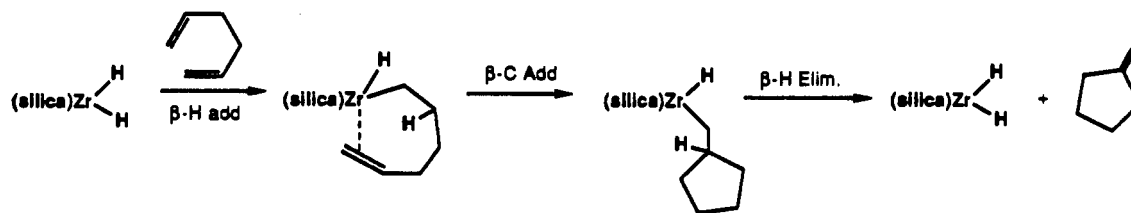
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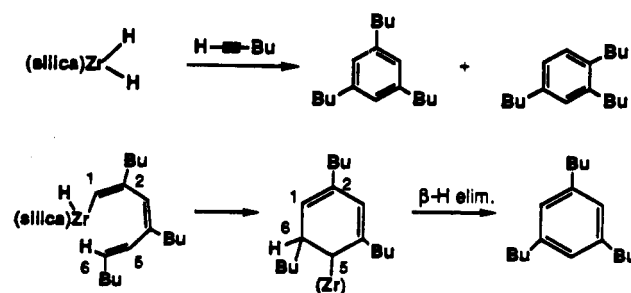
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Scheme I. Fundamental Chemistry of (Silica)ZrH<sub>2</sub>Scheme II. Cyclization of 1,5-Hexadiene Catalyzed by (Silica)ZrH<sub>2</sub>

derivatives are excellent olefin polymerization catalysts.<sup>17</sup> (Silica)ZrH<sub>2</sub> is also an active polymerization catalyst for ethylene and propylene,<sup>2</sup> and it exhibits high activity toward olefin isomerization<sup>3</sup> under mild conditions. When a gastight infrared cell containing **1** was pressurized to 3 atm with 1-butene, formation of the alkyl monohydride could not be observed, yet recovered olefin was isomerized to the thermodynamic mixture of linear butenes. Given the strong donor ligand ability of hydride,<sup>18</sup> stronger  $\pi$ -donation by Cp than by silica should result in a weaker Zr-H bond in monomeric Cp<sub>2</sub>Zr-H systems than in a (SiO<sub>2</sub>)Zr-H unit. This hypothesis is supported by noting IR values for  $\nu_{\text{Zr-H}}$  for monomeric Cp<sub>2</sub>Zr-H species (Cp\*<sub>2</sub>ZrH<sub>2</sub>,<sup>19</sup>  $\nu_{\text{Zr-H}} = 1555 \text{ cm}^{-1}$ ; Cp<sub>2</sub>ZrH(BH<sub>4</sub>),<sup>20</sup>  $\nu_{\text{Zr-H}} = 1945 \text{ cm}^{-1}$ ) compared with (SiO<sub>2</sub>)ZrH<sub>2</sub> ( $\nu_{\text{Zr-H}} = 2254, 2190 \text{ cm}^{-1}$ ). Thus,  $\beta$ -hydride elimination from (SiO<sub>2</sub>)Zr alkyls could be more favorable than from Cp<sub>2</sub>Zr analogues.<sup>21</sup> Both (SiO<sub>2</sub>)ZrHCl and (SiO<sub>2</sub>)ZrH(OEt) failed either to form alkyls or to catalyze olefin isomerization.

That (silica)ZrH<sub>2</sub> is a good olefin polymerization catalyst suggests olefin "insertion" into a growing alkylzirconium chain is facile.<sup>17</sup> An interesting variation on such olefin polyaddition is cyclization insertion of dienes. In fact, (SiO<sub>2</sub>)ZrH<sub>2</sub> catalyzes cyclization of 1,5-hexadiene to methylcyclopentene (methylene-cyclopentane, the expected primary product of cyclization, undergoes double-bond isomerization to methylcyclopentene under the cyclization conditions<sup>3</sup>). (See Scheme II.)

(SiO<sub>2</sub>)ZrH<sub>2</sub> also catalyzes cyclotrimerization of acetylenes to give arenes, a reaction unprecedented in the chemistry of Cp<sub>2</sub>ZrHCl or its analogues. Zirconacycles have been prepared<sup>22</sup> from acetylenes and Zr(II) compounds,<sup>23-25</sup> and late-transition-

Scheme III. Cyclotrimerization of 1-Hexyne Catalyzed by (Silica)ZrH<sub>2</sub>

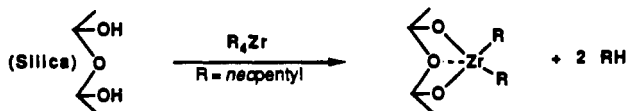
metal acetylene trimerization catalysts may involve analogous metallacycles,<sup>26</sup> but known zirconacycles do not react with acetylenes to give arenes. Perhaps our reaction parallels routes proposed<sup>27</sup> for Pd(II)-catalyzed cyclotrimerization and involves sequential acetylene insertion and  $\beta$ -hydride elimination (via linear trimerization followed by cyclization). (See Scheme III.)

### Discussion

Monomeric Cp<sub>2</sub>ZrXY species are nominally coordinatively unsaturated (16e), but  $\pi$ -donation from X and/or Y, inferred through both crystallography<sup>14,28-30</sup> and mechanistic analysis,<sup>5</sup> can saturate the metal center. Unfortunately, no hard data exist to describe bonding between the -ZrH<sub>2</sub> moiety and the surface of an oxide, but on the basis of structural studies for other oxide-supported Zr systems,<sup>31</sup> it may be that three oxygens of the support

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**Figure 1.** Possible ligation of Zr in (silica)ZrR<sub>2</sub>. Note: This implies that two OH groups of the support have reacted on deposition (as determined by measurement of RH evolution); one  $\mu$ -oxo group is suggested also to be coordinated to Zr resulting in 5-coordinate Zr(IV).

can interact with the metal. In this representation (Figure 1), two oxygen atoms are "doubly" bridged and one is "triply" bridged, and all Zr-O-Si angles are "bent". Electron counting for this arrangement can be done on the basis of structures reported for ZrO<sub>2</sub> (baddeleyite) and for soluble complexes containing Zr-O linkages. Baddeleyite contains two types of oxygen atoms:<sup>28</sup> tetrahedral, quadruply bridging ones ("sp<sup>3</sup>") and planar, triply bridging ones ("sp<sup>2</sup>"). Two of the three triply bridged Zr-O bonds are significantly shorter (2.05, 2.06 Å) than the five others in the unit cell (2.15-2.28 Å), suggesting  $\pi$ -interactions might exist for these oxygens (by "octet rule" electron counting, a  $1/2$   $\pi$ -bond order for each of these short interactions).  $\pi$ -Interactions for doubly Zr-bridging oxygens are also likely for (Cp<sub>2</sub>ZrX)<sub>2</sub>O species (X = Cl,<sup>29a</sup> CH<sub>3</sub>,<sup>29b</sup>) and for (tritox)<sub>2</sub>Zr systems<sup>14</sup> (tritox = [(CH<sub>3</sub>)<sub>3</sub>C]<sub>3</sub>CO<sup>-</sup>); in these cases<sup>14,29</sup> nearly linear Zr-O-Zr and C-O-Zr units and short Zr-O bonds (Zr-O = 1.94 and 1.895 Å, respectively) are consistent with sp O and multiple  $\pi$ -interactions per O. With this notion of multiple bonding, (tritox)<sub>2</sub>ZrCl<sub>2</sub> has been described as a 16e system in which each O of the alkoxide acts as a Cp<sup>-</sup> analogue;<sup>14</sup> similarly, (silica)ZrH<sub>2</sub> can be thought of as a 16e species in which each of the three oxygen atoms of the support ligand serves as a 4e donor and (silica)ZrHCl, through Cl to Zr  $\pi$ -donation, as an 18e species.

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**Supplementary Material Available:** Infrared spectra of silica-supported zirconium complexes (3 pages). Ordering information is given on any current masthead page.

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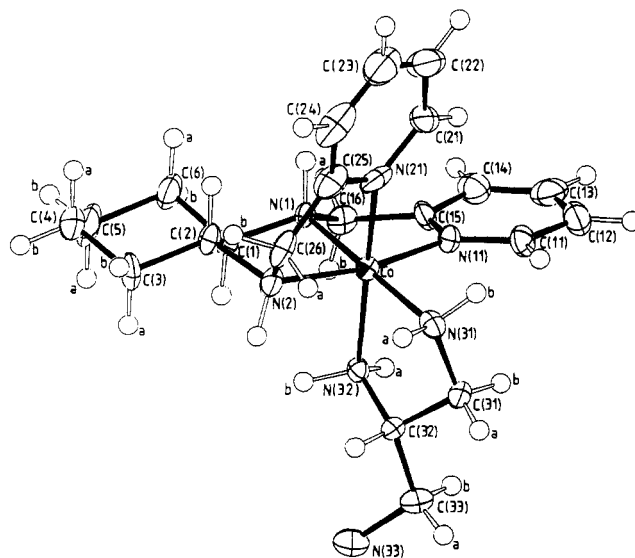
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### Chiral Metal Complexes. 32.<sup>1</sup> Use of an Optically Active Complex for a Nearly Absolute Chiral Induction

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It has been shown<sup>5</sup> that ternary, chiral coordination complexes comprising an optically active tetradentate and a substituted



**Figure 1.** Perspective drawing of the  $\Lambda$ - $\beta$ -<sub>2</sub>-[Co(R,R-picchxn)(tap)]<sup>3+</sup> cation showing the atomic-labeling scheme. Thermal ellipsoids are scaled to include 35% probability. Hydrogen atoms are labeled according to the atom to which they are bonded for example, that to C(11) is H(11) or that to N(1) is H(N1). Where more than one hydrogen atom is bonded to a given atom they are labeled a and b and for clarity only these labels are included for the hydrogen atoms in the diagram.

aminomalonnate ligand (I) may be synthesized in high yield. Considerable discrimination may be obtained with respect to the mode of coordination of the aminomalonnate, depending upon the nature of the tetradentate ligand. This may be employed in subtle ways to produce optically active aminoacidates via decarboxylation of the coordinated aminomalonnate in aqueous acid.<sup>6</sup>



Other prochiral branched terdentates could be used to similar effect. Should subsequent reactions be performed that do not involve the newly created chiral center, completely stereospecific chiral inductions are possible. One such prochiral terdentate is Mann's triamine, 1,2,3-triaminopropane (tap, II), which could be used as a precursor for a number of optically active vicinal diamines providing five-membered chelate ring formation is involved. Some 50 years ago, Mann<sup>7</sup> showed that tap could be coordinated to Pt(II) and Pt(IV), with selective formation of five-membered chelate rings, and that [Pt(tap)Cl<sub>4</sub>]-HCl and [Pt(tap)Cl<sub>2</sub>]-HCl could be resolved into enantiomeric forms.<sup>7</sup> Unfortunately, these resolutions proved to be somewhat tedious, and the optically active complexes racemize in aqueous solution. Other systems may be used to overcome these difficulties, as with the researches of Wild et al.<sup>8</sup> on the stereoselective coordination of glycerol to a chiral Pt(II) complex.

We have examined the coordination behavior of Mann's triamine with a Co(III) complex containing the chiral tetradentate N,N'-bis(2-picolyl)-(1R,2R)-diaminocyclohexane (R,R-picchxn)

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