# Catalytic Oligomerization of Primary Phosphines by the Anionic Zirconocene Trihydride: [Cp\*<sub>2</sub>ZrH<sub>3</sub>]<sup>-</sup>

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## Received August 30, 1995

Interest in the organometallic chemistry of early transition metals has been spurred in the past decade by their applications in organic synthesis<sup>1</sup> and homogeneous catalysis.<sup>2</sup> Recently early metal-main group derivatives or so-called "inorganometallic" systems have also received attention.<sup>3</sup> Of the pnictogenide derivatives of the early metals, much interest has focused on species containing terminal metal-ligand double bonds.<sup>4</sup> While the chemistry of zirconocene phosphinidenes (Zr=PR) is the subject of ongoing study in our group,<sup>4c,f</sup> a parallel study of M-P single bond chemistry continues.<sup>5</sup> In this latter effort, we are studying the established propensity of early metals to mediate P-P bond formation as evidenced by the formation of complexes  $Cp_2M[(PR)_3]$ ,  $Cp_2M[(PR)_2]$  (M = Zr, V), and  $[Cp_2M[(PR_2)]Br]^{-.5}$  In this communication, we describe the use of the new anionic Zr hydride species  $[Cp_{2}^{*}ZrH_{3}]^{-}(1)$  as a catalyst for the oligomerization of  $PRH_2$  (R = Ph, Cy, C<sub>6</sub>H<sub>2</sub>- $2,4,6-Me_3$ ) to the cyclic polyphosphanes (PR)<sub>5</sub>. While a large body of elegant work describes the synthesis and chemistry of these and related polyphosphanes,<sup>6</sup> this is the first report in which a transition metal hydride is employed to effect *catalytic* dehydrocyclooligomerization of primary phosphines.

The reaction of  $Cp*_2ZrCl_2$  with excess KH in THF proceeds at room temperature over the course of several hours to give,



**Figure 1.** ORTEP drawing of the molecule **1**. Methyl and methylene hydrogen atoms have been omitted for clarity while the hydride atoms on Zr were not located.



Figure 2. Proposed intermediates in the catalytic dehydrocoupling of primary phosphines.

upon filtration, addition of hexane, and standing at -30 °C, pale yellow crystals of 1 in 60% yield. The <sup>1</sup>H NMR spectrum of  $1^7$  reveals a typical AX<sub>2</sub> pattern at 1.70(d) and -0.92(t) ppm with  $|J_{H-H}| = 8.3$  Hz. These resonances, attributed to three hydrides in two environments in a ratio of 1:2, show no temperature dependence between 50 and -50 °C while  $T_1$ measurements for the two hydride resonances revealed similar relaxation times for these protons. On the basis of the <sup>1</sup>H and <sup>13</sup>C NMR data, compound **1** was formulated as the salt  $[Cp*_{2} ZrH_3$ [K(THF)<sub>2</sub>]. X-ray crystallography<sup>8</sup> confirmed this formulation as the Cp\*<sub>2</sub>Zr and K(THF)<sub>2</sub> fragments exhibiting typical metric parameters. The structure of 1 is consistent with electrostatic anion-cation pairing in the solid state resulting in what can be loosely termed a "dimer" (Figure 1). The Zr...K and Zr...Zr distances of 4.029(5) and 6.84 Å suggest the presence of bridging hydrides between Zr and K<sup>9</sup> although this could

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<sup>(7)</sup> Spectroscopic data. 1: <sup>1</sup>H NMR (THF- $d_8$ , 25 °C) 3.72 (br, 8H), 1.91 (s, 30H), 1.70(d, 2H,  $|J_{H-H}| = 8.3$  Hz), 1.52 (br, 8H), -0.92 (t, 1H,  $|J_{H-H}| = 8.3$  Hz), <sup>13</sup>C{<sup>1</sup>H} NMR (THF- $d_8$ , 25 °C) 110.6, 67.5, 26.1, 12.1. <sup>31</sup>P NMR (THF- $d_8$ , 25 °C): 7, -49.22 ( $|J_{P-P}| = 335$  Hz,  $|J_{P-H}| = 41$  Hz), -89.15 ( $|J_{P-P}| = 335$  Hz); **8**, -23.59 ( $|J_{P-P}| = 340$  Hz,  $|J_{P-H}| = 28$  Hz), -66.34 ( $|J_{P-P}| = 340$  Hz); **9**, -55.82 ( $|J_{P-P}| = 348$  Hz,  $|J_{P-H}| = 32$  Hz), -87.13 ( $|J_{P-P}| = 348$  Hz); **10**, -34.99 ( $|J_{P-P}| = 172$ , 182 Hz,  $|J_{P-H}| = 71$  Hz), -17.34 ( $|J_{P-P}| = 172$ , 149 Hz), -60.53 ( $|J_{P-P}| = 149$ , 182 Hz). <sup>1</sup>H and <sup>13</sup>C NMR and elemental analysis data are deposited as supporting information.

<sup>(8)</sup> Space group;  $P\bar{1}$ ; a = 12.105(5) Å, b = 13.319(4) Å, c = 10.972(4) Å,  $\alpha = 98.71(3)^{\circ}$ ,  $\beta = 109.24(3)^{\circ}$ ,  $\gamma = 65.35(2)^{\circ}$ , V = 1518(1) Å<sup>3</sup>. R = 8.80%,  $R_{w} = 7.60\%$ .

<sup>(9)</sup> Hydride bridges between Zr and K have been observed previously: Jaciby, D.; Isoz, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. J. Am. Chem. Soc. 1995, 117, 2793.

not be confirmed crystallographically as the hydride hydrogen atoms were not located. Nonetheless, anionic Zr(IV) complexes are rare,<sup>5a</sup> and 1 represents the first anionic Zr(IV) hydride complex to be structurally characterized.

<sup>1</sup>H and <sup>2</sup>D NMR spectra<sup>7</sup> showed no evidence of any exchange of the exo and endo hydrides/deuterides in 1:1 mixtures of 1 and [Cp\*<sub>2</sub>ZrD<sub>3</sub>][K(THF)<sub>2</sub>] (1-d<sub>3</sub>) or [Cp\*<sub>2</sub>ZrDH<sub>2</sub>]<sup>-</sup>  $(1-d_1)$ . The latter species, obtained from the reaction of Cp\*<sub>2</sub>- $ZrH_2$  (2) with KD, also revealed that attack of the dihydride 2 occurs exclusively at the exo position. These data confirm the stereorigidity of the trihydride 1 as well as the absence of an equilibrium between 1 and 2 in solution. Nonetheless, 1 could be converted to 2 via stoichiometric reaction with an ammonium salt or trityl cation.

The reaction of compound 1 with excess PPhH<sub>2</sub> (100 equiv) in dioxane proceeds at 120 °C, resulting in the total consumption of the primary phosphine after 3 days. The resulting phosphoruscontaining product 3 exhibits a broad resonance at -5 ppm in the <sup>31</sup>P NMR spectrum. This product, which crystallizes from solution, was identified as (PPh)5 by high-resolution mass spectra, <sup>31</sup>P NMR, preliminary X-ray crystallographic data, and elemental analysis.<sup>10</sup> Under similar reaction conditions PCyH<sub>2</sub> and  $P(C_6H_2-2,4,6-Me_3)H_2$  are likewise converted to  $(PCy)_5$  (4) and  $(P(C_6H_2-2,4,6-Me_3))_5$  (5), respectively.<sup>11,12</sup> Qualitatively, the rate of formation of 5 is faster as consumption of the primary phosphines is complete in 56 h under similar conditions. This suggests that steric congestion at the metal center accelerates the reaction. The catalytic role of the anionic zirconocene trihydride was confirmed through the use of  $1-d_3$ . Reaction of 1- $d_3$  with excess PPhH<sub>2</sub> at 60 °C in THF (or at 120 °C in dioxane) led to the production and isolation of  $(PPh)_5$  (3) while <sup>1</sup>H and <sup>2</sup>D NMR spectroscopy also verified the consumption of  $1-d_3$  and the re-formation of the trihydride 1.

Monitoring the stoichiometric reaction of 1 with 1 equiv of PPhH<sub>2</sub> by  ${}^{31}P{}^{1}H$  and  ${}^{31}P$  NMR spectra initially revealed a weak singlet resonance at 465.8 ppm along with much stronger doublets at -49.2 and -89.1 ppm having a  $|J_{P-P}|$  coupling of 335 Hz. The former resonance is similar in position to that observed for the phosphinidene hydride  $[Cp_2ZrH(P(C_6H_2-2,4,6$ t-Bu<sub>3</sub>)]<sup>-,13</sup> suggesting the formation of an analogous species  $[Cp*_2ZrH(PPh)]^-$  (6). This species is short-lived and unstable and thus could not be isolated. The unstable species 6 was converted cleanly to 7 via addition of a second equivalent of PPhH<sub>2</sub>. The  ${}^{31}P{}^{1}H$  NMR spectrum of compound 7 exhibited

the two doublets at -49.2 and -89.1 ppm. The lower field half of this pattern also showed a  $|J_{P-H}|$  coupling of 41 Hz.<sup>13</sup> Addition of hexanes to the THF solution afforded the isolation of this compound, identified as [Cp\*<sub>2</sub>Zr((PPh)<sub>2</sub>)H][K(THF)<sub>4</sub>] (7), the anion of which is presumably isostructural to the known complex  $Cp_2Ta((PPh)_2)H$ .<sup>14</sup> In analogous reactions with 2 equiv of  $PCyH_2$  and  $P(C_6H_2-2,4,6-Me_3)H_2$ , the related compounds  $[Cp*_2Zr((PCy)_2)H][K(THF)_4]$  (8) and  $[Cp*_2Zr((P(C_6H_2-2,4,6-4)))]$  $Me_3)_2)H][K(THF)_4]$  (9) were isolated. However, in the case of the reaction of 1 with  $P(C_6H_2-2,4,6-t-Bu_3)H_2$ , the extreme steric bulk resulted in the induction of P-C bond cleavage affording the previously reported substituent-free P complexes  $[Cp*_2Zr]_2(\mu-P_2)$  and  $[Cp*_2Zr]_2(\mu-P)$ .<sup>15</sup>

Reaction of 7 with an additional equivalent of PPhH<sub>2</sub> leads to the clean formation of a new species 10, which exhibits a clean ABC pattern in the  ${}^{31}P{}^{1}H$  NMR spectrum with resonances at -17.34, -34.99, and -60.53 ppm. The central resonances also exhibit a P-H coupling of 71 Hz. These data together with elemental analysis are consistent with the formulation of 10 as  $[Cp*_2Zr((PPh)_3)H][K(THF)_4]$ . The analogous products derived from  $PCyH_2$  and  $P(C_6H_2-2,4,6-Me_3)H_2$  were not observed at 25 °C while at elevated temperatures only the polyphosphane products 4 and 5 were observed. Similarly, addition of more  $PPhH_2$  to 10 resulted in no further reaction at 25°C, while 3 was formed at elevated temperatures,

The isolation and/or observation of 6-10 suggests a mechanism for P-P bond formation in which a primary phosphine reacts sequentially with Zr to yield  $P_1$ ,  $P_2$ , and  $P_3$  intermediates with concomitant loss of  $H_2$ . It appears that further addition of 2 equiv of phosphines occurs with Zr-P bond cleavage and regeneration of the Zr-H bond, although the precise details of the mechanism remain unknown. These aspects as well as the general reactivity and utility of 1 in the catalysis of main group bond formation are the subjects of continuing study.

Acknowledgment. Financial support from the NSERC of Canada and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supporting Information Available: Spectroscopic data and tables of crystallographic parameters, hydrogen atom parameters, and thermal parameters for 1 (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

#### JA9529899

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