pyramidalization angles in **3** are significantly larger than the pyramidalization angles found in the $(Ph_3P)_2Pt$ complexes of other alkenes,[14] except for the $(Ph_3P)_2Pt$ complex of bicyclo[2.2.0]hex-1(4)-ene.[4]

In the latter complex the bond angles within the four-membered rings are constrained to be close to 90°, which causes small amounts of nonplanarity at the carbons bonded to platinum to result in very large pyramidalization angles.[16] A better indicator of the degree of pyramidalization at these carbons in the $(Ph_3P)_2Pt$ complex of bicyclo[2.2.0]hex-1(4)-ene is the flap angle between the two four-membered rings, which has been found to be 123°.[4] This flap angle is considerably less than the 180° that is calculated for the equilibrium geometry of the free alkene,[15,17,18] but significantly larger than the corresponding flap angle in **3**, which is found to be 114° ± 4°. Unlike bicyclo[2.2.0]hex-1(4)-ene, which is calculated to be planar, albeit with a small force constant for pyramidalization at the doubly bonded carbons,[17] **2** is computed to have a highly pyramidalized equilibrium geometry.[15]

Acknowledgment. We thank the National Science Foundation and the Department of Energy for support of this work and Professors James M. Mayer and Nancy M. Doherty for helpful discussions.

Supplementary Material Available: Details of data collection and refinement and tables of crystal parameters, bond lengths and angles, torsional angles, and least-squares planes for **3** (10 pages); tables of observed and calculated structure factors for **3** (10 pages). Ordering information is given on any current masthead page.

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(16) When the C—C—R bond angles in $R_2C{=}CR_2$ are exactly 90°, any deviation of the R—C—R bond angle from 180° gives a pyramidalization angle of 90°.[2]

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Detection of an Alkyl Ethylene Complex during Ethylene Polymerization by a Co(III) Catalyst. Energetics of the β-Migratory Insertion Reaction

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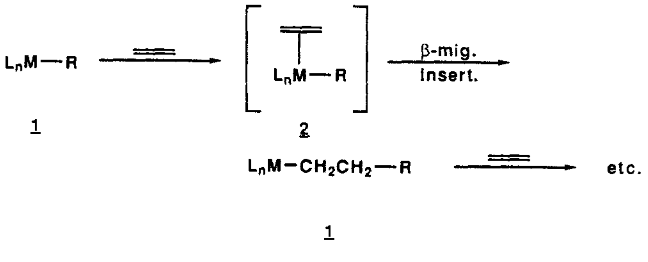
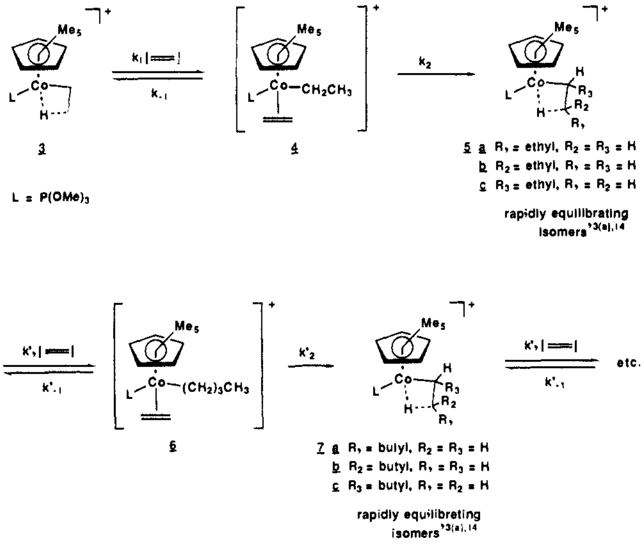
The mechanism of carbon–carbon bond formation in transition-metal-catalyzed olefin polymerization reactions is thought to be a β-migratory insertion reaction occuring via an intermediate alkyl olefin complex, **1** → **2** → **1′** (the Cossee–Arlman mechanism).[1-11] Although the stepwise polymerization of ethylene (and other alkenes) in homogeneous systems has been studied spectroscopically,[3-6,8b,12] intermediate alkyl ethylene complexes have not been detected. Thus, activation energies for the β-migratory insertion reactions of alkyl olefin complexes in polymerizing systems are unknown. We report here spectroscopic detection of an intermediate cobalt alkyl ethylene complex during ethylene polymerization by a Co(III) catalyst together with a kinetic study which allows estimation of $\Delta G^{\ddagger}$ for the β-migratory insertion reaction.



Scheme I



The Co(III) complex $C_5Me_5(P(OMe)_3)CoCH_2CH_2\text{-}\mu\text{-}H^+$ (**3**), has been previously shown to function as an ethylene polymerization catalyst.[13] On the basis of low-temperature ^1H and ^{13}C NMR studies of the polymerization, the mechanism shown in Scheme I was proposed. Agostic species **3**, **5a–c**, **7a–c**, etc. are the "resting state" of the catalyst and were the only species that

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(10) Species **1** (or **1′**) in many cases bridges a β-hydrogen and adopts an agostic structure.

(11) Calculations suggest that in the reaction of $Cp_2Ti{-}CH_3^+$ with C_2H_4 an intermediate alkyl ethylene complex, $Cp_2Ti(C_2H_4)CH_3^+$, is formed and undergoes β-CH_3 migration with an E_a of 10 kcal/mol: Jolly, C. A.; Marynick, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 7968.

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Table I. Comparisons of Free Energies of Activation for β-Migratory Insertions of the Rhodium (**8a**,**b**) and Cobalt (**3** and **4**) Ethylene Complexes

$Cp^*(L)M(C_2H_4)R$	$\Delta G^\ddagger_{H\text{-mig}}$, R = H	$\Delta G^\ddagger_{Et\text{-mig}}$, R = C_2H_5	$\Delta\Delta G^\ddagger$, kcal/mol
Rh[a]	12	22.3	10.3
Co	est 6–8[b]	14.3	est 8–6

[a] Values taken from ref 18. [b] See text for explanation of this value.

could be detected spectroscopically. The alkyl ethylene complexes **4**, **6**, etc. were proposed but unobserved intermediates.

In an effort to detect such alkyl ethylene intermediates, the polymerization was carried out with high concentrations of doubly labeled [^{13}C]ethylene and monitored by ^{13}C NMR spectroscopy. Initial experiments were done at Exxon by using a high-pressure sapphire NMR cell.[15] At a pressure of 70 psi, 97% enriched $^{13}C_2H_4$ was condensed into a 1.5-mL CD_2Cl_2 solution of 0.23 M $3^+BF_4^-$ at −80 °C. After standing for 10 h at −80 °C, additional unlabeled C_2H_4 at 500 psi was condensed into the tube at −80 °C (C_2H_4:$^{13}C_2H_4$ ca. 7:1). The NMR spectrum at −70 °C showed signals at 56.5 ppm (d, $J_{^{13}C-^{13}C}$ = 44 Hz) and 66.5 ppm (d, $J_{^{13}C-^{13}C}$ = 44 Hz). The coupled spectrum showed doublets of triplets at the same chemical shift values ($J_{^{13}C-H}$ = 165 Hz). These resonances are ascribed to the nonequivalent ethylene carbons in the ethyl ethylene complex **4**. (However, signals of the higher ethylene alkyl homologues **6** etc. overlap those of **4** and later in the reaction the bands observed are a composite of **4**, **6**, etc.; see below.[16]) Support for this assignment comes from the value of the $J_{^{13}C-^{13}C}$ coupling constant (44 Hz), which is consistent with an η^2-bound ethylene,[17] and the close correspondence of these shifts with those of the previously characterized rhodium analogues.[18] At −55 °C the doublets broaden due to rotation of the ethylene ligand and exchange of the two sites.[19] Site exchange was verified at −70 °C by irradiation of the doublet at 66.5 ppm, which resulted in saturation of the signal at 56.5 ppm.[20]

Having detected **4**, **6**, etc., we carried out kinetic analyses of the polymerization reaction in normal heavy-walled 5-mm NMR tubes employing 1.0–2.0 M 99% enriched $^{13}C_2H_4$ and 0.1–0.25 M $3^+BF_4^-$. Samples were prepared at −80 °C and monitored by ^{13}C NMR between −70 and −50 °C. At −70 ±2 °C the ethyl ethylene complex **4** builds to a low (ca. 3% of **3**) steady-state concentration after ca. 120 min. Beyond this time, a pseudo-first-order decay of **3** can be measured[21] where $-d[3]/dt = k_{obsd}[^{13}C_2H_4][3]$, $k_{obsd} = (3.7 \pm 0.2) \times 10^{-5}$ L mol^{-1} s^{-1}. Application of steady-state kinetics yields $-d[3]/dt = (k_1/(k_{-1} + k_2))k_2[^{13}C_2H_4][3]$ where $k_1/(k_{-1} + k_2)$ is given by $[4]/([^{13}C_2H_4][3])$.[22] The rate constant, k_2, can thus be calculated as $(1.8 \pm 0.3) \times 10^{-3}$ s^{-1} from $k_2 = k_{obsd}/(k_1/(k_{-1} + k_2))$, which corresponds to a free energy of activation for β-migratory insertion of 14.3 ± 0.2 kcal/mol.

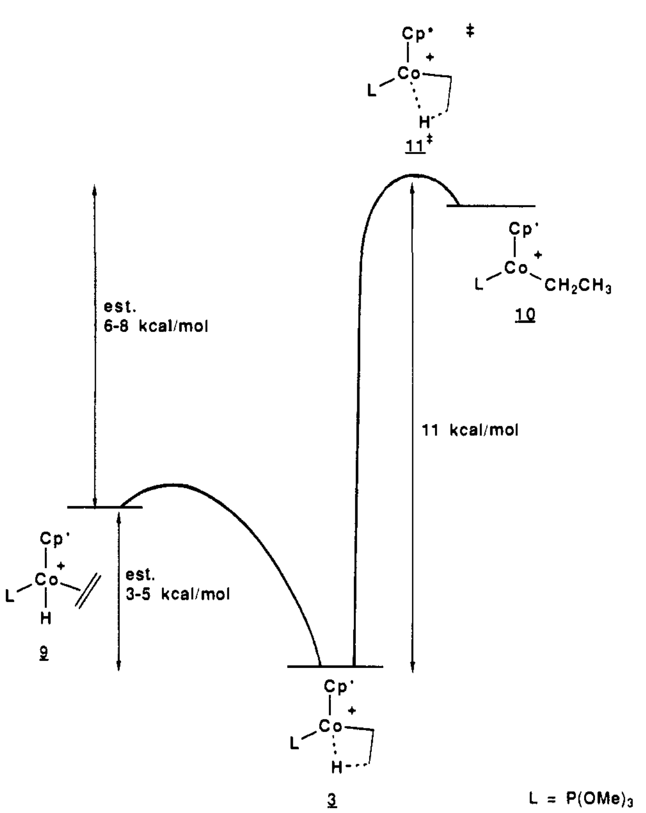
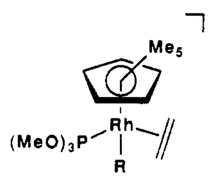


Figure 1.

It is instructive to compare the free energies of activation for the β-migratory insertions of alkyl and hydride rhodium analogues[18] **8a** and **8b** to the cobalt system **4** and its hydride analogue **3**. These comparisons are shown in Table I. An explanation of the $\Delta G^\ddagger_{H\text{-mig}}$ value shown in Table I for the cobalt hydride system is necessary. The stable form of the cobalt hydride is agostic, and the free energy diagram that applies to this system is shown in Figure 1. The $\Delta G^\ddagger$ for "migratory insertion" of agostic **3** is 11.1 kcal/mol;[14] however, to properly compare the Co system with the Rh system, the energy difference between the *terminal* hydride **9** and the transition state for forming **10** (i.e., **11**‡) should be compared. Although the exact energy difference between **3** and **9** is not known, a reasonable estimate is 3–5 kcal/mol.[23] Thus the free energy difference between **9** and **11**‡ is ca. 6–8 kcal/mol, as is entered in Table I.



8 **a** R = Et

b R = H

As is evident from Table I, the barriers to hydride and alkyl migrations for the second row Rh systems are substantially greater

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(15) Roe, C. *J. Magn. Reson.* **1985**, *63*, 388.

(16) The alkyl ethylene complexes observed following the first insertion (**4** → **5**) could be linear $C_5Me_5(L)(C_2H_4)Co{-}CH_2CH_2R^+$ (as shown for **6**) or branched $C_5Me_5(L)(C_2H_4)Co{-}CH(CH_3)R^+$ isomers. If branched, these intermediates could not be on the reaction pathway since linear polyethylene is formed. Low concentrations of these ethylene complexes preclude distinguishing branched from linear structures by NMR. We favor the *n*-alkyl formulation for the following reasons: (a) ^{13}C shifts of the ethylene carbons are identical for **4** ($Co{-}CH_2CH_3$, no branching possible) and the subsequent ethylene alkyl complexes **6** etc. If the α-carbon in **6** were branched, a perturbation of at least one of the ^{13}C resonances of the η^2-ethylene ligand would have been expected. (b) The metal center is sterically crowded, and the stability of the *n*-alkyl complexes is expected to be considerably greater than their branched isomers. (c) The steady-state concentration of **6** can be measured and k'_2 can be determined assuming **6** to be the *n*-butyl-substituted isomer. As expected for CH_2CH_3 vs $CH_2CH_2CH_2CH_3$, the values of k_2 and k'_2 are similar.

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(19) The rate of ethylene rotation has been calculated at −55 °C by line-shape analysis as $k_{rot} = 90$ s^{-1}, $\Delta G^\ddagger = 10.5 \pm 0.5$ kcal/mol.

(20) Spin saturation experiments indicate no exchange between free and coordinated ethylene.

(21) The first insertion is slower than the subsequent insertions by a factor of ca. 4, and thus ethylene consumption accelerates as **3** yields **5**, **7**, etc. Since we can use only 5–20-fold excesses of $^{13}C_2H_4$, the consumption of **3** can be followed for only ca. 1.5 half-lives. Best kinetic plots are obtained by making point-by-point corrections for the decrease in $^{13}C_2H_4$ concentration. (See supplementary material.)

(22) The determination of the concentration of **4** throughout the reaction is complicated by the fact that the ^{13}C signals of the η^2-$^{13}C_2H_4$ in **4** overlap those for the alkyl ethylene complexes formed after 1 + *n* insertions (**6** etc.). Knowing the ratio of [**3**]/[**5** + **7** + ...] and assuming that $k'/(k'_{-1} + k'_2)$ is the same for all 1 + *n* species, the value of both $k/(k_{-1} + k_2)$ and $k'/(k'_{-1} + k'_2)$ can be determined from a plot of [**4** + **6** + ...] vs [**5** + **7** + ...]. (See supplementary material.)

(23) Lincoln, D. M.; Brookhart, M.; Bennett, M.; Pelling, S. *J. Am. Chem. Soc.* **1990**, *112*, 2691.

than the first row cobalt analogues. The difference in free energies of activation for ethyl migration in the Co complex **4** relative to the Rh analogue **8a** of 8 kcal/mol corresponds to a rate difference of 10^5–10^6 at 25 °C. The difference in $\Delta G^*_{\text{R-mig}}$ and $\Delta G^*_{\text{H-mig}}$, $\Delta\Delta G^*$, for the Rh systems is 10.3 kcal/mol, while this number is less for the cobalt systems, ca. 8–6 kcal/mol. This is consistent with the expectation that as the barriers to H and R migration decrease, the *difference* between them will decrease. The detailed comparisons that can now be made between the Rh and Co systems provide quantitative support for our earlier suggestion[13a] that barriers for alkyl migrations will be lower for cases in which the hydride analogues exist as bridged (agostic) isomers rather than as terminal hydrides.

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Supplementary Material Available: Description of the low-temperature ^{13}C NMR kinetics experiment, sample spectra, and kinetic plots (5 pages). Ordering information is given on any current masthead page.

Synthesis of Homoleptic Silylphosphido Complexes $\{M[P(SiMe_3)_2][\mu\text{-}P(SiMe_3)_2]\}_2$, Where M = Zn and Cd, and Their Use in Metalloorganic Routes to Cd_3P_2 and $MGeP_2$

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Several recent reports have described solution-phase metalloorganic procedures for the preparation of III-V ($A^{III}B^{V}$) and II-VI ($A^{II}B^{VI}$) semiconductors.[1] Such studies are motivated by at least two goals: (1) to develop alternatives to chemical-vapor deposition with group V hydrides for semiconductor-film production and (2) to provide syntheses of semiconductor clusters having sizes and properties intermediate between those of molecular compounds and nonmolecular solids.

We describe a new strategy for the synthesis of phosphide semiconductors that is analogous to the sol–gel synthesis of oxides. The latter, a well-established metalloorganic technique, proceeds by hydrolysis of homoleptic alkoxide precursors and polycondensation of the resulting M–OH intermediates.[2] Our strategy is based on the alcoholysis of homoleptic silylphosphido precursors, $M[P(SiMe_3)_2]_x$, and polycondensation of the resulting M–PH_2 intermediates. We now report the synthesis of the title silylphosphido precursors and the preparation of Cd_3P_2 by alcoholysis and polycondensation. We also describe the synthesis of the ternary compounds $ZnGeP_2$ and $CdGeP_2$ by a related condensation reaction.

The precursors were prepared according to eq 1 and isolated as air-sensitive, sublimable, crystalline solids.[3] The solid-state structure of $\{Zn[P(SiMe_3)_2][\mu\text{-}P(SiMe_3)_2]\}_2$ (**1**) is shown in Figure 1;[4] $\{Cd[P(SiMe_3)_2][\mu\text{-}P(SiMe_3)_2]\}_2$ (**2**) is isomorphous. Compounds **1** and **2** appear to be the first homoleptic phosphido complexes of zinc[5] and cadmium[6] and the first homoleptic $P(SiMe_3)_2$ complexes in general.[7]

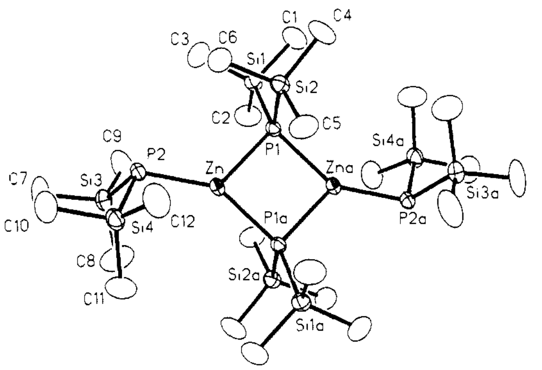

Figure 1. An ORTEP representation of $\{Zn[P(SiMe_3)_2][\mu\text{-}P(SiMe_3)_2]\}_2$ (**1**); hydrogen atoms were omitted for clarity. Selected distances (Å): Zn–P(1), 2.421 (1); Zn–P(2), 2.295 (1); Zn–P(1A), 2.419 (1); Zn–Zn(A), 3.401 (1). Selected angles (deg): P(1)–Zn–P(2), 124.1 (1); P(1)–Zn–P(1A), 90.7 (1); P(2)–Zn–P(1A), 144.9 (1); Zn–P(1)–Zn(A), 89.3 (1); Zn–P(2)–Si(3), 107.0 (1); Zn–P(2)–Si(4), 103.6 (4); Si(3)–P(2)–Si(4), 106.2 (1).

$$M[N(SiMe_3)_2]_2 + 2HP(SiMe_3)_2 \rightarrow \tfrac{1}{2}\{M[P(SiMe_3)_2]_2\}_2 + 2HN(SiMe_3)_2 \quad (1)$$

M = Zn (**1**), 87%
M = Cd (**2**), 90%

Solutions of **2** and methanol gave a light-yellow slurry (<2 min), which gradually darkened through orange and brown to black (ca. 1.5 h).[8] Amorphous Cd_3P_2[9] formed according to eq 2 and was collected as a very air sensitive, black powder. Coproducts Me_3SiOMe and PH_3 were observed by NMR spectroscopy; however, the putative intermediate $Cd(PH_2)_2$ was not detected, and the actual pathway may be more complex than eq 2 indicates. Polycrystalline Cd_3P_2 was obtained by heating the amorphous material to 600 °C.[10] In related work, Theopold and co-workers previously described the synthesis of GaAs by alcoholysis of $(\eta^1\text{-}C_5Me_5)_2Ga[As(SiMe_3)_2]$;[1c] intermediates containing AsH_2 or AsH ligands are conceivable.

$$\tfrac{1}{2}\mathbf{2} + 4MeOH \xrightarrow{-4MeOSiMe_3} \text{“}Cd(PH_2)_2\text{”} \rightarrow \tfrac{1}{3}Cd_3P_2 + \tfrac{4}{3}PH_3 \quad (2)$$

In contrast to eq 2, the reaction of **1** and methanol gave zinc dimethoxide[11] by methanolysis of Zn–P rather than Si–P bonds; see eq 3. Both zinc and cadmium are more electropositive than silicon and should be susceptible to nucleophilic attack by

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[3] Satisfactory elemental analyses were obtained (C, H, Cd, Zn). ^{31}P NMR (ppm, benzene-d_6): **1**, −183.0 (br s), −237.3 (br s); **2**, −180.1 (v br s), −229.5 (v br s). Sublimation point [°C (yield), 10^{-4} Torr]: **1**, 140 (50%); **2**, 140 (75%).

[4] Crystal data for **1**: $C_{24}H_{72}Si_8P_4Zn_2$, $M_r = 840.2$, triclinic, $P\bar{1}$, $a = 9.831$ (2) Å, $b = 10.813$ (2) Å, $c = 12.692$ (3) Å, $\alpha = 80.97$ (3)°, $\beta = 67.62$ (3)°, $\gamma = 80.20$ (3)°, $V = 1223.1$ (4) Å^3, $T = 295$ K, $Z = 1$, $D_{\text{calcd}} = 1.141$ g cm^{-3}, λ(Cu Kα) = 1.541 78 Å. Of the 3353 unique intensities measured, 3065 with $F_o > 6.0\sigma(F_o)$ yielded $R(F) = 0.0741$ and $R_w(F) = 0.1102$.

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[9] No diffraction intensities were observed by X-ray powder diffraction (XRD). Anal. Calcd for Cd_3P_2: C, 0; H, 0; Cd, 84.47; Si, 0. Found: C, 0.69; H, 0.38; Cd, 81.76; Si, <0.1.

[10] (a) The XRD pattern matched the simulated pattern.[10b] Anal. Found: C, 0.00; H, 0.00; Cd, 83.06. (Cd was determined by EDTA titration; 1–2% *relative* errors are typical of our procedure.) (b) Wyckoff, R. W. G. *Crystal Structures*, 2nd ed.; Wiley-Interscience: New York, 1964; Vol. 2, pp 33–36.

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