

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  $\Delta G^*_{R-mig}$  and  $\Delta G^*_{H-mig}$ ,  $\Delta\Delta G^*$ , 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<sup>13a</sup> 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.

**Acknowledgment** is made to the National Science Foundation (Grant No. CHE-8705534) for support of this research.

**Supplementary Material Available:** Description of the low-temperature <sup>13</sup>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 $\{M[P(SiMe_3)_2][\mu-P(SiMe_3)_2]\}_2$ , Where M = Zn and Cd, and Their Use in Metalloorganic Routes to $Cd_3P_2$ and $MGeP_2$

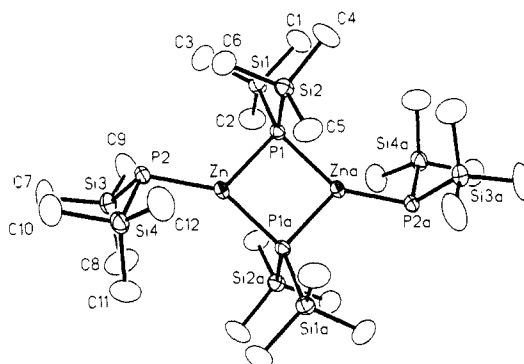
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Several recent reports have described solution-phase metalloorganic procedures for the preparation of III–V ( $A^{III}B^V$ ) and II–VI ( $A^{II}B^VI$ ) semiconductors.<sup>1</sup> Such studies are motivated by at least two goals: (1) to develop alternatives 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.

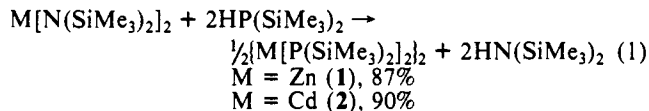
We describe a new strategy for the synthesis of phosphide semiconductors that is analogous to the sol-gel synthesis of oxides. The latter, a well-established metalloorganic technique, proceeds by hydrolysis of homoleptic alkoxide precursors and polycondensation of the resulting M–OH intermediates.<sup>2</sup> Our strategy is based on the alcoholysis of homoleptic silylphosphido precursors,  $M[P(SiMe_3)_2]_x$ , and polycondensation of the resulting M–PH<sub>2</sub> 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.<sup>3</sup> The solid-state

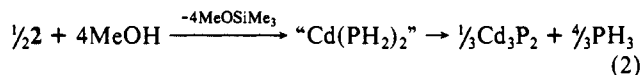


**Figure 1.** An ORTEP representation of  $\{Zn[P(SiMe_3)_2][\mu-P(SiMe_3)_2]\}_2$  (**1**); hydrogen atoms were omitted for clarity. Selected distances (Å): Zn–P(1), 2.421 (1); Zn–P(2), 2.295 (1); Zn–P(1A), 2.419 (1); Zn–Zn(A), 3.401 (1). Selected angles (deg): P(1)–Zn–P(2), 124.1 (1); P(1)–Zn–P(1A),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

structure of  $\{Zn[P(SiMe_3)_2][\mu-P(SiMe_3)_2]\}_2$  (**1**) is shown in Figure 1;<sup>4</sup>  $\{Cd[P(SiMe_3)_2][\mu-P(SiMe_3)_2]\}_2$  (**2**) is isomorphous. Compounds **1** and **2** appear to be the first homoleptic phosphido complexes of zinc<sup>5</sup> and cadmium<sup>6</sup> and the first homoleptic P–(SiMe<sub>3</sub>)<sub>2</sub> complexes in general.<sup>7</sup>



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).<sup>8</sup> Amorphous  $Cd_3P_2$ <sup>9</sup> 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.<sup>10</sup> In related work, Theopold and co-workers previously described the synthesis of GaAs by alcoholysis of  $(\eta^1-C_5Me_5)_2Ga[As(SiMe_3)_2]$ ; intermediates containing  $AsH_2$  or  $AsH$  ligands are conceivable.



In contrast to eq 2, the reaction of **1** and methanol gave zinc dimethoxide<sup>11</sup> 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

(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<sup>3</sup>,  $T = 295$  K,  $Z = 1$ ,  $D_{calc} = 1.141$  g cm<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.54178$  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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(10) (a) The XRD pattern matched the simulated pattern.<sup>10b</sup> 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.

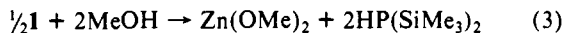
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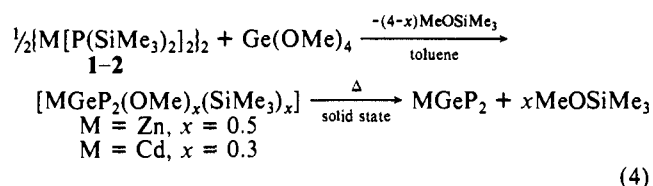
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(3) Satisfactory elemental analyses were obtained (C, H, Cd, Zn). <sup>31</sup>P NMR (ppm, benzene-*d*<sub>6</sub>): **1**, –183.0 (br s), –237.3 (br s); **2**, –180.1 (v br s), –229.5 (v br s). Sublimation point [°C (yield), 10<sup>-4</sup> Torr]: **1**, 140 (50%); **2**, 140 (75%).

methanol. However, the relative softness of cadmium(II) apparently disfavors attack of the hard, methanol nucleophile at cadmium. Equations 2 and 3 together suggest that the alcoholysis-and-polycondensation strategy may generally fail with precursors having hard, electropositive cations.



Precursors **1** and **2** gave the ternary phosphides  $\text{ZnGeP}_2$  and  $\text{CdGeP}_2$  according to eq 4. Intermediates were precipitated from refluxing toluene solutions of **1** or **2** and  $\text{Ge}(\text{OMe})_4$  that contained  $\text{SiMe}_3$  and  $\text{OMe}$  groups;<sup>12</sup> these were substantially removed by heating the dry solids to 300–350 °C in vacuo. Conversion to polycrystalline  $\text{ZnGeP}_2$ <sup>13</sup> and  $\text{CdGeP}_2$ <sup>13</sup> was achieved at temperatures of 800 and 600 °C, respectively, which are 200 °C below the melting points of the compounds<sup>14</sup> and are mild conditions.<sup>15</sup> However, the  $\text{ZnGeP}_2$  and  $\text{CdGeP}_2$  contained residual-carbon impurities of ca. 3% and 1%, respectively.<sup>13</sup> Efforts to decrease carbon levels by optimizing precursors and processing conditions are in progress.



The  $\text{A}^{II}\text{B}^{\text{IV}}\text{V}_2$  and  $\text{A}^{\text{III}}\text{B}^{\text{IV}}\text{C}^{\text{V}}\text{V}_2$  families have potential applications in photovoltaics ( $\text{Zn}_3\text{P}_2$ ),<sup>16</sup> IR-transmitting ceramics ( $\text{ZnGeP}_2$ ),<sup>17</sup> nonlinear optics ( $\text{ZnGeP}_2$ ),<sup>18</sup> and variable-band-gap devices ( $\text{ZnSnP}_2$ ).<sup>19</sup> Photophysical studies describing the novel properties of colloidal  $\text{Cd}_3\text{P}_2$  have recently appeared.<sup>20</sup> By analogy to the sol-gel process for oxides, rational metallorganic syntheses may become useful for preparing phosphide particles, films, or monoliths.

**Acknowledgment.** Support was provided by Washington University and the donors of the Petroleum Research Fund, administered by the American Chemical Society. The Washington University X-ray Crystallography Facility was funded by the NSF Chemical Instrumentation Program (Grant CHE-8811456). The Washington University High-Resolution NMR Service Facility was funded in part by NIH Biomedical Research-Support Shared-Instrument Grant 1 S10 RR02004 and a gift from the

Monsanto Co. We are also grateful to Dr. Charles Campana, Siemens Analytical X-Ray Instruments, Inc., for assistance with crystallography and Drs. D. Kremser and T. Huston for technical assistance.

**Supplementary Material Available:** Listings of the details of the data collection, final positional and equivalent isotropic thermal parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters for **1** and a description of experimental details (10 pages); a listing of observed and calculated structure factors for **1** (12 pages). Ordering information is given on any current masthead page.

## Stabilization of Mononuclear Five-Coordinate Iron(IV)

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High oxidation state middle transition metal compounds are of considerable importance, especially for the first-row metals. These rare species provide a major source of metallooxidants. In the case of iron, highly oxidized complexes are significant as reactive intermediates in many biological and biomimetic redox processes.<sup>2</sup> Despite this significance, high valent iron coordination chemistry is limited. Few stable, well-defined compounds of iron(IV) exist,<sup>3</sup> and the V and VI oxidation states are established only for the tetraoxo polyanions.<sup>3</sup> The coordination chemistry of high-valent middle and later first row transition metals can be expanded by the use of oxidation-resistant, strongly donating ligand complements.<sup>4</sup> The donor capacity and resistance to oxidative destruction of tetradentate tetraanionic ligands has been refined<sup>4</sup> to give the innocent macrocyclic tetraamide,  $\text{H}_4[\mathbf{1}]$  (Scheme I). The resistance of the macrocycle to oxidative degradation and the strong donor capacity of the amido-*N* donors are central features of this system. The ability of amido-*N* ligands to stabilize higher oxidation states was first demonstrated by Margerum and co-workers in extensive studies of copper and nickel chemistry,<sup>5</sup> studies that are a foundation of the current work. Here we report the initial results of a study of the iron chemistry of  $\text{H}_4[\mathbf{1}]$ ,

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