Catalytic Oligomerization of Primary Phosphines by the Anionic Zirconocene Trihydride: $[Cp^*_2ZrH_3]^-$

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Interest in the organometallic chemistry of early transition metals has been spurred in the past decade by their applications in organic synthesis[1] and homogeneous catalysis.[2] Recently early metal−main group derivatives or so-called "inorganometallic" systems have also received attention.[3] Of the pnictogenide derivatives of the early metals, much interest has focused on species containing terminal metal−ligand double bonds.[4] While the chemistry of zirconocene phosphinidenes (Zr=PR) is the subject of ongoing study in our group,[4c,f] a parallel study of M−P single bond chemistry continues.[5] 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 $[Cp^*_2ZrH_3]^-$ (**1**) as a catalyst for the oligomerization of PRH_2 (R = Ph, Cy, C_6H_2-2,4,6-Me_3) to the cyclic polyphosphanes $(PR)_5$. While a large body of elegant work describes the synthesis and chemistry of these and related polyphosphanes,[6] 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, upon filtration, addition of hexane, and standing at −30 °C, pale yellow crystals of **1** in 60% yield. The ^{1}H NMR spectrum of **1**[7] reveals a typical AX_2 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 ^{1}H and ^{13}C NMR data, compound **1** was formulated as the salt $[Cp^*_2ZrH_3][K(THF)_2]$. X-ray crystallography[8] confirmed this formulation as the Cp^*_2Zr and $K(THF)_2$ 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[9] although this could

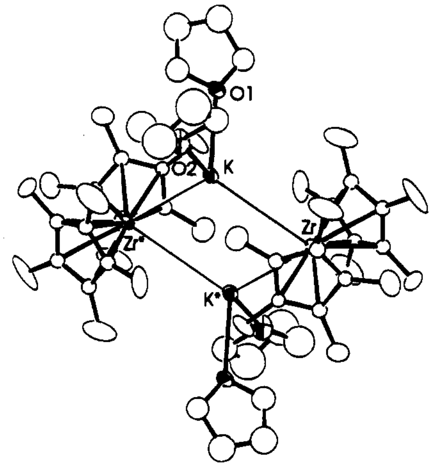

Figure 1. ORTEP drawing of the molecule **1**. Methyl and methylene hydrogen atoms have been omitted for clarity while the hydride atoms on Zr were not located.

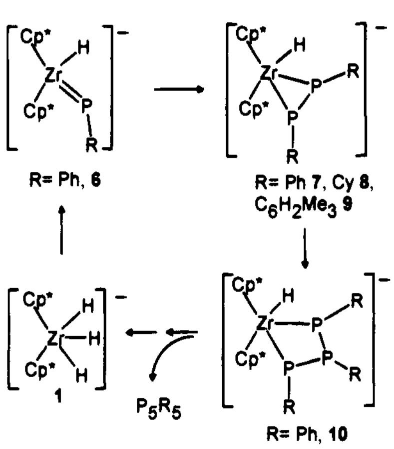

Figure 2. Proposed intermediates in the catalytic dehydrocoupling of primary phosphines.

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[1] Some of the leading refererences in this area include the following: (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (b) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981. (c) Doxsee, K. M.; Dhen, G. S.; Knobler, C. B. *J. Am. Chem. Soc.* **1989**, *111*, 9129. (d) Buchwald, S. L.; Watson, B. T.; Wannamaker, W. M.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (e) McGrane, P. L.; Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1992**, *114*, 5459. (f) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 1590. (g) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171. (h) Buchwald, S. L.; Fisher, R. A.; Davis, W. M. *Organometallics* **1989**, *8*. 2082. (i) Fisher, R. A.; Nielsen, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 165. (j) Geissler, B.; Wettling, T.; Barth, S.; Binger, P.; Regitz, M. *Synthesis* **1994**, 1337. (k) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (l) Walsh, P. J.; Carney, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6343. (m) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Organomet. Chem.* **1992**, *428*, 13. (n) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 2179. (o) Schaller, C. P.; Bonanno, J. B.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 4133. (p) Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985. (q) Banaszak Hall, M. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1992**, *114*, 3854. (r) Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 391. (s) Carney, M. J.: Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751. (t) Whinnery, L. L.; Hening, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 7575. (u) Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6426.

[2] (a) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (b) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57. (c) Erker, G. *Pure Appl. Chem.* **1992**, *64*, 393.

[3] *Inorganometallics*; Fehlner, T. P., Ed.; Plenum Press: New York, 1992.

[4] (a) Hitchcock, P. B.; Lappert, M. F.; Leung, W. P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282. (b) Cowley, A. H.; Pellerin, B.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* **1990**, *112*, 6734. (c) Hou, Z.; Stephan, D. W. *J. Am. Chem. Soc.* **1992**, *114*, 10088. (d) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 756. (e) Bonanno, J. B.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1994**, *116*, 11159. (f) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914.

[5] (a) Ho, J.; Breen, T. L.; Ozarowski, A.; Stephan, D. W. *Inorg. Chem.* **1994**, *33*, 865. (b) Hou, Z.; Breen, T. L.; Stephan, D. W. *Organometallics* **1993**, *12*, 3158.

[6] (a) Baudler, M. *Angew. Chem.* **1982**, *94*, 520. (b) Baudler, M. *Angew. Chem.* **1987**, *99*, 429.

[7] Spectroscopic data. **1**: ^{1}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); $^{13}C\{^1H\}$ NMR (THF-d_8, 25 °C) 110.6, 67.5, 26.1, 12.1. ^{31}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). ^{1}H and ^{13}C NMR and elemental analysis data are deposited as supporting information.

[8] Space group; $P\bar{1}$; $a = 12.105(5)$ Å, $b = 13.319(4)$ Å, $c = 10.972(4)$ Å, $\alpha = 98.71(3)°$, $\beta = 109.24(3)°$, $\gamma = 65.35(2)°$, $V = 1518(1)$ Å^3. $R = 8.80\%$, $R_w = 7.60\%$.

[9] 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.

0002-7863/95/1517-12645$09.00/0

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

^1H and ^2D NMR spectra[7] showed no evidence of any exchange of the *exo* and *endo* hydrides/deuterides in 1:1 mixtures of **1** and $[Cp^*_2ZrD_3][K(THF)_2]$ (**1**-d_3) or $[Cp^*_2ZrDH_2]^-$ (**1**-d_1). The latter species, obtained from the reaction of $Cp^*_2ZrH_2$ (**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 $PPhH_2$ (100 equiv) in dioxane proceeds at 120 °C, resulting in the total consumption of the primary phosphine after 3 days. The resulting phosphorus-containing product **3** exhibits a broad resonance at −5 ppm in the ^{31}P NMR spectrum. This product, which crystallizes from solution, was identified as $(PPh)_5$ by high-resolution mass spectra, ^{31}P NMR, preliminary X-ray crystallographic data, and elemental analysis.[10] Under similar reaction conditions $PCyH_2$ and $P(C_6H_2\text{-}2,4,6\text{-}Me_3)H_2$ are likewise converted to $(PCy)_5$ (**4**) and $(P(C_6H_2\text{-}2,4,6\text{-}Me_3))_5$ (**5**), respectively.[11,12] 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 $PPhH_2$ at 60 °C in THF (or at 120 °C in dioxane) led to the production and isolation of $(PPh)_5$ (**3**) while ^1H and ^2D 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 $PPhH_2$ by $^{31}P\{^1H\}$ 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 $[Cp_2ZrH(P(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3))]^-$,[13] 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 $PPhH_2$. The $^{31}P\{^1H\}$ 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.[13] Addition of hexanes to the THF solution afforded the isolation of this compound, identified as $[Cp^*_2Zr((PPh)_2)H][K(THF)_4]$ (**7**), the anion of which is presumably isostructural to the known complex $Cp_2Ta((PPh)_2)H$.[14] In analogous reactions with 2 equiv of $PCyH_2$ and $P(C_6H_2\text{-}2,4,6\text{-}Me_3)H_2$, the related compounds $[Cp^*_2Zr((PCy)_2)H][K(THF)_4]$ (**8**) and $[Cp^*_2Zr((P(C_6H_2\text{-}2,4,6\text{-}Me_3))_2)H][K(THF)_4]$ (**9**) were isolated. However, in the case of the reaction of **1** with $P(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)H_2$, the extreme steric bulk resulted in the induction of P−C bond cleavage affording the previously reported substituent-free P complexes $[Cp^*_2Zr]_2(\mu\text{-}P_2)$ and $[Cp^*_2Zr]_2(\mu\text{-}P)$.[15]

Reaction of **7** with an additional equivalent of $PPhH_2$ leads to the clean formation of a new species **10**, which exhibits a clean ABC pattern in the $^{31}P\{^1H\}$ 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 $P(C_6H_2\text{-}2,4,6\text{-}Me_3)H_2$ 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.

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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.

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[10] (a) Daly, J. J. *J. Chem. Soc.* **1964**, 6147. (b) Albrand, J. P.; Gagnaire, D. *J. Am. Chem. Soc.* **1972**, *94*, 8930. (c) Baudler, M.; Carlsohm, B. *Chem. Ber.* **1977**, *110*, 2404.

[11] Baudler, M.; Pinner, C.; Gruner, C.; Heilmann, J.; Schwaraborn, M.; Kloth, B. *Z. Naturforsch.* **1977**, *32b*, 1244.

[12] $^{31}P\{^1H\}$ NMR (THF-d_8, 25C): broad multiplet resonance centered at −2 ppm. ^1H and ^{13}C NMR and elemental analysis data are deposited as supporting information.

[13] Fermin M. C.; Ho, J.; Stephan, D. W. *Organometallics* **1995**, *14*, 4247.

[14] ^{31}P NMR data for compound $Cp_2Ta((PPh)_2)H$, −146, −164 ppm ($|J_{P-P}|$ = 327 Hz, $|J_{P-H}|$ = 42 Hz), is reported in the following: Leblanc, J. C.; Moise, C. *J. Organomet. Chem.* **1989**, *364*, C3.

[15] Fermin M. C.; Ho, J.; Stephan, D. W. *J. Am. Chem. Soc.* **1994**, *116*, 6033.