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Communications

Spectral Evidence for Dimerization of Titanium Tetrachloride at Cryogenic Temperatures

Sir:

Although Ti(IV) preferably forms four- or six-coordinated halogen complexes, several compounds that contain five-coordinated titanium have been identified.[1] The monomeric tbp pentachloride $TiCl_5^-$ is stabilized by large cations while most systems contain the six-coordinated dimers $Ti_2Cl_{10}^{2-}$ or $Ti_2Cl_9^-$, besides the common $TiCl_6^{2-}$. Thus, it may be adequate to formulate the reactions leading to the dimers as

$$2TiCl_5^- = Ti_2Cl_{10}^{2-} \tag{1}$$

and

$$TiCl_5^- + TiCl_4 = Ti_2Cl_9^- \tag{2}$$

Formation of the neutral dimer

$$2TiCl_4 = Ti_2Cl_8 \tag{3}$$

has not yet been reported. In the present work, spectral evidence is presented for the existence of five-coordinated titanium when $TiCl_4(g)$ is cocondensed with argon at 12 K. The most consistent interpretation of the data strongly indicates that Ti_2Cl_8 is stable at cryogenic temperatures.

The titanium species have interest in connection with our recent studies of matrix-isolated aluminum alkyls.[2] In an effort to react trimethylaluminum (TMAL) or triethylaluminum with titanium tetrachloride, several new bands in the Ti–Cl stretching region were observed (Figure 1). No change, however, of the pure alkyl spectrum appeared.[3] Moreover, it turned out to be possible to obtain the new bands in pure $TiCl_4$/Ar mixtures, i.e., without presence of an aluminum alkyl. Hence, the attempted reaction did *not* proceed at low temperatures, but still a modification of the tetrahedral $TiCl_4$ molecule took place.

The applied apparatus and procedures have been described in detail elsewhere.[2] Here, it is only appropriate to point out that high-quality argon was employed (Norsk Hydro; 99.9997%) and that the pressure in the deposition chamber was less than 5×10^{-6} torr before, and less than 5×10^{-7} torr after the cryocooler was started. The $TiCl_4$ (Fluka; p.a., 99%) and TMAL (Alfa; electronic grade, 98%) were distilled prior to use. The alkyl was deposited from a Knudsen effusion cell at ca. 300 °C, producing mainly the monomer $(CH_3)_3Al$ (m-TMAL), whereas $TiCl_4$ was premixed with argon in a gas-mixing system in the ratios 1:25 to 1:100. A reverse procedure, with 1:100 TMAL/Ar from the gas-mixing system and $TiCl_4$ from the Knudsen cell (decomposition of $TiCl_3$(s) at 400 °C or $TiCl_2$(s) at 800 °C), produced similar results that will not be discussed further. Spectra in the 250–4000 cm^{-1} region were recorded with a Perkin-Elmer 580B infrared (IR) spectrometer.

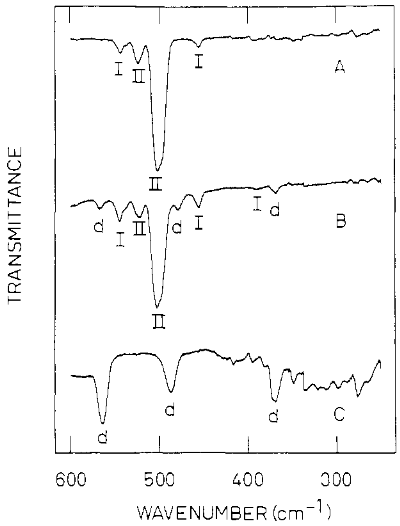

Figure 1. Infrared spectra of $TiCl_4$ in argon matrices: A, 1:50 $TiCl_4$/Ar (deposition rate 9.1 mmol/h); B, $(CH_3)_3Al$ (ca. 10% dimerized) + 1:75 $TiCl_4$/Ar (6, 1 mmol/h); C, matrix B annealed for 5 h at 35 K with simultaneous 281-nm UV irradiation. I = Ti_2Cl_8, II = $TiCl_4$, and d = $(CH_3)_6Al_2$.

On the basis of absorbance measurements for 13 different matrices, with or without TMAL, the frequencies (cm^{-1}) assigned to titanium chlorides could be ascribed to two different species: I, 544 m (shoulder at 538), 456 w, and 390 vw; II ($TiCl_4$, T_d), 524 w and 503 vs (shoulder at 497). In particular, it was found that the band positions were independent of the matrix preparation conditions and that the absorbance ratios $A_{503}:A_{524} \approx 18$ (II) and $A_{544}:A_{456} \approx 1.6$ (I) were constant within 10% for all experiments. Variations of the ratio $A_{544}:A_{503}$ (I:II) indicated that species I was relatively more abundant at high deposition rates (total range 5–15 mmol/h) and when m-TMAL was codeposited.

Annealing of the matrices at 35 K for 2–5 h did not cause any change in the Ti–Cl band structure. Diffusion in the system at this temperature, however, was demonstrated by alkylaluminum dimerization for the samples containing m-TMAL. Attempts to induce reactions were made by broad-band or selective electronic excitation of $TiCl_4$, in the latter case by 281-nm UV light, which corresponds to the ligand ($p\pi$) → metal (3d) transition $1t_1 \rightarrow 2e$.[4]

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(1) Creaser, C. S.; Creighton, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1402.

(2) (a) Kvisle, S.; Rytter, E. *J. Mol. Struct.* **1984**, *117*, 51. (b) *Spectrochim. Acta, Part A* **1984**, *40A*, 939. (c) To be submitted for publication in *Inorg. Chem.*

(3) Two minor spectral changes indicate a $TiCl_4$–TMAL interaction. One is a new very weak band at 1367 cm^{-1}. The second indication can be seen in Figure 1B where a band at 480 cm^{-1}, tentatively attributed to $(TMAL)_2$, shifts upon annealing (Figure 1C) to its normal position at 487–490 cm^{-1}.

(4) Iverson, A. A.; Russell, B. R. *Spectrochim. Acta, Part A* **1973**, *29A*, 715.

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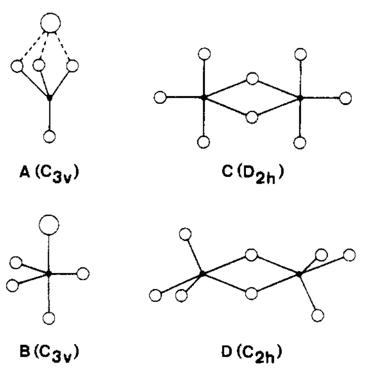

Figure 2. Models for titanium(IV) chloride in argon matrices: A, perturbation; B, coordination; C and D, dimerization. • = Ti, o = Cl, and ○ = other ligand.

Simultaneous annealing and UV irradiation only caused all Ti–Cl bands attributed to I and II to disappear gradually in exchange for a broad feature around 300–350 cm^{-1}, probably due to the reactions

$$\mathrm{TiCl_4\ (I,\ II)} \xrightarrow{h\nu} \mathrm{TiCl_3} + \mathrm{Cl\cdot} \rightarrow \mathrm{TiCl_3(s)} + \mathrm{Cl_2} \qquad (4)$$

The formation of a lower valent titanium chloride is supported by the appearance of a brown-yellow color of the matrix. It can be concluded that species I is as stable as species II at 12–35 K and that neither interact with the strong Lewis acid trimethylaluminum.

Species II is the well-known tetrahedral $\mathrm{TiCl_4}$ molecule with matrix bands at 524 ($\nu_1 + \nu_4$, F_2) and 503 cm^{-1} (ν_3, F_2).[5] The antisymmetric stretching, ν_3, has a low-frequency shoulder due to isotopic splitting. The same interpretation is offered for the shoulder on the 544-cm^{-1} band of I. The remaining bands of the new compound may be explained by any of the four I(A–D) models in Figure 2. They all give three IR-active $\mathrm{TiCl_t}$ terminal stretching fundamentals as observed. Deformations and bridge stretches are expected well below 300 cm^{-1}.[6,7] Distribution of the $\mathrm{TiCl_t}$ modes among the irreducible representations of the appropriate point groups are given in eq 5–8, where IR and R

$$\Gamma(T_d) = \mathrm{A_1\ (R) + F_2\ (IR,\ R)} \qquad (5)$$

$$\Gamma(C_{3v}) = \mathrm{2\ A_1\ (IR,\ R) + E\ (IR,\ R)} \qquad (6)$$

$$\Gamma(D_{2h}) = \mathrm{2\ A_g\ (R) + B_{2g}\ (R) + B_{1u}\ (IR) + 2\ B_{3u}\ (IR)} \qquad (7)$$

$$\Gamma(C_{2h}) = \mathrm{2\ A_g\ (R) + B_g\ (R) + A_u\ (IR) + 2\ B_u\ (IR)} \qquad (8)$$

denote infrared and Raman activity, respectively. One of the frequencies, 390 cm^{-1}, is in the same position as ν_1 ($\mathrm{A_1}$) of $\mathrm{TiCl_4}$ (T_d).[5] This Raman mode is activated in the IR region by a perturbation model such as I(A) in Figure 2, e.g., caused by a weak interaction with a solvent atom. However, the considerable splitting of ν_3 ($\mathrm{F_2}$), 503 → 544 + 456 cm^{-1}, can only have its origin in the formation of a normal chemical bond, as in I(B). Nevertheless, this model appears improbable because an impurity donor like $\mathrm{N_2}$, $\mathrm{O_2}$, or CO is required. Carbon monoxide is not found in the matrices, and $\mathrm{N_2}$ or $\mathrm{O_2}$ is hardly present in large enough amounts to give the observed effect. Besides, no ligand bands that may be attributed to such complex formation can be identified.[6]

The possibilities left are models I(C) and I(D), which both imply a bridged dimer with five-coordinated titanium atoms. Of these, I(D) definitely is assumed to be the more stable. Since it forms the bridges by employing one axial and one equatorial bond of each tbp $\mathrm{TiCl_5}$ part of the dimer, the ideal $\mathrm{Cl_b}$–Ti–$\mathrm{Cl_b}$ angle is 90° compared to 120° for I(C). Observed angles,[8,9] in other complexes with similar Ti–$\mathrm{Cl_2}$–Ti bridges are 80 ± 2°, and I(D) therefore requires a far less distortion of the ideal structure. In addition, similar structures have been found for the oxygen-bridged molecules $\mathrm{Ti_2Cl_4(OC_6H_5)_4}$ and $\mathrm{Ti_2Cl_4(OC_2H_5)_4}$.[10]

From eq 8, it is seen that the IR-active $\mathrm{Ti_2Cl_8}$ terminal stretching modes belong to $\mathrm{A_u} + 2\ \mathrm{B_u}$. The corresponding assignments are 544 (axial Ti–$\mathrm{Cl_t}$ stretch ($\mathrm{B_u}$)), 456 (antisymmetric equatorial $\mathrm{TiCl_t}$ stretch ($\mathrm{A_u}$)), and 390 cm^{-1} (symmetric equatorial Ti–$\mathrm{Cl_t}$ stretch ($\mathrm{B_u}$)), where axial and equatorial refer to the tbp $\mathrm{TiCl_5}$ units. The highest frequency deserves special attention. On the basis of a splitting of the 503-cm^{-1} band (ν_3, $\mathrm{F_2}$) of $\mathrm{TiCl_4}$, 544 cm^{-1} does not seem unreasonable. It should be noted, however, that this is the highest frequency assigned to a Ti(IV)–Cl normal mode.[1,6–8] Therefore, it is gratifying that a strong axial Ti–Cl terminal bond is compatible with the trans influence found in octahedral Ti(IV) complexes;[8] cf. the short $\mathrm{TiCl_t}$ distance (2.258 (2) Å) trans to bridging atoms with the other terminal bond lengths (2.296 (3) Å) in $\mathrm{Ti_2Cl_{10}}^{2-}$.[9]

To summarize, the $\mathrm{Ti_2Cl_8}$ molecule is proposed to be stable at cryogenic temperatures, although the dependency on the deposition parameters suggests that the kinetics for production of dimers is important. A very limited stability range is indicated by the failure to initiate dimerization at liquid-$\mathrm{N_2}$ temperature.[11] We may continue the efforts to characterize the new complex by employing an all-vacuum, matrix-isolation FTIR system.[12]

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(12) Apparatus under construction.

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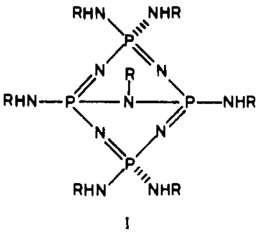
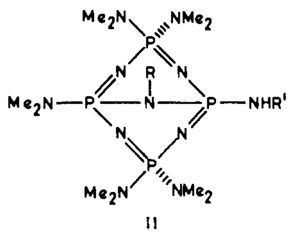
Mechanism of Formation of Bicyclic Phosphazenes. Isolation of a Versatile Tetrakis(amino) Intermediate, $\mathrm{N_4P_4Cl_4(NMe_2)_2(NHEt)_2}$

Sir:

Novel bicyclic phosphazenes of types $\mathrm{N_4P_4(NHR)_6(NR)}$ (I) and $\mathrm{N_4P_4(NMe_2)_5(NR)(NHR')}$ (II) have been isolated in the


I

R = Me, Et, Pr^n, Pr^i, Bu^n


II

R = R' = Me, Et, Pr^n, Bu^n, CH$_2$Ph
R = Et, R' = Bu^t

aminolysis reactions of octachlorocyclotetraphosphazene ($\mathrm{N_4P_4Cl_8}$) and its bis(primary amino) derivatives, $\mathrm{N_4P_4(NHR)_2Cl_6}$ or $\mathrm{N_4P_4(NHR)(NHR')Cl_6}$.[1–4] The effects of solvent, substituent,

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