Inorg. Chem. **1996,** *35,* 4090−4092

Infrared Spectroscopic Study of the Matrix-Isolated Complexes of $TiCl_4$ with PH_3 and AsH_3

Jennifer B. Everhart and Bruce S. Ault*

Department of Chemistry, University of Cincinnati,
Cincinnati, Ohio 45221

Received December 21, 1995

Introduction

Chemical vapor deposition (CVD) is used extensively for the production of thin films for the semiconductor industry and other industries. In CVD, a solid thin film is deposited on a heated substrate from the reaction of gaseous precursors in the vapor phase or on the surface of the substrate.[1] $TiCl_4$ and NH_3 have been used[2] as precursors in the chemical vapor deposition of TiN thin films, and the decomposition of the 1:2 complex $TiCl_4{\cdot}2NH_3$ to form TiN thin films has also been reported.[3] Recently, a matrix isolation and cryogenic thin film study of the $TiCl_4/NH_3$ system led to the formation and characterization of the 1:1 $TiCl_4{\cdot}NH_3$ complex.[4] In this study, the 1:1 complex was observed to undergo further reactions, including addition of a second NH_3 group to form the 1:2 complex and loss of HCl to form amido or imido species.

Beattie and Collis[5] have obtained the low-temperature infrared and Raman spectra of the 1:1 $TiCl_4{\cdot}PH_3$ complex while Holtje[6] claims formation of both 1:1 (vapor pressure at 0 °C *ca.* 5 mm) and 1:2 (vapor pressure at 0 °C *ca.* 138 mm) complexes. The 1:1 complex has not been fully characterized by vibrational spectroscopy while the 1:2 complex has never been observed spectroscopically. Formation of a complex of $TiCl_4$ with AsH_3, another group V hydride, has never been reported yet is likely to be stable under low-temperature matrix conditions.

The matrix isolation technique[7−9] is ideally suited for the spectroscopic characterization of reactive intermediates. A study of the reaction products of $TiCl_4$ with PH_3 and AsH_3 should provide further information on the reaction pathways of these systems. Isolation of the 1:1 complexes of $TiCl_4$ with PH_3 and AsH_3 should also provide information on the effects of base strength on the $TiCl_4$ subunit in the complex. Consequently, a matrix isolation study was undertaken to examine the reaction products of these two systems.

Experimental Section

The experiments conducted in this study were carried out on conventional matrix isolation equipment that has been described.[10] PH_3 (Matheson), AsH_3 (Alphagaz), and HCl (Matheson) were introduced to the vacuum system as gases and were purified by repeated freeze−thaw cycles at 77 K. $TiCl_4$ (MCB) was introduced to the system by means of a glass finger and distilled using a dry ice/ acetone bath at −77 °C to partially remove impurity HCl. Argon was used as the matrix gas in all experiments and was used without further purification.

Table 1. Band Positions[a] and Assignments for the Reaction Products of PH_3 and AsH_3 with HCl in Argon Matrices

PH_3/HCl[b]	PH_3/HCl[c]	AsH_3/HCl[b]	AsH_3/HCl[c]	assignment
984	983	903	901	sym def[d]
2358	2360	2161	2162	sym str[d]
2367	2368	2174	2176	asym str[d]
2596	2596			ν(H−Cl)[e]
2646	2646	2699	2701	ν(H−Cl)

[a] Band positions in cm^{-1}. [b] This work. [c] Reference 13. [d] Vibrations of base subunit. [e] 1:2 complex.

In a typical matrix experiment the gaseous samples were prepared in separate vacuum manifolds and then deposited on the 14 K cold window employing twin jet or merged jet deposition. In the twin jet mode, the two deposition lines were each pointed at 45° to the cold window so that sample mixing occurred directly in front of or on the cold surface. In the merged jet mode, the two deposition lines were joined with an Ultratorr tee 25 cm from the cold window and the samples flowed together for this distance before depositing onto the cold window. Pyrolysis experiments were also conducted in which the merged region was wrapped with heat tape and the samples were heated to temperatures as high as 350 °C before deposition. Samples were deposited for 19−24 h at a flow rate of approximately 2 mmol/h before final spectra were recorded at 1 cm^{-1} resolution on a Mattson Cygnus Fourier transform infrared spectrometer.

Results

Prior to the study of the reactions of $TiCl_4$ with PH_3 and AsH_3, blank experiments were conducted on each reactant in solid argon. The blank spectra were in good agreement with literature spectra.[11−13] Bands observed in the 2800−2900 cm^{-1} region correspond to those reported in the literature matrix spectra[14,15] of HCl which was present as an impurity in all experiments involving $TiCl_4$.

$TiCl_4$ + PH_3. When a sample of Ar/$TiCl_4$ = 500 was codeposited with a sample of Ar/PH_3 = 250 in a twin jet experiment, several infrared absorptions were observed which were not present in the blank spectra. When similar samples were codeposited in a merged jet experiment, the same product bands were observed with the same approximate intensity. Further merged jet experiments were performed in which the concentration ratio of $PH_3/TiCl_4$ was changed to 1/1 and 1/2. The same product bands were observed under these conditions. However, these bands did **not** maintain a constant intensity ratio, indicating that more than one product was being formed. Since HCl was present as an impurity in all samples of Ar/$TiCl_4$, an experiment was conducted in which a sample of Ar/HCl was codeposited with a sample of Ar/PH_3 = 500. Several product bands observed in this experiment were also seen in the $TiCl_4$/PH_3 codeposition experiments; these match bands reported for $PH_3{\cdot}HCl$ complexes in Ar matrices[13] and are listed in Table 1. The remaining product bands are listed in Table 2 and representative spectra are shown in Figure 1.

Several pyrolysis experiments were performed in which the merged samples of varying concentrations were heated stepwise from 100 to 350 °C before deposition on the cold window. The same two sets of product bands were observed in all of the pyrolysis experiments with yields similar to those obtained in

---

(1) Pierson, H. O. *Handbook of Chemical Vapor Deposition*; Noyes Publications: Park Ridge, NJ, 1992.
(2) (a) Kurtz, S. R.; Gordon, R. G. *Thin Solid Films* **1986**, *140*, 277. (b) Buiting, M. J.; Otterloo, A. F.; Montree, A. H. *J. Electrochem. Soc.* **1991**, *138*, 500.
(3) Winter, C. H.; Lewkebandara, T. S.; Proscia, J. W.; Rheinbold, A. L. *Inorg. Chem.* **1994**, *33*, 1227.
(4) Everhart, J. B.; Ault, B. S. *Inorg. Chem.* **1995**, *34*, 4379.
(5) Beattie, I. R.; Collis, R. *J. Chem. Soc.* **1969**, 2960.
(6) Holtje, R. *Z. Anorg. Chem.* **1930**, *190*, 241.
(7) Whittle, E.; Dows, D. A.; Pimentel, G. C. *J. Chem. Phys.* **1954**, *22*, 1943.
(8) Craddock, S.; Hinchliffe, A. *Matrix Isolation*; Cambridge University Press: New York, 1975.
(9) Hallam, H. E., Ed. *Vibrational Spectroscopy of Trapped Species*; Wiley: New York, 1973.
(10) Ault, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2426.
(11) Koniger, F.; Carter, R. O.; Muller, A. *Spectrochim. Acta* **1976**, *32A*, 891.
(12) Rytter, E.; Kvisle, S. *Inorg. Chem.* **1985**, *24*, 639.
(13) Arlinghaus, R. T.; Andrews, L. *J. Chem. Phys.* **1984**, *81*, 4341.
(14) Mann, D. E.; Acquista, N.; White, D. *J. Chem. Phys.* **1966**, *44*, 3453.
(15) Barnes, A. J.; Hallam, H. E.; Scrimshaw, G. F. *Trans. Faraday Soc.* **1969**, *65*, 3150.

S0020-1669(95)01631-4 CCC: $12.00

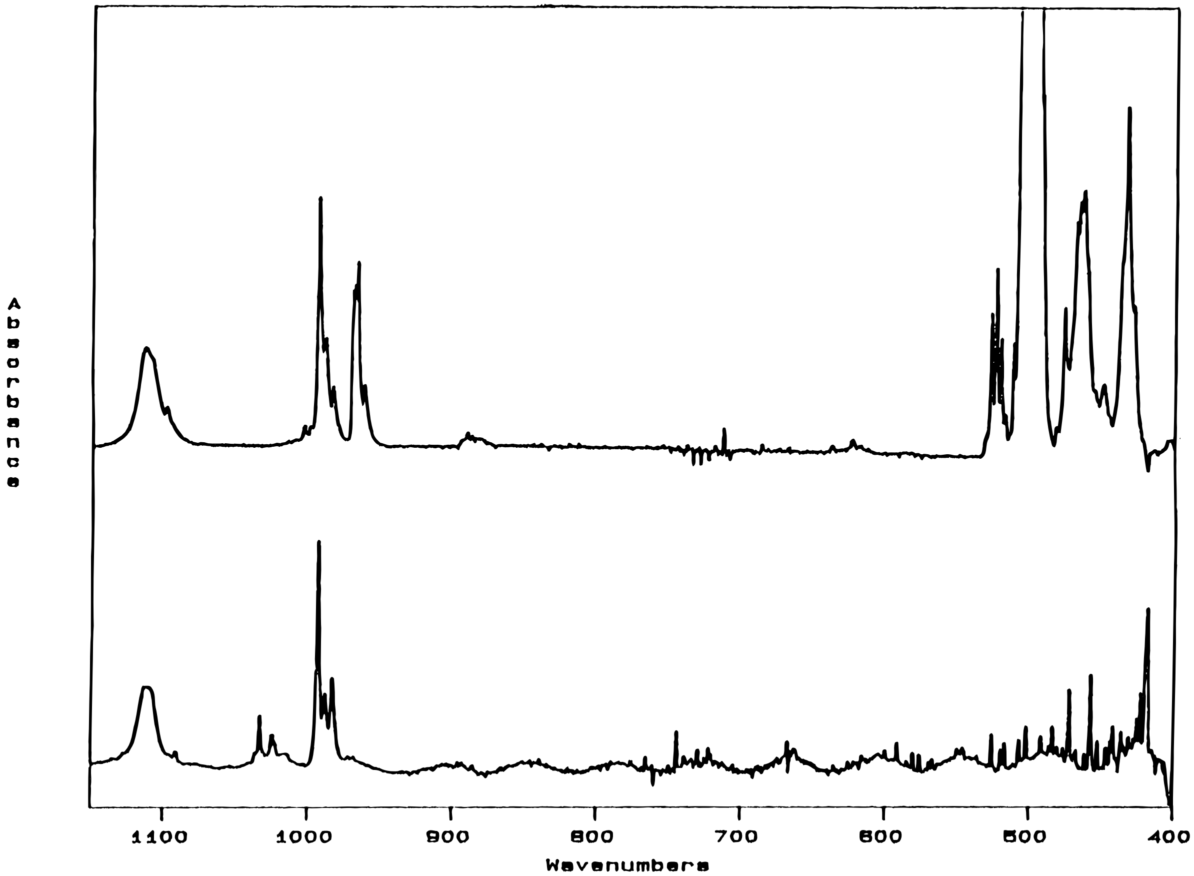

Figure 1. Infrared spectrum of the products of the codeposition of $TiCl_4$ and PH_3 in solid argon (upper trace) compared to a spectrum of the products of the codeposition of PH_3 and HCl in solid argon (lower trace).

the corresponding room temperature experiments at the same concentration.

$TiCl_4$ + AsH_3. When a sample of $Ar/TiCl_4 = 500$ was codeposited with a sample of $Ar/AsH_3 = 500$ in a twin jet experiment, several new infrared absorptions were observed. One set of product bands listed in Table 1 matched product bands obtained in a twin jet codeposition of Ar/HCl and Ar/AsH_3 (run as a part of this study) and bands reported for AsH_3•HCl complexes in Ar matrices.[13] The remaining product bands listed in Table 2 were observed consistently in several twin jet and merged jet experiments in which the $TiCl_4/AsH_3$ concentration ratio was varied and the total concentration was also changed. The overall yield of product increased somewhat in the merged experiments The spectrum of a pyrolysis experiment performed at 315 °C showed little difference from the spectrum of a similar experiment performed at the same concentration with a room-temperature merged jet deposition line. Representative spectra for the $Ar/TiCl_4/AsH_3$ system are shown in Figure 2.

Discussion

Product Identification. The codeposition of $TiCl_4$ with PH_3 and AsH_3 into argon matrices led to the observation of several new infrared absorptions which could not be attributed to either parent species. As noted above, several of these bands were observed in experiments in which PH_3 and AsH_3 were codeposited with HCl and are assigned to the known[13] products arising from these pairs of reactants. These bands and assignments are listed in Table 1. The remaining product bands were quite similar for the $TiCl_4/PH_3$ and $TiCl_4/AsH_3$ systems and will be discussed together.

The product bands in each system were all located near the absorptions of one or the other of the precursor species. This is indicative of the formation of a molecular complex where the two reactants are perturbed in the product complex yet retain their structural identity.[16] Only one reaction product was isolated for each system despite differing absolute and relative precursor concentrations, alteration of mixing zone lengths, and variation of mixing zone temperature. This suggests that the product bands are due to the initial reaction product for each system. Previous studies have indicated that a 1:1 complex between $TiCl_4$ and PH_3 forms readily[5] although 1:2 complex formation has also been claimed.[6] Although formation of complexes with higher stoichiometries is certainly possible, it is unlikely that these complexes would be observed without also observing the 1:1 complex. Furthermore, the 1:1 complex of $TiCl_4$ with NH_3 was isolated[4] under the conditions of high dilution and limited reaction time similar to those used in the present twin jet experiments. These arguments strongly support the identification of the product obtained in these experiments as the 1:1 complexes of $TiCl_4$ with PH_3 and AsH_3.

Band Assignments. The band assignments for the matrix-isolated 1:1 complexes are relatively straightforward based on proximity to parent absorptions and comparison to previously reported $TiCl_4$ complexes. The intense bands at 434 and 467 cm^{-1} and 436 and 471 cm^{-1} for the PH_3 and AsH_3 complexes, respectively, are located near the parent $TiCl_4$ antisymmetric stretching mode at 503 cm^{-1}. These bands fall in the region in which the Ti−Cl antisymmetric stretching modes were observed for the $TiCl_4$•NH_3 complex and are assigned to the corresponding modes for the $TiCl_4$•PH_3 and $TiCl_4$•AsH_3 complexes. In the 77 K spectrum of the 1:1 $TiCl_4$•PH_3 complex, Beattie and Collis[5] reported antisymmetric Ti−Cl stretching vibrations at 426 and 481 cm^{-1} which are in adequate agreement with the present matrix results. Beattie and Collis studied the complex as a solid thin film, a very different and more strongly interacting environment than the complex isolated in an argon matrix. This

---

(16) Ault, B. S. *Rev. Chem. Intermed.* **1988**, *9*, 233.

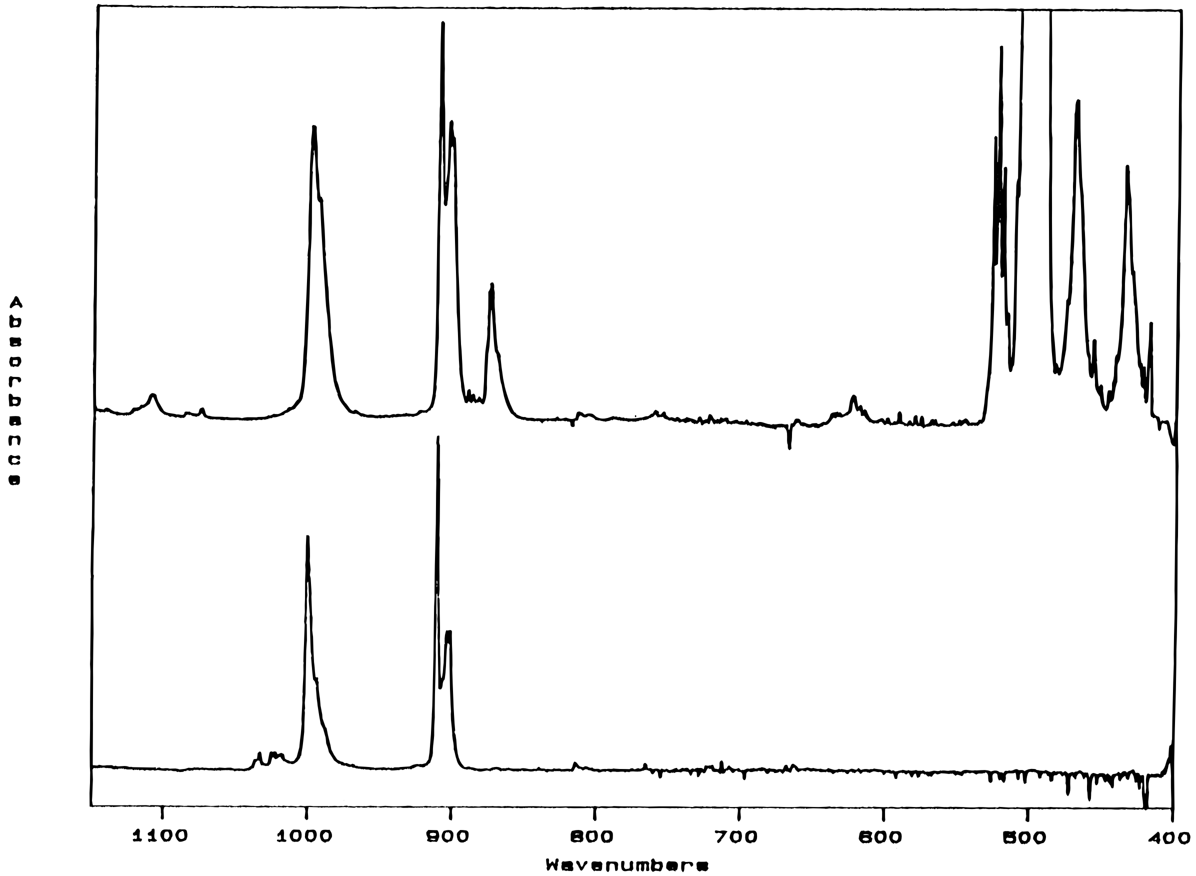

Figure 2. Infrared spectrum of the products of the codeposition of $TiCl_4$ and AsH_3 in solid argon (upper trace) compared to a spectrum of the products of the codeposition of AsH_3 and HCl in solid argon (lower trace).

Table 2. Band Positions[a] and Assignments for the 1:1 Complexes of $TiCl_4$ with PH_3 and AsH_3 in Argon Matrices

Ar/PH_3	Ar/$TiCl_4$/PH_3	Ar/AsH_3	Ar/$TiCl_4$/AsH_3	assignment
	434		436	ax Ti−Cl str
	467		471	eq Ti−Cl str
994	967	911	876	sym def[b]
1114	1099	1001		asym def[b]
2340	2383	2139	2195	sym str[b]
2346	2392	2149	2216	asym str[b]

[a] Band positions in cm^{-1}. [b] Vibrations of base subunit.

Table 3. Variation of Ti−Cl Stretching Band Positions[a] with Base Strength

base	ν_{eq}	ν_{ax}	ν_{avg}	PA,[c] kcal/mol
NH_3	456[b]	440[b]	448	204
PH_3	467	434	450.5	189
AsH_3	471	436	453.5	179

[a] Band positions in cm^{-1}. [b] Reference 4. [c] Reference 17.

difference in the environment of the two samples readily accounts for the difference in band positions. The band positions of the 1:1 $TiCl_4 \cdot PD_3$ complex also studied by Beattie and Collis were virtually unshifted from those of the normal isotopic complex; this further confirms the assignments of the matrix bands to vibrations of the $TiCl_4$ subunit.

The remaining product bands observed for the complexes each fall within a few wavenumbers of a parent mode of PH_3 or AsH_3. These are readily assigned to the corresponding mode of the coordinated base as listed in Table 2. For example, the symmetric deformation (umbrella mode) of the hydride shifted approximately 30 cm^{-1} to lower energy in each isolated 1:1 complex.

Further Considerations. The Ti−Cl stretching vibrations were observed to shift slightly as the base was changed from NH_3 to PH_3 and AsH_3 as shown in Table 3. The position of the Ti−Cl stretching bands would be expected to be shifted to lower energy as the mass of the coordinated base increased, but the opposite trend was observed for the group V bases. The basicity of these bases is known to decrease down the group with proton affinity used as the measure.[17] A higher basicity indicates a great ability to donate electron density to the acid subunit in the complex ($TiCl_4$ in this study). The electron density enters an antibonding orbital on the $TiCl_4$ subunit, decreasing the overall bonding in the acid subunit and lowering the Ti−Cl stretching force constants. This argument accounts for the decrease in Ti−Cl stretching frequency with increased basicity of the group V hydride and also is consistent with many previous studies of Lewis acid/base complexes (see, for example, ref 16).

Finally, it is noteworthy that the perturbations to the vibrational modes of the Lewis base (PH_3 and AsH_3) as a result of complexation with $TiCl_4$ were significantly greater than perturbations to the same modes in the 1:1 complexes[13] with HCl. This suggest that $TiCl_4$ is a quite strong Lewis acid, more so than HCl. In a similar comparison, the shift of this mode in complexes of PH_3 and AsH_3 with metal alkyls has been tabulated;[18] the shifts in the present study of 1:1 complexes with $TiCl_4$ were distinctly larger, again suggesting greater Lewis acidity than the metal alkyls.

Acknowledgment. The National Science Foundation is gratefully acknowledged for their support of this research through grant CHE 92-22622.

IC951631A

---

(17) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(18) Bai, H.; Ault, B. S. *J. Mol. Struct.*, in press.