compared to Ni(DPPE)Cl$_2$. However, Pd(DPPE)Cl$_2$ (70:30, HT:HH) was not nearly as effective as Ni(DPPE)Cl$_2$. The smaller ionic radius of Ni^{2+} vs Pd^{2+} along with the higher steric demands for DPPE indicate that the degree of stereoregularity is controlled by steric congestion of the reductive elimination step. This is further supported by the fact that **3** is apparently isomerized into **2** (by a series of transmetalation–reductive elimination followed by oxidative addition) faster than it is polymerized.

The ^{1}H and ^{13}C NMR spectra of PHT provide sensitive probes of the substitution pattern in the polymer backbone. In a mixture of the four possible triad regioisomers (Figure 1a structures), all of the vinyl carbon atoms (16 peaks are theoretically possible) and all of the vinyl protons (4 total) can be resolved.[1a,b,7] This is clearly demonstrated in the ^{1}H and ^{13}C NMR spectra of **4** (Figures 1a and 2a). The observed spectra are consistent with a totally random (1:1:1:1, HT-HT:HT-HH:TT-HT:TT-HH linkages based on NMR integration) mixture of the four triad structures depicted.

In contrast, only one sharp band for the vinyl proton, which denotes the HT-HT structure, and four sharp bands for the vinyl carbon atoms (one band for each carbon), which also denotes the HT-HT structure, are observed in the ^{1}H and ^{13}C NMR spectra of **5** (Figures 1b and 2b). The resolution and signal:noise ratio characterize **5** as pure HT-PHT (98.5 ± 1.5%). The two doublet peaks (7.15, 6.93 ppm) and one singlet peak at 6.91 ppm (Figure 1a) are assigned as the terminal ring protons Ha, Hb, and Hc of PHT.[8]

The molecular weights were determined by GPC (relative to polystyrene standard). Random PHT has M_w = 2.44 × 10^4 and M_n = 5.65 × 10^3, corresponding to a polydispersity index of 4.32. HT-PHT does not completely dissolve in THF at the same concentration; the soluble part has M_w = 1.50 × 10^4. UV–vis data shows that HT-PHT has the longest wavelength of maximum absorption either in solution (CHCl$_3$, 456 nm) or in the solid state (film, 560 and 610 nm) when compared with the values of other PHT.[1a,b,2b,9] This indicates that HT-PHT has the greatest effective conjugation length in the polymer chain, apparently due to complete head-to-tail regularity.[10] Random PHT has maximum absorption with the relatively shorter wavelengths of 427 (CHCl$_3$) and 438 nm (film). The physical properties for the two polymers are quite different.[11]

Neither regioregular HT-PHT, such as **5**, nor equally regiorandom PHT, such as **4**, has previously been reported.[1a,b,2c] We expect the regioregular HT-PHT to have a large improvement not only in electrical conductivity but also in magnetic, nonlinear optical properties and other physical properties, and we are currently pursuing such characterizations. Likewise we are examining aspects of this polymerization which may explain the difference in control of regiochemistry observed in Ni and Pd catalysis.

Supplementary Material Available: Synthetic procedures for **4** and **5**, ^{1}H and ^{13}C NMR spectra, and tables of IR, GC, and elemental analysis data (9 pages). Ordering information is given on any current masthead page.

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(11) The solubility of random PHT in chloroform is at least 3 times greater than that of regioregular HT-PHT apparently due to the reduced crystallinity of the polymer chain. More interestingly, a film of the regular HT-PHT is gold-yellow in color, with a metallic luster and a strong fluorescence; the random polymer only forms a red-brown transparent film.

Generation and Reactivity of the First Mononuclear Early Metal Phosphinidene Complex, Cp*$_2$Zr=P(C$_6$H$_2$Me$_3$-2,4,6)

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The wide-ranging applications of metal carbenes (M=C) in organometallic chemistry[1] have spawned interest in transition metal complexes containing metal–heteroatom double bonds. While many metal–oxo and –sulfido systems are generally robust, recent work has shown that early metal systems containing metal–imido (M=NR),[2-4] –oxo (M=O),[5-8] and –sulfido (M=S)[8] have a rich chemistry. Development of related early metal phosphinidene (M=PR) chemistry faces several obstacles. Firstly, synthetic routes to known phosphinidene complexes typically involve either use of metal complex anions or thermal degradation of coordinated phosphinidene precursors.[9] Neither of these methods is amenable to early metals. A second problem is the propensity of phosphinidene moieties to bridge two or more metal centers. Thus, while V[10] and Zr[11] phosphinidene-bridged complexes have been characterized, related mononuclear systems are unknown.[12] Herein, we describe the preparation of the primary phosphide complex Cp*$_2$Zr(PH(C$_6$H$_2$Me$_3$))$_2$ (**1**). This species is a synthon for a transient mononuclear Zr=PR moiety which reacts intramolecularly with sp^3 C–H bonds, with P–H bonds or MeCN affording phosphametallocycles.

The reaction of Cp*$_2$ZrCl$_2$ with 2 equiv of LiPH(C$_6$H$_2$Me$_3$) in benzene at 25 °C gave the wine-red diphosphido species **1**[13,14] in 90% isolated yield. In the solid state the pseudotetrahedral zirconium center resides on a crystallographically imposed 2-fold

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(12) Only two transition metal complexes containing terminal phosphinidene moieties have been structurally characterized: (a) Cowley, A. H.; Pellerin, B. *J. Am. Chem. Soc.* **1990**, *112*, 6734. (b) Hitchcock, P. B.; Lappert, M. F.; Leung, W. P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282. (c) The ^{31}P NMR chemical shifts of the "bent" terminal phosphinidene complexes are as follows: Cp$_2$Mo=P(C$_6$H$_2$(t-Bu)$_3$), 799.5 ppm; Cp$_2$W=P-(C$_6$H$_2$(t-Bu)$_3$), 661.1 ppm. (d) DME may stabilize the adduct Cp*$_2$Zr(μ-P-(C$_6$H$_2$Me$_3$))(μ-Cl)Li(DME).

(13) In all cases, C$_6$H$_2$Me$_3$ refers to the 2,4,6-trimethylphenyl substituent. NMR data (all recorded in C$_6$D$_6$ at 25 °C, δ (ppm) relative to TMS and 85% H$_3$PO$_4$ for ^{1}H and ^{31}P data, respectively), **1**: ^{31}P{^{1}H} NMR δ 39.0; ^{1}H NMR δ 6.91 (s, 4 H), 4.43 (d of m, 2 H, $|J_{P-H}|$ = 268 Hz, $|J_{P-H}|$ = 50 Hz), 2.73 (br s, 6 H), 2.60 (br s, 6 H), 2.26 (s, 6 H), 1.72 (s, 30 H). **2**: ^{31}P{^{1}H} NMR δ -42.6; ^{1}H NMR δ 6.86 (s, 1 H), 6.73 (s, 1 H), 3.54 (d, 1 H, $|J_{P-H}|$ = 180 Hz), 2.75 (s, 3 H), 2.26 (s, 3 H), 1.72 (s, 30 H), 1.25 (s, 2 H). **3**: ^{31}P{^{1}H} NMR δ 134.9; ^{1}H NMR δ 6.93 (s, 2 H), 6.73 (s, 2 H), 3.33 (s, 6 H), 2.29 (s, 6 H), 1.78 (s, 30 H), 1.24 (s, 6 H). **4**: ^{31}P{^{1}H} NMR δ 0.2; ^{1}H NMR δ 6.89 (s, 2 H), 2.15 (s, 3 H), 1.99 (d, 3 H, $|J_{P-H}|$ = 4.5 Hz), 1.89 (s, 30 H), 1.87 (br s, 6 H). **5**: ^{31}P{^{1}H} NMR δ -71.9; ^{1}H NMR δ 6.88 (s, 1 H), 6.58 (s, 1 H), 5.36 (d, 1 H, $|J_{P-H}|$ = 225 Hz), 2.29 (s, 3 H), 2.19 (s, 3 H), 2.08 (d, 3 H, $|J_{P-H}|$ = 3.6 Hz), 1.76 (s, 15 H), 1.54 (s, 15 H), 1.26 (s, 2 H). **6**: ^{31}P{^{1}H} NMR δ -30.1; ^{1}H NMR δ 6.80 (s, 4 H), 6.49 (s, 4 H), 3.03 (s, 6 H), 2.40 (s, 6 H), 2.07 (t, 6 H, $|J_{P-H}|$ = 1.5 Hz), 1.99 (s, 30 H), 1.94 (s, 6 H). Satisfactory combustion analyses have been obtained for **1–6**.

Scheme I
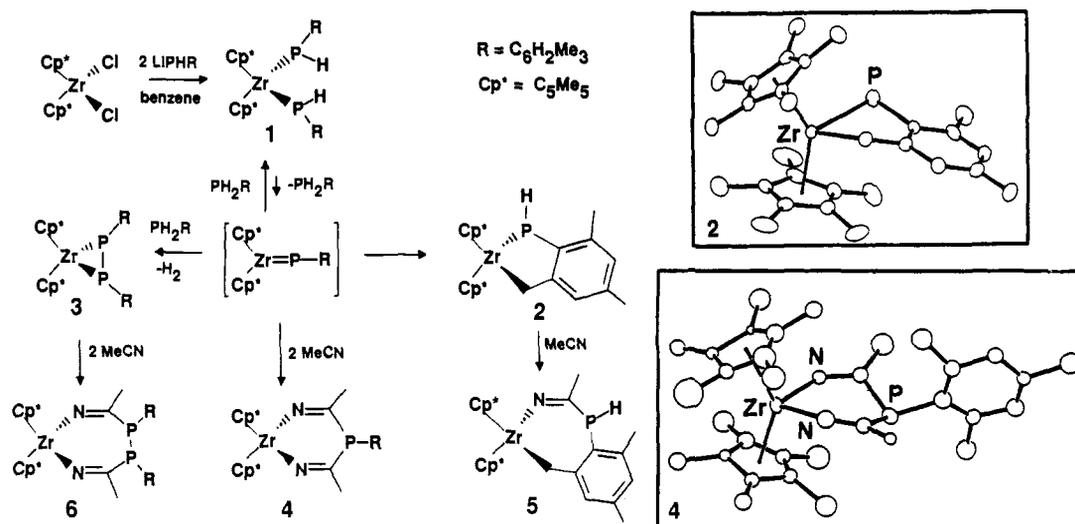
axis of symmetry with a Zr–P bond length of 2.63 (2) Å, which is typical of pyramidal phosphides on Zr(IV).

Compound **1** is a synthon for the highly reactive phosphinidene intermediate Cp*$_2$Zr=P(C$_6$H$_2$Me$_3$) as judged by its subsequent trapped products. Monitoring of a benzene solution of **1** by ^{31}P NMR showed the slow loss of the resonance attributable to **1** and the growth of signals attributable to two new Zr complexes, free primary phosphine PH$_2$(C$_6$H$_2$Me$_3$), and traces of (PH-(C$_6$H$_2$Me$_3$))$_2$. The new Zr complexes were isolated by fractional crystallization. After 2 days, red-brown crystals of **2** were deposited. The NMR spectra[13] and crystallographic data[13] confirmed **2** as the phosphametallocycle Cp*$_2$Zr(CH$_2$C$_6$H$_2$Me$_2$PH). Upon further standing for several days, a second new Zr derivative, Cp*$_2$Zr(PC$_6$H$_2$Me$_3$)$_2$ (**3**), was obtained.[13]

Bergman et al.[2] have described the generation of Cp$_2$Zr=NR from Cp$_2$Zr(NHR)$_2$. In our case, a similar equilibrium between **1** and the highly reactive phosphinidene intermediate accounts for the conversion of **1** to **2** and **3**. Intramolecular C–H bond activation of an *o*-methyl group in the transient phosphinidene accounts for the formation of **2**. Formation of **3** requires addition of the P–H bond of the primary phosphine to the Zr=P double bond with the opposite regiochemistry to that which permits re-formation of **1**. This yields a P–P bond, and subsequent elimination of H$_2$ drives the irreversible formation of **3**. Compound **2** is stable in solution, even in the presence of excess phosphine (PH$_2$(C$_6$H$_2$Me$_3$)) and is thus not involved in the formation of **3**. Interception of the transient phosphinidene was achieved via the reaction of a solution of **1** with MeCN in benzene at 25 °C. The products include free primary phosphine PRH$_2$ as well as the yellow-orange six-membered metallocycle Cp*$_2$Zr(NCMe)$_2$P-(C$_6$H$_2$Me$_3$) (**4**).[13,14] The geometry at the phosphorus atom in **4** is pseudopyramidal. Mechanistically, this reaction may be viewed as a 2 + 2 cycloaddition of MeCN to the phosphinidene with subsequent insertion of a second equivalent of acetonitrile into the Zr–P bond. Attempts to observe the initial cycloaddition product led only to the observation of **1**, **4**, and free phosphine. Although attempts to isolate the phosphinidene intermediate have been unsuccessful to date, direct spectroscopic evidence for a phosphinidene species is derived from the reaction of LiPH-

(C$_6$H$_2$Me$_3$) and Cp*$_2$ZrCl$_2$ in DME at 25 °C. In addition to **1**, a ^{31}P NMR resonance at 537 ppm with no P–H coupling is seen. This downfield resonance is attributed to the unstable bent phosphinidene intermediate.[12c,d] Addition of MeCN to this DME solution led to the disappearance of both the resonance at 537 and that from **1** and the appearance of the signal from **4**. Attempts to trap this species employing dative donors such as PMe$_3$ were unsuccessful, affording instead mixtures of **2** and **3**.

It was also found that reactions of **2** and **3** with MeCN give quantitatively the seven-membered metallocycles Cp*$_2$Zr-(CH$_2$C$_6$H$_2$Me$_2$PH(C(Me)N)) (**5**) and Cp*$_2$Zr(NC(Me)P-(C$_6$H$_2$Me$_3$))$_2$ (**6**), respectively.[13]

The chemistry described herein illustrates that generation of a reactive phosphinidene intermediate offers a route to a variety of new phosphametallocycles and thus a point of entry for metal-mediated organophosphorus chemistry.

(14) Crystal data, **1**: C$_{38}$H$_{54}$P$_2$Zr, *Pbcn*, *a* = 10.941 (4) Å, *b* = 15.719 (6) Å, *c* = 21.047 (9) Å. **2**: C$_{29}$H$_{41}$PZr, *P2$_1$/n*, *a* = 11.724 (8) Å, *b* = 15.613 (6) Å, *c* = 14.791 (3) Å, *β* = 102.81 (3)°. **4**: C$_{33}$H$_{47}$N$_2$PZr, *Pbca*, *n* = 23.328 (6) Å, *b* = 18.777 (5) Å, *c* = 14.583 (6) Å. **6**: C$_{42}$H$_{58}$N$_2$P$_2$Zr, *Cc*, *a* = 16.722 (33) Å, *b* = 14.003 (3) Å, *c* = 17.652 (9) Å, *β* = 104.04 (9)°. Mo Kα radiation, λ = 0.710 69 Å, and a Rigaku AFC6-S diffractometer were employed to collect the data (4.5° < 2θ < 50°). The solutions were obtained and refined employing the TEXSAN software package from MSC. Refinement (data *I* > 3σ(*I*), variables *R*, *R$_w$*), **1**: 309, 55, 0.0962, 0.0967. **2**: 2740, 280, 0.0480, 0.0554. **4**: 916, 111, 0.0857, 0.0850. **6**: 1570, 212, 0.0411, 0.0482.

Is the Structure of Selenoformamide Similar to Those of Formamide and Thioformamide?

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Formamide and its thio and seleno analogs can formally exist in two tautomeric forms, **1** and **2** (Chart I). However, it is experimentally well documented that the amide form **1** of both formamide (F) and thioformamide (SF) is a dominating species in the vapor phase, an inert environment, and a polar medium.[1]

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