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The reactions of pentamethylcyclopentadienylindium(I) $In(C_5Me_5)$ with white phosphorus (P_4) at 175°C and of neopentylgallium(I) $[Ga(CH_2CMe_3)]_n$ with P_4 at 350-400°C and with NH_3 at 460-480°C in sealed tubes provide routes to indium phosphide, gallium phosphide and hexagonal gallium nitride, respectively. The formation of these group 13-15 materials as black solids was confirmed by their X-ray photoelectron spectra, X-ray powder diffraction patterns and physical properties. The other products were $(C_5Me_5)_2$ in the case of the reaction of $In(C_5Me_5)$ with P_4, neopentane and H_2 in the case of the $[Ga(CH_2CMe_3)]_n$ - NH_3 reaction, and unidentified hydrocarbons and H_2 in the case of $[Ga(CH_2CMe_3)]_n$ - P_4. These products were isolated and identified by ^1H NMR spectroscopy or their physical properties, as appropriate. Carbon contamination in all materials was indicated by their XPS spectra and confirmed by combustion analysis.

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ABSTRACT

The reactions of pentamethylcyclopentadienylindium(I) In(C_5Me_5) with white phosphorus (P_4) at 175 °C and of neopentylgallium(I) $[Ga(CH_2CMe_3)]_n$ with P_4 at 350 - 400 °C and with NH_3 at 460 -480 °C in sealed tubes provide routes to indium phosphide, gallium phosphide and hexagonal gallium nitride, respectively. The formation of these group 13-15 materials as black solids was confirmed by their X-ray photoelectron spectra, X-ray powder diffraction patterns and physical properties. The other products were $(C_5Me_5)_2$ in the case of the reaction of In(C_5Me_5) with P_4, neopentane and H_2 in the case of the $[Ga(CH_2CMe_3)]_n$ - NH_3 reaction, and unidentified hydrocarbons and H_2 in the case of $[Ga(CH_2CMe_3)]_n$ - P_4. These products were isolated and identified by ^{1}H NMR spectroscopy or their physical properties, as appropriate. Carbon contamination in all materials was indicated by their XPS spectra and confirmed by combustion analysis.

Two pathways have been proposed for the formation of group 13-15 electronic materials such as GaAs and InP by using the organometallic chemical vapor deposition (OMCVD) process with the simplest precursors, a group 13 trialkyl compound and a group 15 hydride. One pathway requires a series of elimination reactions[1,2] with formation of species of the types, R_2MEH_2 and RMEH (M = group 13 element, E = group 15 element) whereas the other involves the formation and reactions of low oxidation state species[3,4] such as MR, E_n and EH. Even though many workers favor the low oxidation state pathway, very few synthetic studies have used low oxidation state compounds to prepare group 13-15 materials. However, cyclopentadienylindium(I) compounds have been reacted with PH_3 at 675 °C to form InP by using a OMCVD process.[5] In this paper we report the results of our studies of reactions of low oxidation state organo-indium and -gallium compounds to prepare InP, and GaP and GaN, respectively. This study was prompted by our previous observations in indium(I) chemistry which had shown that pentamethylcyclopentadienylindium(I)[6,7] reacted readily with simple Lewis bases[6] such as THF and pyridine at room temperature to form indium metal and decamethylfulvene. Therefore, we investigated the reactions of $In(C_5Me_5)$ with white phosphorus (P_4), a nominal Lewis base with a lone pair of electrons on each phosphorus atom, in order to determine if InP could be formed at a temperature which would be significantly lower than that typically used for the OMCVD process. The success of the reaction of $In(C_5Me_5)$ with P_4 prompted additional experiments with the low oxidation state organogallium(I) compound[8] $[Ga(CH_2CMe_3)]_n$ in order to learn more about the usefulness of low oxidation state compounds for the formation of materials. Thus, the reactions of $[Ga(CH_2CMe_3)]_n$ with P_4 and with NH_3 in order to prepare GaP and GaN were investigated.

The reaction of $In(C_5Me_5)$ with P_4 in a simple break-seal tube in the absence of solvent at the relatively low temperature of 175 °C provides a new route to indium phosphide. Subsequent studies[9] have also demonstrated that the identical reagents can be used to prepare thin films of InP under OMCVD conditions at temperatures as low as 125 °C. In the sealed tube experiments, two distinctly different products, a shiny black crystalline solid and a yellow-orange liquid which was nonvolatile at room temperature, were formed. The black product was identified, after it was washed with pentane, ground with a mortar and pestle in the dry box and then washed again with pentane, by its X-ray photoelectron spectrum[10] (XPS) and X-ray powder diffraction pattern[11] as InP. The XPS surface scan of the InP indicated the presence of In, P, C and O. With the possible

$$\mathrm{In(C_5Me_5)} + 1/4\ \mathrm{P_4} \longrightarrow \mathrm{InP_{(s)}} + 1/2\ \mathrm{(C_5Me_5)_2} \tag{1}$$

exception of phosphorus, each element was present in only one environment. The observed binding energies for indium and phosphorus are in good agreement with those previously reported for InP[10]. The presence of carbon in the InP was confirmed by combustion analysis (3.74%). Oxygen contamination might be related to the presence of either P_4O_6 or P_4O_{10}, compounds which would be readily formed by a reaction of P_4 with oxygen (impurity) in the dry box. However, if a phosphorus oxide were present, the XPS line for phosphorus would have to be very small and lost in the noise of the spectrum. The nonvolatile, yellow-orange liquid which was separated by washing the initial reaction product with pentane was identified by ^{1}H NMR spectroscopy as $(C_5Me_5)_2$.[6,12] Even though this product can be envisioned to be formed by coupling of two C_5Me_5 radicals, we have no data to confirm or deny the presence of radicals.

The general usefulness of the reaction of a cyclopentadienylindium(I) compound with P_4 was tested further by investigating the corresponding reactions of $In(C_5H_5)$[13-16], $In(C_5H_4Me)$[16], and $In(C_5H_4CMe_3)$[17] by using the identical conditions as described for the $In(C_5Me_5)$ reaction. A shiny black solid and a nonvolatile liquid were formed in each case. The XPS spectra of each black solid was consistent with InP. However, the black products from these reactions had carbon impurities which were higher than observed for the In(C_5Me_5) - P_4 reaction. The percent carbon in the shiny black solid (combustion analyses) increased in the order In(C_5Me_5) (3.74 %) << In($C_5H_4CMe_3$) (15.95 %) < In(C_5H_4Me) (21.77 %) < In(C_5H_5) (26.18%). The liquid products isolated from the reactions of these cyclopentadienylindium(I) compounds had complicated ^1H NMR spectra. Even though these organic products were not conclusively identified, they can be envisioned to be compounds related to $(C_5Me_5)_2$ which had either polymerized and/or decomposed as would be consistent with the chemistry of a cyclopentadiene derivative. The order for the carbon contamination suggests that it might be related to the ease of decomposition of the organic product and the reaction conditions. A reaction in a sealed tubes eliminates the possibility of removing the organic product as it is formed.

Although all four indium(I) reagents produced approximately the same results, the reaction between In(C_5Me_5) and P_4 provided some significant observations that suggest that it might be the best reagent to use to prepare InP. First, the reaction between In(C_5Me_5) and P_4 appears to occur, at least in part, in the gas phase. Even though the starting materials were placed in the bottom of the break-seal tube and liquified at the reaction temperature of 175 °C, the entire surface of the glass tube became mirrored with the shiny black film of InP. In contrast, the reactions of the other indium(I) derivatives produced shiny black solids where the original reagents had liquified rather than films on the entire glass surfaces of the tubes. Second, the organic product from the In(C_5Me_5) and P_4 reaction was readily removed from the indium phosphide with one pentane wash to leave a very fine powder. The XPS spectrum of the black solid had a very smooth base line from which it was easy to detect the lines for the contaminants as well as the Auger peaks for indium and phosphorus. The X-ray powder pattern confirmed the black shiny solid to be InP.[11] However, the powder pattern also revealed the presence of indium metal.[18] It is noteworthy that the XPS spectrum did not suggest indium in two different environments. Either the XPS spectrometer could not resolve a peak for InP at 444.2 eV and for indium metal at 443.1 eV or the amount of indium metal was too small to detect.

The low oxidation state organogallium(I) compound[8] $[Ga(CH_2CMe_3)]_n$ has been used to prepare hexagonal gallium nitride and gallium phosphide but at higher temperatures than those used for the reactions of the cyclopentadienyindium(I) compounds. The reaction with NH_3 at 460 - 480 °C (heating for 1 d) and the reaction with P_4 at the slightly lower temperature of 350 - 400 ° C (heating for 8 d) can be summarized by the following chemical equations (eq 2 and 3). Both shiny black solids were crystalline and were identified by their X-ray photoelectron spectra[10, 19,20] and X-ray powder diffraction patterns.[21]

$$1/n\ [Ga(CH_2CMe_3)]_n + NH_3 \longrightarrow GaN_{(s)} + H_2 + CMe_4 \quad (2)$$

$$1/n\ [Ga(CH_2CMe_3)]_n + 1/4\ P_4 \longrightarrow GaP_{(s)} + H_2 + \text{hydrocarbons} \quad (3)$$

The binding energies observed from XPS spectra identified Ga, N, C and O for the sample believed to be gallium nitride and Ga, P, C and O for the gallium phosphide. The presence of carbon was confirmed by combustion analyses. The gallium nitridehad a lower carbon impurity (1.24 % C) than did the gallium phosphide (9.97 % C). The amount of oxygen in the samples as detected by XPS was small. In the case of the reaction of $[Ga(CH_2CMe_3)]_n$ with NH_3, the volatile products were isolated by using the vacuum line and identified as only H_2 and neopentane (CMe_4). The percent yields of H_2 and CMe_4, as based on eq 2, were 70.3 and 86.6, respectively. The neopentane was identified by ^1H NMR spectroscopy as the only hydrocarbon product. In the case of the reaction of $[Ga(CH_2CMe_3)]_n$ with P_4, the ^1H NMR spectrum suggested the volatile product to be a mixture of hydrocarbons.

The experimental results from this study support the hypothesis that low oxidation state species might be important to the formation of group 13 - 15 materials. Cyclopentadienylindium(I) compounds react with P_4 at a relatively low temperature. Even though a similar low temperature could not initiate the corresponding reaction of $[Ga(CH_2CMe_3)]_n$, the surprisingly clean and straightforward reaction of this gallium(I) compound with ammonia at a temperature lower than is typical for trialkylgallium(III) - ammonia reactions (600 - 1000 °C)[22] is significant. The differences between the temperatures needed for reactions of the gallium(I) and indium(I) compounds might reflect major differences between these two types of reagents. Cyclopentadienylindium(I) compounds have very weak intermolecular interactions between the simplest formula units in the solid state, are volatile at room temperature[6,7,13-17] and are monomeric in the gas phase.[6,16] In contrast, $[Ga(CH_2CMe_3)]_n$, is nonvolatile at room temperature and is believed to exist as clusters[8] of gallium atoms with gallium-gallium bonding. Cryoscopic molecular weight studies for benzene solutions suggest that the clusters might have from six to twelve gallium atoms. Thus, the higher temperature needed for reactions of gallium(I) than for indium(I) might be related to the existence of these gallium-gallium bonds. The significance of the low oxidation state gallium reactant can be appreciated when the experimental observations for the reaction of P_4 with a gallium(III) reagent $Ga(CH_2CMe_3)_3$ and with the gallium(I) compound $[Ga(CH_2CMe_3)]_n$ under the same conditions are compared. When $Ga(CH_2CMe_3)_3$ was reacted with P_4 at 350 - 400 °C, the black solid product was composed of GaP and gallium metal, had higher carbon contamination (12.11 %) than when the gallium(I) reagent was used, and had broad XRD lines. Silver-colored specks of gallium metal which were observed by microscopic examination melted at 31 - 37 °C. The melting point of pure gallium metal is 29.8 °C.

EXPERIMENTAL

Cyclopentadienylindium(I) compounds, $In(C_5H_5)$[16], $In(C_5H_4Me)$[16], $In(C_5H_4CMe_3)$[17], and $In(C_5Me_5)$[6,7], and neopentylgallium(I)[8] $[Ga(CH_2CMe_3)]_n$ were prepared and purified by the literature methods. These compounds are exceedingly sensitive to oxygen and moisture and must be manipulated in either a standard vacuum line or in a purified argon atmosphere by using the procedures described previously.[6,7] White phosphorus under water was purchased from Strem Chemicals, Inc.. Small chunks of the white phosphorus were cut from the larger piece and placed in a small flask. Water was then removed by vacuum distillation. The smaller pieces used for the reactions were cut from the larger pieces in the dry box. Ammonia was dried over sodium metal before use. All manipulations of the shiny black products, InP, GaP and GaN, were carried out in the drybox. Elemental analyses for carbon were performed by E+R Microanalytical Laboratories, Inc., Corona, NY. The ^{1}H NMR spectra were recorded by using a Varian Gemini 300 FT-NMR spectrometer operating at 300 MHz. Chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ at 0.00 and C_6H_6 at 7.15. Each sample for XPS analysis was first ground into a fine powder in the dry box and then the sample was placed on one side of two-sided clear sticky tape which was fixed to the circular metal mounting stage. The mounting stage was then placed in the XPS manipulator chamber in the dry box in order to transfer the sample to the spectrometer without exposure to air. The XPS analysis was performed by using a Perkin-Elmer Physical Electronics (PHI) Model 5100 ESCA spectrometer with a Mg $K_{\alpha 1,2}$ X-ray source (1253.6 eV) with a 180 ° hemispherical detector. The spectrometer was calibrated to the Ag $_{3d5/2}$ peak at 367.9 eV with full width at half maxium of 900,000 counts per second. The linearity of the binding scale was calibrated by using $Cu_{2p3/2}$ and $Cu_{3p3/2}$ at 932.5 and 75.0 eV, respectively. The operating parameters of the X-ray source were 300 W, 15kV, and 20 mA. The base pressure of the instrument was 2×10^{-9} Torr with an operating pressure of 2×10^{-8} Torr. The spectra were collected with a take-off angle of 45°. The identity of the different elements present at the surface of the sample were qualitatively evaluated by low resolution (89.45 eV) survey spectra. High resolution (35.75 eV) spectra were taken to establish the binding energy. X-ray powder diffraction patterns were obtained by using a Siemans D-500 X-Ray Diffractometer. The powder sample was irradiated with monochromatic Cu K_α radiation at a wavelength of 1.54 Å. Power settings were 30 mA and 40 kV. The powder pattern was generated as 2θ versus intensity. The peak locations were translated into d spacings and then compared to ASTM standards.

Reaction of In(C_5Me_5) with P_4. A break-seal tube was charged with 1.71 g of In(C_5Me_5) (6.45 mmol) and 0.209 g of P_4(1.68 mmol), was evacuated with the tube at -196 °C and then was sealed by fusion. The tube was the placed in an oven at 175 °C. Since P_4 melts at ~41 °C and In(C_5Me_5) melts at ~92 °C, the contents became liquid in a matter of minutes and turned black. After approximately 15 min, the entire internal surface of the tube was coated with a black film. The tube was heated for a total of 3 d in order to ensure complete reaction. The seal was broken, the tube was evacuated and the solid was washed with pentane to separate a yellow-orange pentane soluble liquid from the black solid. The solid was scraped from the tube and weighed (0.766 g, 5.25 mmol InP, 81.4 % yield based on In(C_5Me_5)). The ^{1}H NMR spectrum of the yellow-orange liquid was comparable to the spectrum previously observed for decamethylfulvene but additional lines were also evident. **InP** ESCA (Binding energy, eV; corrected to C_{1s}): 444.7 (In $_{d5/2}$); 452.3 (In $_{d3/2}$); 129.2 (P_{2p}); 285.0 (C_{1s}); 532.6 (O_{2p}) (Lit.[10] $In_{d5/2}$ 444.2; P_{2p} 129.0; C_{1s} 285.0; O_{2p} 531.9). X-ray Powder Pattern (d spacings): 3.36 (InP); 2.70 (In) (Lit. InP 3.39[11]; In 2.72[18]). Anal. Found: C, 3.74.

Reaction of Other Cyclopentadienylindium(I) Derivatives with P_4. All other reactions of cyclopentadienylindium(I) compounds with P_4 were run in a manner similar to that described previously for In(C_5Me_5). Thus, only quantities of reagents and of InP which were isolated after it was transferred from the reaction tube and washed with pentane as well as significant experimental observations are described. **In[C_5H_4(CMe$_3$)]:** 0.407 g (1.73 mmol) In[C_5H_4(CMe$_3$)], 0.0560 g (0.452 mmol) P_4, 0.193 g of the black solid (InP). The reaction appeared to occur in the liquid phase as the product was located at the bottom of the tube where the reagents mixed. ESCA (Binding energy, eV; corrected to C_{1s}): 444.5 (In $_{d5/2}$); 452.2 (In $_{d3/2}$); 129.3 (P_{2p}); 285.0 (C_{1s}); 532.6 (O_{2p}). Anal. Found: C, 15.95. **In[C_5H_4(Me)]:** 0.248 g (1.28 mmol) In[C_5H_4(Me)], 0.0386 g (0.313 mmol) P_4, 0.194 g of the black solid (InP). The reaction appeared to occur as soon as the reagents were in the liquid phase; the product was located at the bottom of the tube where the reagents initially mixed. ESCA (Binding energy, eV; corrected to C_{1s}): 445.1 (In $_{d5/2}$). 452.5 (In $_{d3/2}$); 130.2 (P_{2p}); 285.0 (C_{1s}); 532.9 (O_{2p}). Anal. Found: C, 21.77. **In(C_5H_5):** 0.430 g (2.39 mmol) In(C_5H_5), 0.0740 g (0.610 mmol) P_4, 0.253 g of the black solid (InP). The reaction appeared to occur as soon as the reagents were in the liquid phase; the product was located at the bottom of the tube where the reagents initially mixed. ESCA (Binding energy, eV; corrected to C_{1s}): 445.1 (In $_{d5/2}$); 452.6 (In $_{d3/2}$); 129.9 (P_{2p}); 285.0 (C_{1s}); 532.2 (O_{2p}). Anal. Found: C, 26.18.

Reaction of $[Ga(CH_2CMe_3)]_n$ with NH_3. A break-seal tube was charged with 0.440 g of $Ga(CH_2CMe_3)$ (3.13 mmol) and 3.44 mmol of NH_3 , sealed and heated at 460 - 480 °C for 24 h. As heating occurred, the contents of the tube changed color from dark reddish-brown, to light grey, to yellow-grey, and finally to black. After the tube was cooled to -196 °C, the noncondensable gas was measured with a Toepler pump - gas buret assembly (2.20 mmol H_2, 70.3% based on $Ga(CH_2CMe_3)$ and eq 3). The volatile, condensable materials were removed from the reaction tube by vacuum distillation and identified by ^1H NMR spectroscopy as neopentane, CMe_4 (0.195 g, 2.71 mmol, 86.6 % based on $Ga(CH_2CMe_3)$ and eq 3). The nonvolatile, shiny black solid was isolated and identified as GaN (0.232 g, 2.77 mmol, if entirely GaN, 88.5 % based on $Ga(CH_2CMe_3)$ and eq 3). **GaN:** ESCA (Binding energy, eV; corrected to C_{1s}): 20.3 ($Ga_{3d3/2}$); 1119.5 ($Ga_{2p3/2}$); 398.3 (N_{1s}); 285.0 (C_{1s}); 531.7 (O_{1s}) (Lit.[10, 19, 20] 19.8 ($Ga_{3d3/2}$); 1124.1 ($Ga_{2p3/2}$); 397.0 (N_{1s}); 285.0 (C_{1s}); 531.9 (O_{1s})). X-ray Powder Pattern: high quality, crystalline sample, hexagonal GaN structure; d spacings: 2.76, 2.58, 2.44, 1.89,1.60, 1.46,1.37 (Lit.[21] 2.76, 2.59, 2.43, 1.88, 1.59, 1.46 1.38). Anal. Found: C, 1.24; H, 0.69.

Reaction of $[Ga(CH_2CMe_3)]_n$ with P_4. A break-seal tube was charged with 0.461 g of $Ga(CH_2CMe_3)$ (3.27 mmol) and 0.102 g of white phosphorus P_4 (0.820 mmol) and then heated at 350 - 400 °C for 8 d. As reaction occurred, the tube became coated (appeared like a mirror) while the material at the bottom of the tube changed from the dark reddish-brown color of the gallium(I) reagent to shiny black. The tube was cooled to -196 °C, opened and the noncondensable gas (H_2) (1.41 mmol) was measured with a Toepler pump-gas buret assembly. The remaining materials which were volatile at room temperature were vacuum distilled into a small tube, weighed (0.115 g) and characterized by ^{1}H NMR spectroscopy. The nonvolatile, shiny black solid was scraped from the tube, ground into a fine powder ,washed with 50 mL pentane and weighed in the drybox (0.343g, 3.40 mmol, if entirely GaP, 104 % yield based on $Ga(CH_2CMe_3)$). **GaP:** ESCA (Binding energy, eV; corrected to C_{1s}): 19.6 ($Ga_{3d3/2}$); 1118.8 ($Ga_{2p3/2}$); 129.5 (P_{2p}); 285.0 (C_{1s}); 532.9 (O_{1s}) (Lit.[10, 19, 20] 19.8 ($Ga_{3d3/2}$); 1124.1 ($Ga_{2p3/2}$); 128.8 (P_{2p}); 285.0 (C_{1s}); 531.9 (O_{1s})). X-ray Powder Pattern: high crystalline quality; d spacings: 3.14, 2.72, 1.93, 1.65, 1.26, 1.23 (Lit.[21] 3.15, 2.73, 1.93, 1.25, 1.22). Anal. Found: C, 9.97; H, 0.94.

Reaction of $Ga(CH_2CMe_3)_3$ with P_4. A break-seal tube was charged with 0.887 g of $Ga(CH_2CMe_3)_3$ (3.13 mmol) and 0.0998 g of P_4 (0.805 mmol), sealed and heated at 350 - 400 °C for 24 h. As heating occurred, the the tube became coated with a light brown mirror-like coating while a shiny black material formed in the bottom of the tube. After the tube was cooled to -196 °C, the noncondensable gas was measured with a Toepler pump - gas buret assembly (2.92 mmol H_2). The volatile materials (0.482 g) were removed by vacuum distillation and characterized by ^{1}H NMR spectroscopy. The presence of numerous lines between 0.00 and 5.00 ppm (C_6D_6) suggested the sample to be a mixture of unidentifyable hydrocarbons. The nonvolatile, shiny black solid was scraped out of the reaction tube in the drybox, washed with 50 mL of pentane and weighed (0.302 g). This material appeared as a shiny black solid to the naked eye but microscopic examination revealed a mixture of a shiny black solid with silver-colored specks. Characterization data identified a mixture of GaP and gallium metal. Mp: Silver-colored specks melted at 31 - 37 °C, but the black solid did not melt up to 260 °C. ESCA (Binding energy, eV; corrected to C_{1s}): 20.0 ($Ga_{3d3/2}$); 1119.3 ($Ga_{2p3/2}$); 130.3 (P_{2p}); 285.0 (C_{1s}); 532.9 (O_{1s}). X-ray Powder

Pattern: broad lines, poor crystalline quality; d spacings: 3.12, 1.92 1.64, 1.25, 1.22. Anal. Found: C, 12.11; H, 1.64.

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