tegration of the gated-{^{1}H}-decoupled ^{31}P resonances for the various species in equilibrium in CH_2Cl_2 gave equilibrium constants of 2.8 for **3a** in equilibrium with **4** and 3.9 for **3b**. Thus, the pK_a-{Ru(η^2-H_2)} value for **3a** is estimated to be 4.3 on the basis of the pK_a value of 3.85 (aqueous scale)[16] for [HP(p-tol)$_3$]$^+$ whereas the pK_a{Ru(H)$_2$} value for **3b** is estimated to be 4.4.[17]

A 2-equiv amount of **3** reacts with 1 equiv of **1** in THF to give 2 equiv of **4** and 1 equiv of [W(NNH$_2$)(F)(dppe)$_2$]BF$_4$ (**2**)[6] according to Scheme I. The reaction occurs in less than 10 min and is quantitative as indicated by ^{31}P NMR spectroscopy. Thus, when **1** (45.5 ppm) is added to the solution of **3** in THF, resonances at 81.1 (**3a**) and 70.0 (**3b**) and 93.0 ppm (**4**, small) are replaced by just the resonance at 93.0 ppm (**4**) together with the appearance of a new resonance at 35.3 ppm (**2**, doublet with ^{183}W satellites, ^2J(P,F) = 41 Hz, ^1J(P,W) = 288 Hz).

No reaction occurs between **1** and 2 equiv of *trans*-[Ru(H)(η^2-H_2)(PEt$_2$CH$_2$CH$_2$PEt$_2$)$_2$]BF$_4$ (**6**). The pK_a of the latter complex is estimated to be near 16, since its conjugate base, Ru(H)$_2$(PEt$_2$CH$_2$CH$_2$PEt$_2$)$_2$, is protonated by neat EtOH, which has a pK_a of 15.8, to give **6** but is not protonated by ^{i}PrOH (pK_a ~16).[18] The pK_a of the related complex [Fe(H)(η^2-H_2)(PMe$_2$CH$_2$CH$_2$PMe$_2$)$_2$]$^+$ has been estimated to be 15.8.[19]

Thus, the heterolytic cleavage of dihydrogen can lead to the protonation of coordinated dinitrogen when the dihydrogen/dihydride complex is sufficiently acidic. The dihydrogen form is expected to transfer protons more quickly than the dihydride form.[20] Methods to prepare complex **3** directly from H_2 gas are being investigated. We have recently found that a related complex, [Ru(H)(H$_2$)(dtfpe)$_2$]BF$_4$,[5] which can be prepared from H_2(g), also converts **1** into **2**, although in lower yield than the reaction involving **3**.

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Molecular Precursors for Indium Phosphide and Synthesis of Small III-V Semiconductor Clusters in Solution

The preparation and physical characterization of semiconductor clusters in the nanometer-size regime is currently attracting considerable attention.[1] While most studies in this area focus on II-VI semiconductors[2] (e.g. CdS, CdSe), the technological importance of III-V semiconductors (e.g. GaAs, InP)[3] makes an investigation of "quantum size effects" in these materials desirable.[4] We have previously reported the chemical conversion of the organometallic arsinogallane Cp*$_2$Ga-As(SiMe$_3$)$_2$ into small gallium arsenide clusters.[5] Herein we describe some results of related work on indium phosphide colloids.

Precursor molecules **1-4** containing covalently bound indium and phosphorus in a 1:1 ratio were synthesized by combining alkylindium chlorides R(R′)InCl with either P(SiMe$_3$)$_3$ or LiP(SiMe$_3$)$_2$ (see Scheme I).[6,7] Virtual coupling of the trimethylsilyl protons to two phosphorus nuclei in the ^{1}H NMR spectrum revealed the dimeric nature of the compounds in solution. The solid-state structure of the representative [Cp*(Cl)In(μ-P(SiMe$_3$)$_2$)]$_2$ (**I**)[8] was determined by X-ray diffraction (see Figure 1).[9] The molecule is a head-to-tail dimer and exhibits crystallographic inversion symmetry. Its In$_2$P$_2$ core is a nearly perfect square with an average In-P distance of 2.62 Å, slightly longer than the sum of the covalent radii (2.50 Å). The bulky Cp* ligands are situated trans to each other and are bonded to indium in a η^1-fashion. The five-membered ring shows the expected bond length alternation and angles of a localized cyclopentadiene. However, their rotation is rapid on the NMR time scale in solution and leads to observation of one and two Cp* resonances in the ^{1}H and ^{13}C spectra, respectively.

Addition of 3.0-5.0 equiv of methanol to solutions of precursors **1-4** in a closed vessel ultimately resulted in the precipitation of

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[9] Yellow rectangular prisms from pentane; monoclinic $\bar{P}2_1/n$; a = 9.722 (3) Å, b = 18.073 (5) Å, c = 12.983 (11) Å, β = 97.9 (3)°, and Z = 4; R = 0.044 and R_w = 0.047.

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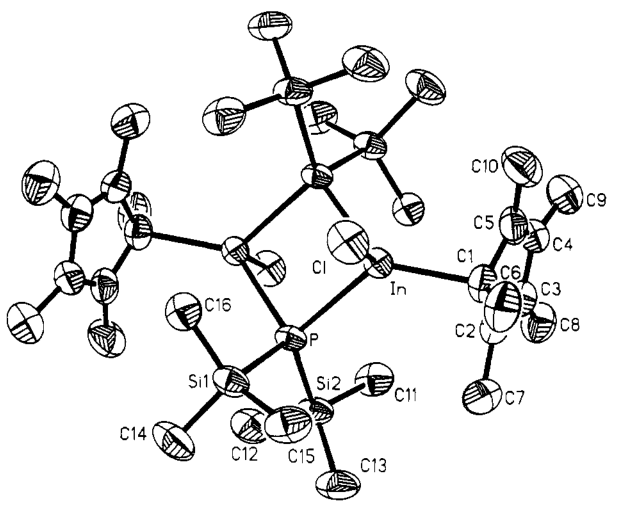
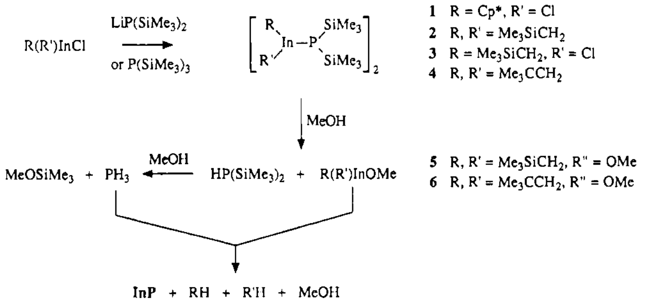


Figure 1. Molecular structure of $[Cp^*(Cl)In(\mu\text{-}P(SiMe_3)_2]_2$ (**1**). Selected bond distances (Å): In–P, 2.648 (2); In–P_a, 2.594 (1); In–Cl, 2.242 (5); In–Cl, 2.441 (2); P–Si1, 2.269 (2); P–Si2, 2.281 (2). Selected interatomic angles (deg): In–P–In_a, 92.2 (1); P–In–P_a, 87.8 (1); Cl–In–P, 104.4 (1); Cl–In–Pa, 99.9 (1); Cl–In–Cl, 101.0 (2); Si1–P–Si2, 109.9 (1).

Scheme I



a fine orange powder in all cases, although the rates of the transformations differed dramatically (**1** reacts within seconds at −70 °C, while **2** requires heating to ca. 60 °C over several hours to complete the reaction). The organic products of these reactions were hydrocarbons (i.e. Cp*H, NpH, $SiMe_4$) and the ether $MeOSiMe_3$ in near-quantitative yield (by NMR and GC). Elemental analyses[10] of the solids prepared from dialkyl precursors showed them to be pure indium phosphide (InP), while samples prepared by alcoholysis of chloride-containing molecules retained varying levels of chloride. As the reaction of $[(Me_3SiCH_2)_2In(\mu\text{-}P(SiMe_3)_2]_2$ (**2**)[11] yielded analytically pure InP and was slow enough to be monitored spectroscopically, we selected it for further investigation.

The ^{1}H NMR spectrum of a C_6D_6 solution of **2** and 4.0 equiv of methanol exhibited the resonances of $[(Me_3SiCH_2)_2InOMe]_n$ (**5**),[12] PH_3 (^{31}P NMR: δ −243 ppm, quartet, J_{PH} = 182 Hz), and $MeOSiMe_3$. However, when *tert*-butyl alcohol was added to **2**, $[(Me_3SiCH_2)_2InO^tBu]_n$ and $HP(SiMe_3)_2$ were produced, indicating heterolytic cleavage of the In–P bond as the first—and seemingly counterproductive—step of the reaction. Heating of the MeOH-containing solution to 60 °C for 10 h produced $SiMe_4$ (by ^{1}H NMR) and eventually InP. On the basis of these observations, we suggest the reaction mechanism outlined in Scheme I. We note that the alcoholysis of $H_nP(SiMe_3)_{3-n}$ is apparently catalyzed by chloride, providing some rationale for the varying reaction rates noted above.[13]

The progress of the reaction was accompanied by a gradual change in the color of the heated solution from colorless through various shades of yellow and orange to a dark red-brown. However, during this progression the solution appeared perfectly homogeneous, and precipitation of solid InP took place only after several hours. UV–vis spectra of such a solution after various intervals of heating (see supplementary material) displayed a featureless absorption and a gradual red-shift (from ca. 450 to 650 nm) of the absorption onset. This behavior is strikingly similar to that observed in our related gallium arsenide (GaAs) work,[5] and here too we attribute it to the growth of semiconductor clusters beginning at the molecular level and never quite reaching the size required for establishing the band gap of the bulk material (1.3 eV; 976 nm). On the basis of an estimated "band gap" of 615 nm (see UV–vis data, supplementary material), a simple calculation[1a,3a] yields an estimated diameter of the clusters responsible for this absorption of 5.4 nm.

TEM pictures of a sample prepared by evaporating a seemingly homogeneous solution of clusters on a formvar-covered copper grid (supplementary material) showed some crystalline particles (sizes up to ca. 10 nm) on a featureless background. However, the spacing between their visible lattice planes (2.93 Å) and electron diffraction patterns of these crystallites were most consistent with In_2O_3.[14a] STEM examination of a sample that had been annealed at 180 °C showed much larger particles and electron diffraction rings and spots attributable to InP (see supplementary material).[14b] Energy dispersive X-ray analysis indicated the presence of indium, phosphorus, and silicon in the former sample, while the annealed material no longer contained silicon. Neither sample exhibited a discernible X-ray diffraction pattern. We conclude that the indium phosphide particles formed in the alcoholysis reaction are amorphous and begin to develop crystalline order only upon heating. Traces of water in the reaction medium were likely responsible for the contamination of the product with indium oxide, a material that apparently crystallizes easily.

This contribution describes a convenient synthesis of small clusters of III–V semiconductors. We are now developing protocols to arrest the growth and improve solubility and stability of these particles by surface functionalization.[15] In this vein, we have found that addition of primary phosphines (RPH_2) to the reaction mixtures suppressed the precipitation and yielded highly colored and stable solutions of indium phosphide clusters. The characterization of these soluble III–V semiconductor clusters will be the subject of future reports.

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(10) Samples were heated under vacuum followed by digestion with HNO_3 according to: Buresch, O.; von Schnering, H. G. *Fresenius' Z. Anal. Chem.* **1984**, *319*, 418. They underwent analysis for In, P, Si, and Cl by ICP-AA. **2**: In, 78.04; P, 20.09; Si, 0.07. **3**: In, 76.93; P, 17.31; Si, 0.20; Cl, 4.34. Calcd for InP: In, 78.75; P, 21.25. Control with authentic InP: In, 78.39; P, 20.33; Si, 0.0; Cl, 0.0.

(11) Analytical data for **2** are as follows. ^{1}H NMR (C_6D_6): δ 0.45 (t, 18 H, J_{PH} = 2.5 Hz), 0.31 (s, 18 H), 0.19 (s, 4 H). ^{13}C NMR (C_6D_6): δ 5.3 (t, J_{PC} = 4 Hz), 4.1 (s), 3.7 (s). ^{31}P NMR (C_6D_6): δ −229.2 (s). IR (KBr): 2951 (s), 2895 (m), 1438 (w), 1400 (w), 1354 (w), 1242 (s), 952 (s), 852 (s), 835 (s), 750 (s), 723 (s), 684 (m), 626 (m), 551 (w), 478 (w), 455 cm^{-1} (w). Mp: 244–248 °C dec. Anal. Calcd for $C_{14}H_{40}InPSi_4$: C, 36.04; H, 8.64. Found: C, 36.09; H, 8.13.

(12) Analytical data for **5** are as follows. ^{1}H NMR (C_6D_6): δ 3.39 (s, 3 H), 0.19 (s, 18 H), −0.17 (s, 4 H). ^{13}C NMR (C_6D_6): δ 52.34 (s), 2.55 (s), 2.07 (s). IR (KBr): 2949 (s), 2887 (m), 2812 (w), 1444 (w), 1400 (w), 1294 (w), 1246 (s), 1039 (m), 1022 (m), 962 (m), 852 (s), 827 (s), 752 (s), 717 (m), 684 (m), 609 (w), 580 (w), 511 (w), 478 cm^{-1} (m). Mp: 32–37 °C. Anal. Calcd for $C_9H_{25}InOSi_2$: C, 33.75; H, 7.87. Found: C, 33.35; H, 7.67.

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(14) *Powder Diffraction File* (Joint Committee on Powder Diffraction Standards, International Centre for Diffraction Data, Swarthmore, PA, 1974: (a) file No. 6-416; (b) file No. 32-453. The (111), (200), (220), and (311) lines of InP were identified.

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Supplementary Material Available: Tables of X-ray structure determination data for $[Cp^*(Cl)In(\mu\text{-}P(SiMe_3)_2]_2$ and figures showing UV–vis spectra of growing clusters in solution, a transmission electron micrograph, and electron diffraction patterns of In_2O_3 particles and of annealed InP (10 pages). Ordering information is given on any current masthead page.

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Articles

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Concerning the Dependence of the Volume of Activation for a Limiting D Substitution Mechanism on the Size of the Leaving Group. The Aquation of Pentacyano(amine)ferrate(II) Complexes

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A series of limiting dissociative substitution reactions of complexes of the type $Fe(CN)_5(NH_2R)^{3-}$ (R = H, CH_3, C_2H_5, *i*-C_3H_7, and CH_2Ph) were studied as a function of pressure in order to investigate the dependence of the associated volume of activation on the size of the leaving group (NH_2R). The volumes of activation have an average value of +18 $cm^3\ mol^{-1}$ and do not exhibit a meaningful correlation with the size of NH_2R. The results are compared to data available in the literature for other limiting dissociative substitution reactions of octahedral complexes, and a similar conclusion is reached. Possible reasons for this observation are presented.

Introduction

Our group has a longstanding interest in the application of high-pressure techniques in the elucidation of inorganic and organometallic reaction mechanisms.[2-4] It has been one of our goals in the past to find quantitative correlations between the volume of activation ($\Delta V^{\ddagger}$) and the partial molar volume (V) of reactant and product species in terms of a reaction volume profile analysis. With the large quantity of $\Delta V^{\ddagger}$ data presently available for substitution reactions of octahedral and square-planar complexes in particular, such volume correlations have been useful in the interpretation of the absolute size of $\Delta V^{\ddagger}$.[5-12] For instance, in the case of a limiting associative mechanism for square-planar substitution, $\Delta V^{\ddagger}$ becomes more negative with increasing size of the entering nucleophile due to the more effective overlap of the molecular spheres, as defined by the van der Waals radii.[11,12] In the case of interchange mechanisms (I_a and I_d) for ligand-substitution processes on octahedral metal centers, such correlations are not significant in terms of the size of the entering or leaving groups since only partial bond formation and bond breakage occurs in the transition state. An unanswered question concerns the possibility of such a correlation in the case of limiting dissociative substitution mechanisms.

We therefore studied a series of aquation reactions of octahedral complexes that are known to follow a limiting D mechanism, and for which it was possible to vary the size of the leaving group. For this purpose we selected a series of pentacyano(amine)iron(II) complexes and studied the pressure dependence of their aquation reactions under conditions where iron–amine bond breakage is the rate-determining step.[13-15] The selected amines are NH_3 and NH_2R, where R = methyl, ethyl, isopropyl, and benzyl. The results are discussed in reference to other series of data reported in the literature.

Experimental Section

$Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was prepared from sodium nitroprusside (Merck, reagent grade) according to standard procedures[13] and characterized by UV–vis spectroscopy and elemental analysis.[16] Pyridine (Janssen), methylamine (Fluka, 25% solution), ethylamine (Raedel de Haen, 50% solution), isopropylamine (Raedel de Haen), and benzylamine (Fluka) were used as supplied. All other chemicals were of analytical reagent grade.

Solutions of $Fe(CN)_5(NH_2R)^{3-}$ (10^{-4} M) were prepared by dissolving $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ in solutions containing 0.02 M NH_2R, 0.01 M HCl, and NaCl (to adjust the ionic strength) and thermostating for 20–25 min. to allow for the complete displacement of NH_3 by NH_2R.[13,14]

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