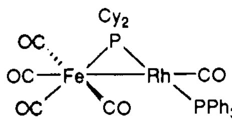
ligand cis ($^2J_{PP}$ = 14.6 Hz) to the μ-PCy_2 group with the PR_3 ligands distinguished by their relative chemical shifts (δ 30.2 (PPh_3), 8.0 (PEt_3)).

The presence of **6** and **7** in the product mixture is more difficult to rationalize since each is formulated as having five CO groups and this requires a source of CO. It is possible that CO abstraction occurs from some other species in solution, for example, any $Fe(CO)_4PR_3$ that might be present. These two complexes are easily characterized by $^{31}P\{^1H\}$ NMR and by comparison with **2**, **5**, **8**, and **9** and are identified as the complexes $(CO)_4Fe(\mu$-$PCy_2)Rh(CO)(PPh_3)$ (**6**) and $(CO)_4Fe(\mu$-$PCy_2)Rh(CO)(PEt_3)$ (**7**). Both complexes show a single PR_3 group bound to Rh with



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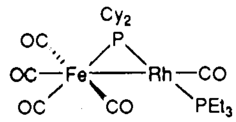

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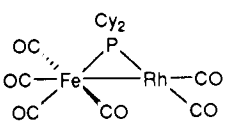
$^1J_{PRh}$ (**6**, 136.0 Hz; **7**, 136.8 Hz) and $^2J_{PP}$ indicative of a trans geometry for the phosphorus ligands (**6**, 212.2 Hz; **7**, 214.8 Hz). **6** and **7** are coordinatively unsaturated at Rh, and the change in geometry from a cis arrangement of PPh_3 and μ-PCy_2 in **2** is probably due to decreased steric congestion at adjacent sites on Fe and Rh opposite the PCy_2 bridge.

The reaction of $(CO)_4Fe(\mu$-$PCy_2)Rh(1,5$-COD) (**3**) with CO(g) produced three products, **10**–**12**, as evidenced by $^{31}P\{^1H\}$ NMR. Two of these species have a downfield chemical shift (**10**, δ 157.0 (d); **11**, δ 172.9 (d)) indicating retention of the FeRh interaction. However, for the first time we observe an upfield chemical shift (**12**, δ 16.2 (d)), which suggests complete saturation of the coordination sites on both metals, including the loss of the Fe–Rh bond. $^{13}C\{^1H\}$ NMR showed no evidence of coordinated 1,5-COD, so these three products are tentatively formulated as being the result of 1,5-COD displacement and the coordination of one, two, and three CO molecules at Rh to give $(CO)_4Fe(\mu$-$PCy_2)Rh(CO)_2$ (**10**), $(CO)_4Fe(\mu$-$PCy_2)Rh(CO)_3$ (**11**), and $(CO)_4Fe(\mu$-$PCy_2)$-$Rh(CO)_4$ (**12**), respectively.



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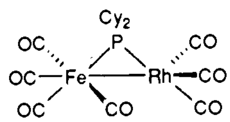

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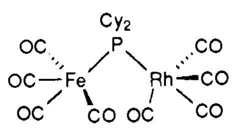

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Discussion

Coordinatively unsaturated heterobimetallic complexes containing Fe and Rh can be prepared by using the sterically demanding μ-PCy_2 bridging ligand. The observation of a semibridging carbonyl group for **3** in both solution and solid state and for **2** in only the solid state is interesting. However, it is unclear why the solution structure for **2** appears to be anomalous in this type of complex. It is conceivable that, for **2**, a solution process is occurring which rapidly exchanges the Rh–CO group with the Fe–CO ligands, thus preventing direct observation of the semibridging CO group in solution. This process would be less likely for **3**, since **3** contains no CO ligands bound to Rh. The unsaturated nature of these complexes makes exchange processes of this type facile, and the type described here has been observed for other heterobimetallic carbonyl complexes such as $(CO)_3$-$(PEt_3)Fe(\mu$-$PPh_2)Rh(PEt_3)(CO)$.[2]

In the case of $(CO)_3Fe(\mu$-$PCy_2)Rh(PPh_3)(CO)$ (**2**), for which the μ-PPh_2 analogue is known, it appears that the presence of the more sterically demanding PCy_2 bridging ligand allows for facile dissociation of PPh_3 from Fe evidenced by the formation of $(CO)_4Fe(\mu$-$PCy_2)Rh(PPh_3)(CO)_2$ (**4**) under CO(g). This is of course a well-known feature of monometallic complexes containing bulky phosphine ligands. The complex $(CO)_4Fe(\mu$-$PCy_2)Rh$-(1,5-COD) (**3**) is a potential precursor to a variety of related complexes since it contains a readily displaced 1,5-COD ligand. It is also an example of a heterobimetallic complex that undergoes ligand substitution for a donor–acceptor metal–metal bond under mild conditions. The reaction chemistry associated with these complexes is of ongoing interest and will be the subject of further publications.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work. The Chemistry Department of the University of Manitoba is gratefully acknowledged for use of their NMR facilities and as the home department of graduate studunt H.A.J.

Registry No. **1**, 113809-78-2; **2**, 119909-51-2; **3**, 119909-59-0; **4**, 119909-52-3; **5**, 119909-53-4; **6**, 119909-54-5; **7**, 119909-55-6; **8**, 119909-56-7; **9**, 119909-57-8; **10**, 119909-60-3; **11**, 119909-61-4; **12**, 119909-58-9; $Fe_2(CO)_9$, 15321-51-4; *trans*-$RhCl(CO)(PPh_3)_2$, 15318-33-9; $[RhCl(1,5\text{-COD})]_2$, 12092-47-6; Fe, 7439-89-6; Rh, 7440-16-6.

Supplementary Material Available: Tables S-I–S-IV, listing details of the crystallographic investigation, thermal parameters, hydrogen atom positions, and bond distances and angles associated with the cyclohexyl groups (5 pages); Table S-V, listing observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

Highly Condensed Titanoxanes: Synthesis of *closo*-$(Cp^*Ti)_4O_6$ and Its Transformation to *bicyclo*-$(Cp^*Ti)_4O_5Cl_2$ with $TiCl_4$ as an Oxide Acceptor Reagent

L. M. Babcock and W. G. Klemperer*

Received July 22, 1988

Hydrolysis of Cp^*TiCl_3, $Cp^* = \eta^5\text{-}C_5(CH_3)_5$, under basic conditions yields a titanoxane cage compound, $(Cp^*Ti)_4O_6$ (**1**), having an adamantane-like, tetrahedral Ti_4O_6 core structure. This compound reacts with 0.5 equiv of $TiCl_4$ in toluene solution to form the bicyclic species $(Cp^*Ti)_4O_5Cl$ (**2**) in quantitative yield. Here, one oxygen of the Ti_4O_6 tetrahedron in **1** has been replaced by two terminal chlorine ligands. Compound **2** reacts with $TiCl_4$ unselectively to produce three new compounds, $(Cp^*Ti)_4O_4Cl_4$ (**3**), $(Cp^*Ti)_3O_3Cl_3$ (**4**), and $(Cp^*Ti)_2OCl_4$ (**5**), plus Cp^*TiCl_3. Compound **5** can be isolated from this mixture in analytically pure, crystalline form. Compound **4** can be prepared in high yield from Cp^*TiCl_3 and excess water in acetone solution.

Introduction

The hydrolysis/condensation of titanium(IV) complexes according to eq 1 serves as the basis of many low-temperature route to titania and mixed-metal titanium oxides.[1-3] Although the

$$TiX_4 + 2H_2O = TiO_2 + 4HX \qquad (1)$$

course of this and other sol–gel processes is known to be very sensitive to reaction conditions such as solution pH and solvent, it is difficult to control in a systematic fashion since virtually nothing is known at a molecular level concerning the molecular growth pathways involved. This lack of understanding is due to the complexity of an overall process that involves countless numbers of polynuclear intermediates $Ti_aX_bO_c(OH)_d$. In order to simplify this complex process, we have turned our attention to the titanium(IV) derivatives $RTiX_3$, where R is an inert group, that might undergo a less complex sequence of hydrolysis/condensation reactions according to eq 2. The pentamethylcyclopentadienyl ligand, $C_5(CH_3)_5$ or Cp*, was selected as the inert group R in eq 2 due to its stability toward both acid and base as well as its steric bulk. The chloride ligand was selected as the reactive group X.

$$2RTiX_3 + 3H_2O = (RTi)_2O_3 + 6HX \qquad (2)$$

This paper is primarily concerned with the synthesis and characterization of the new family of compounds $(Cp^*Ti)_4O_6$ **1**,[4] $(Cp^*Ti)_4O_5Cl_2$ (**2**), $(Cp^*Ti)_4O_4Cl_4$ (**3**), $(Cp^*Ti)_3O_3Cl_3$ (**4**),[4] and $(Cp^*Ti)_2OCl_4$ (**5**), all formally derived from Cp^*TiCl_3 (**6**)[5] by hydrolysis/condensation. These materials have been prepared by standard hydrolysis/condensation techniques under acidic and basic conditions, as well as by a new approach, titanoxane degradation with $TiCl_4$ as an oxide transfer reagent (see eq 3).

$$2\ {-}\overset{|}{\underset{|}{\mathrm{Ti}}}{-}\mathrm{O}{-}\overset{|}{\underset{|}{\mathrm{Ti}}}{-} + TiCl_4 = 4\ {-}\overset{|}{\underset{|}{\mathrm{Ti}}}{-}\mathrm{Cl} + TiO_2 \qquad (3)$$

Experimental Section

Reagents, Solvents, and General Procedures. The following were purchased from commercial sources and used without further purification: *tert*-butyllithium, 1.7 M in pentane (Aldrich); $TiCl_4$ (Fisher); $TiCl_3$ (Alfa); ^{17}O-enriched water (Monsanto); aluminum oxide, activity 1, basic (Brinkman). Triethylamine (J. T. Baker) was distilled from Na metal and stored over Na metal pieces. The following were prepared by literature procedures: $TiCl_3{\cdot}3THF$,[6] $TiCl_4{\cdot}2CH_3CN$,[7] $C_5(CH_3)_5H$,[8] $[\eta^5\text{-}C_5(CH_3)_5]TiCl_3$.[5] Moist silver oxide was precipitated from an aqueous solution of silver nitrate (Aldrich) that was added to excess potassium hydroxide (Fisher) in aqueous solution.[9]

Pentane and toluene (both Fisher) and acetonitrile and tetrahydrofuran (both Mallinckrodt) were dried over sodium/potassium alloy, sodium metal, calcium hydride, and sodium benzophenone ketyl, respectively, and were freshly distilled prior to use. Chloroform and acetone (both Fisher) were used as received without further purification. Deuteriochloroform (Aldrich) was distilled from CaH_2 and stored under a nitrogen atmosphere over activated 4-Å molecular sieves. Molecular sieves were activated at 350 °C over 48 h and stored in tightly sealed containers.

All reactions involving ^{17}O-enriched water, moist Ag_2O, and $TiCl_4$ were handled under a dry nitrogen atmosphere by using standard Schlenk-line and drybox techniques. Nitrogen gas was deoxygenated and dried by passing it through a column of BASF oxygen-scavenging catalyst and then through a second column of activated 4-Å molecular sieves.

Analytical Procedures. Elemental analyses were performed by the University of Illinois School of Chemical Sciences Microanalytical Laboratory. Field desorption mass spectra were obtained by the University of Illinois School of Chemical Sciences Mass Spectroscopy Laboratory. Infrared spectra were measured from mineral oil (Nujol) mulls between KBr plates on a Perkin-Elmer 1330 spectrophotometer. The spectra were referenced to the 1601- or 1028-cm^{-1} band of a 0.05 mm thick polystyrene film.

Proton and $^{13}C\{^1H\}$ NMR spectra were recorded at 300 and 75.5 MHz, respectively, on a General Electric QE-300 NMR spectrometer equipped with a deuterium lock. All ^1H NMR chemical shift values were internally referenced to tetramethylsilane. All $^{13}C\{^1H\}$ NMR chemical shift values were referenced to the central peak of the $CDCl_3$ triplet, 77.0 ppm.

Oxygen-17 NMR spectra were measured at 33.9 MHz in a 12-mm vertical sample tube without sample spinning on an unlocked FTNMR system equipped with a 5.87-T Oxford Instruments magnet and a Nicolet NIC-1280 data processor. The spectra were externally referenced to 22 °C fresh tap water by the sample replacement method.

Preparation of $(Cp^*Ti)_4O_6$ (1). Method 1. (Pentamethylcyclopentadienyl)titanium trichloride (1.00 g, 3.45×10^{-3} mol) was dissolved in 100 mL of toluene. Triethylamine (3 mL) and aqueous NH_4OH (5 mL of a 10% solution by volume) were added to the reaction solution with vigorous stirring. After 3 days, the yellow toluene solution was separated from the aqueous layer and dried over anhydrous Na_2SO_4. The solvent and any remaining triethylamine were removed from the crude product under vacuum. The product was purified by elution of a toluene solution through a column containing 20 g of basic alumina until the eluate was colorless. The volume of this solution was reduced to 50 mL, and the remaining solvent was allowed to evaporate slowly to precipitate the yellow crystalline product $(Cp^*Ti)_4O_6$ (0.49 g, 5.92×10^{-4} mol, 68%). Anal. Calcd for $C_{40}H_{60}Ti_4O_6$: C, 57.99; H, 7.30; Ti, 23.13. Found: C, 58.13; H, 7.34; Ti, 23.34. IR (Nujol, 1000–400 cm^{-1}): 785 (s, br), 735 (sh), 645 (w), 565 (w), 430 (m), 410 (m). ^1H NMR ($CDCl_3$, 0.02 M, 17 °C): δ 1.97. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 0.02 M, 17 °C): $\eta^5\text{-}C_5(CH_3)_5$, δ 121.47; $\eta^5\text{-}C_5(CH_3)_5$, δ 11.37. Field desorption mass spectrum: m/z 828.

Method 2. A solution of triethylamine (0.72 mL, 0.52 g, 5.19×10^{-3} mol) and 26 atom % ^{17}O-enriched water (0.05 mL, 0.05 g, 2.78×10^{-3} mol) in 25 mL of toluene was added to (pentamethylcyclopentadienyl)titanium trichloride (0.50 g, 1.73×10^{-3} mol) dissolved in 25 mL of toluene. The reaction solution was stirred at 22 °C for 2 days and filtered. The solvent was removed from the filtrate under vacuum. The crude product obtained was then dissolved in 30 mL of toluene and eluted through a basic alumina column with toluene as in method 1. The volume of the eluate was reduced to 30 mL and allowed to evaporate in air. The yellow crystalline product was collected and dried under vacuum to give $(Cp^*Ti)_4O_6$ (0.09 g, 1.09×10^{-4} mol, 25%). ^{17}O NMR ($CHCl_3$, 0.02 M, 22 °C): δ 645.

Method 3. (Pentamethylcyclopentadienyl)titanium trichloride (0.50 g, 1.73×10^{-3} mol) was dissolved in 100 mL of toluene. Excess silver oxide (2.00 g) was added to the solution with stirring. The color of the reaction solution turned from red to yellow within 10 min. The reaction mixture was stirred for 15 h and filtered into a second flask containing Ag_2O (2.00 g). This mixture was stirred for an additional 15 h, filtered, and eluted through a basic alumina column as in method 1. The crystalline product, $(Cp^*Ti)_4O_6$ (100 mg, 1.21×10^{-4} mol, 28%), was crystallized by allowing a saturated toluene solution to slowly evaporate.

Method 4. Silver oxide (0.13 g) was added to $(Cp^*Ti)_4O_5Cl_2$ (0.10 g, 1.13×10^{-4} mol) dissolved in 50 mL of toluene. The reaction mixture was heated to 50 °C with stirring for 24 h, filtered into a second flask containing excess Ag_2O (0.13 g), and stirred at 50 °C for an additional 24 h. The solution was then filtered away from the remaining solid and eluted through a basic alumina column as in method 1. The product $(Cp^*Ti)_4O_6$ (28 mg, 3.38×10^{-5} mol, 29.9%) was crystallized by allowing a saturated toluene solution to slowly evaporate.

Preparation of $(Cp^*Ti)_4O_5Cl_2$. Titanium tetrachloride (23 mg, 13 μL, 1.2×10^{-4} mol) was added to 50 mL of toluene in a dropping funnel. This solution was added dropwise over a 30-min period to $(Cp^*Ti)_4O_6$ (0.2 g, 2.4×10^{-4} mol) dissolved in 75 mL of toluene. The solution turned from bright yellow to orange-yellow. After it was stirred 30 min, the reaction solution was filtered from the fine precipitate that formed and the solvent was removed under vacuum. This crude product was dissolved in 20 mL of toluene, and the solvent volume was reduced to 5 mL. Yellow block-shaped crystals formed after cooling the solution to 4 °C for 10 h. A second crop of crystals was obtained by reducing the solvent volume to 3 mL. The crystals were combined and dried under vacuum to give $(Cp^*Ti)_4O_5Cl_2$ (101 mg, 1.2×10^{-4} mol, 50%). Anal. Calcd for $C_{40}H_{60}Ti_4Cl_2O_5$: C, 54.38; H, 6.85; Ti, 21.69; Cl, 8.03. Found: C, 54.39; H, 6.85; Ti, 21.75; Cl, 7.99. IR (Nujol, 1000–400 cm^{-1}): 785 (s), 725 (s), 625 (w), 515 (w), 435 (m). ^1H NMR ($CDCl_3$, 0.01 M, 17 °C): δ 2.08 and 1.99 with an integrated intensity ratio of 1:1. $^{13}C\{^1H\}$

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NMR ($CDCl_3$, 0.05 M, 17 °C): η^5-$C_5(CH_3)_5$, δ 125.33, 125.00; η^5-$C_5(CH_3)_5$, δ 12.30, 11.47. Field desorption mass spectrum: m/z 882.

Preparation of $(Cp^*Ti)_3O_3Cl_3$ (4). (Pentamethylcyclopentadienyl)titanium trichloride (1.00 g, 3.46×10^{-3} mol) was dissolved in 50 mL of acetone, and the solution was heated to reflux with stirring. Deionized water (8 mL) was added to the refluxing reaction solution dropwise over 15 min. An orange crystalline precipitate formed during the course of water addition. This product was collected by filtration and allowed to air-dry, giving $(Cp^*Ti)_3O_3Cl_3$ (0.74 g, 1.05×10^{-3} mol, 91.4%). Anal. Calcd for $C_{30}H_{45}Ti_3Cl_3O_3$: C, 51.19; H, 6.40; Ti, 20.44; Cl, 15.15. Found: C, 51.13; H, 6.24; Ti, 20.33; Cl, 15.24. IR (Nujol, 1000–400 cm^{-1}): 780 (s, br), 730 (sh), 630 (w), 455 (m), 445 (sh). ^1H NMR ($CDCl_3$, 0.01 M, 17 °C): δ 2.12 and 2.10 with an integrated intensity ratio of 2:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 0.02 M, 17 °C): η^5-$C_5(CH_3)_5$, δ 128.90 and 128.22; η^5-$C_5(CH_3)_5$, δ 12.40 and 12.11. Field desorption mass spectrum: m/z 704.

Reaction of $(Cp^*Ti)_4O_5Cl_2$ with $TiCl_4$. Titanium tetrachloride (5.4 mg, 3.1 μL, 2.8×10^{-5} mol) was added to 50 mL of toluene in a dropping funnel. This solution was added dropwise over 30 min to $(Cp^*Ti)_4O_5Cl_2$ (0.1 g, 1.1×10^{-4} mol) dissolved in 100 mL of toluene. The solution changed color from yellow to orange. After it was stirred for 15 min, the reaction solution was filtered from the fine precipitate that formed and the solvent was removed under vacuum. The solid was dissolved in 20 mL of toluene, and the solvent volume was reduced to 5 mL. Yellow block-shaped crystals of **2** formed after cooling the solution to 4 °C for 10 h. After the solvent volume was reduced to 3 mL and cooled to 4 °C for 10 h, red block-shaped crystals of $(Cp^*Ti)_2OCl_4$ (**5**; 8 mg, 1.53×10^{-5} mol, 7%) formed. Anal. Calcd for $C_{20}H_{30}Ti_2Cl_4O$: C, 45.84; H, 5.77; Ti, 18.28; Cl, 27.06. Found: C, 45.85; H, 5.79; Ti, 18.23; Cl, 27.08. ^1H NMR ($CDCl_3$, 0.02 M, 17 °C): δ 2.28. Field desorption mass spectrum: m/z 524. The volume of the remaining solution was reduced to 2 mL and cooled to −20 °C for 10 h. An orange powder precipitated from solution. The components of this material were identified by ^1H NMR and mass spectroscopy as $(Cp^*Ti)_2OCl_4$ (**5**) and $(Cp^*Ti)_4O_4Cl_4$ (**3**). ^1H NMR ($CDCl_3$, 17 °C): δ 2.28 and 2.15. Field desorption mass spectrum: m/z = 524, 938.

Reaction of $(Cp^*Ti)_4O_6$ with >0.5 Equiv of $TiCl_4$. Titanium tetrachloride (22.8 mg, 13.2 μL, 1.2×10^{-4} mol) was added to 50 mL of toluene in a dropping funnel. This solution was added dropwise over 30 min to $(Cp^*Ti)_4O_6$ (0.1 g, 1.2×10^{-4} mol) dissolved in 100 mL of toluene. The solution turned from yellow to orange. After it was stirred for 15 min, the reaction solution was filtered to remove the fine precipitate that formed, and the solvent was removed under vacuum. The ^1H NMR spectrum of this material ($CDCl_3$, 17 °C, see Figure 2) showed resonances at 2.88, 2.15, 2.12, 2.10, 2.08, and 1.99 ppm with relative integrated intensities 3.8, 3.7, 2.0, 1.0, 4.8, and 5.0, respectively.

Results

Synthesis and Characterization of $(Cp^*Ti)_4O_6$ (1). Although $(Cp^*Ti)_4O_6$ can be prepared from moist silver oxide and halide complexes such as Cp^*TiCl_3 and $(Cp^*Ti)_4O_5Cl_2$, it is obtained in best yield (>65%) as a yellow crystalline material by hydrolysis/condensation under basic conditions according to eq 4.

$$4Cp^*TiCl_3 + 12OH^- = (Cp^*Ti)_4O_6 + 12Cl^- + 6H_2O \qquad (4)$$

Compound **1** is formulated on the basis of elemental analysis and mass spectral data. The tetrahedral structure shown in Figure 1 has been established for compound **1** in the solid state[4] and contains the same Ti_4O_6 observed in $[Ti_4(C_6H_{15}N_3)_4O_6]Br_4 \cdot 4H_2O$.[10] Multinuclear ($^1H$, $^{13}C\{^1H\}$, and ^{17}O) NMR spectral data provide support for the same structure in solution.

The $(Cp^*Ti)_4O_6$ molecule is very stable toward bases such as potassium hydroxide and methyllithium in toluene at ambient temperature. It does react, however, with acids such as HCl and $TiCl_4$ to ultimately form Cp^*TiCl_3.

Synthesis and Characterization of $(Cp^*Ti)_3O_3Cl_3$ (4). Hydrolysis/condensation of Cp^*TiCl_3 in refluxing acetone proceeds according to eq 5, where the product has been formulated by using elemental analysis and mass spectral data. Since its ^1H NMR

$$3Cp^*TiCl_3 + 3H_2O = Cp^*_3Ti_3O_3Cl_3 + 6HCl \qquad (5)$$

spectrum displays two resonances having relative intensities of 2:1 in the pentamethylcyclopentadienyl region, compound **4** is

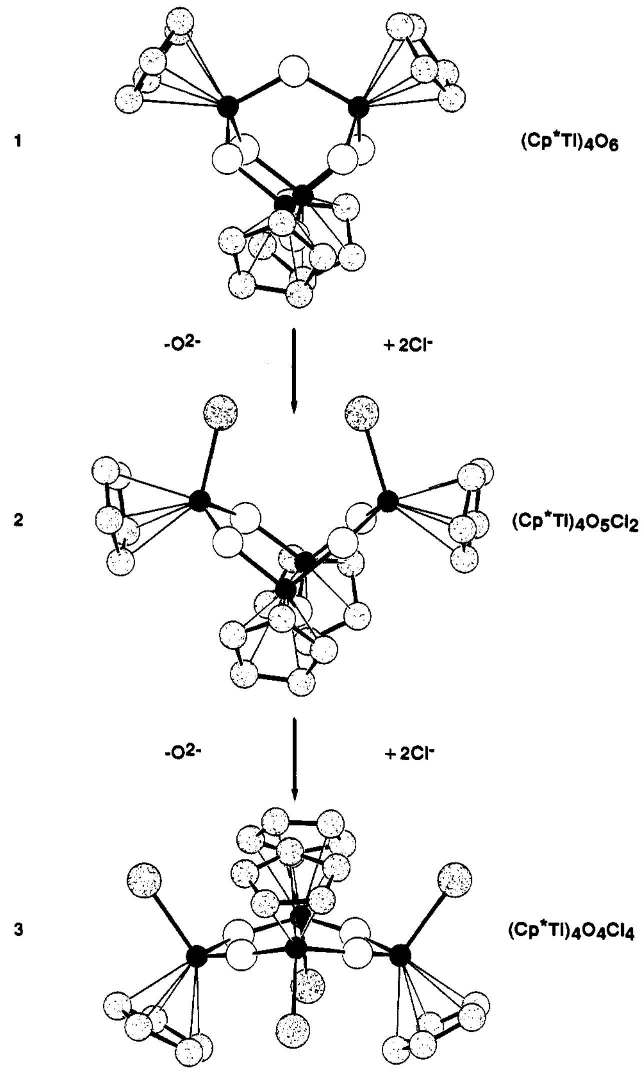
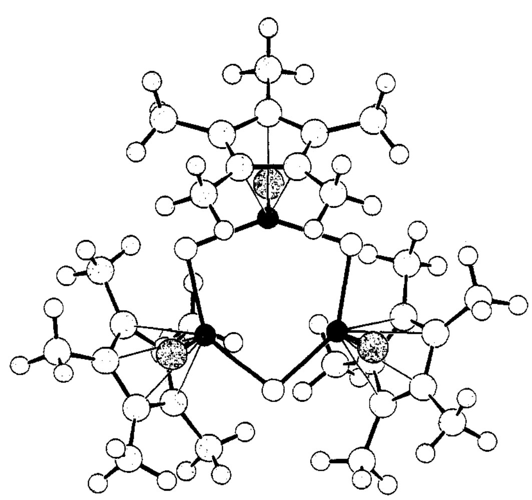


Figure 1. Scheme showing the structures and stoichiometric relationships between $(Cp^*Ti)_4O_6$ (**1**), $(Cp^*Ti)_4O_5Cl_2$ (**2**), and $(Cp^*Ti)_4O_4Cl_4$ (**3**). Titanium atoms are represented by small filled spheres, oxygen atoms by larger open spheres, carbon atoms by lightly shaded spheres, and chlorine atoms by heavily shaded spheres. Methyl groups have been omitted from the pentamethylcyclopentadienyl groups for clarity.

assigned the structure established crystallographically for $Cp^*_3Ti_3O_3(CH_3)_3$:[11]



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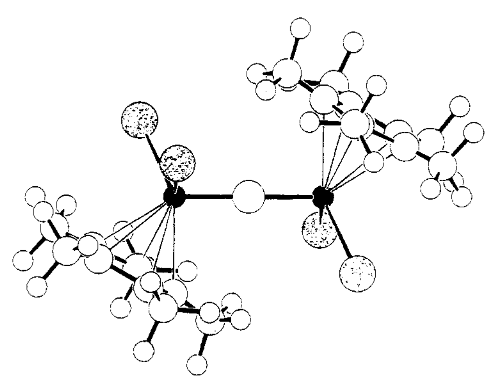
Two unusual features of eq 5 deserve special mention. First, the product observed under acidic conditions is different from the product obtained under basic conditions (see eq 4). Second, the product observed when $C_5H_5TiCl_3$ or $C_5H_4CH_3TiCl_3$ is hydrolyzed in acetone is tetrameric, not trimeric as in eq 5.[12,13]

Synthesis and Characterization of $(Cp^*Ti)_4O_5Cl_2$ (2). Reaction of $(Cp^*Ti)_4O_6$ with up to 0.5 equiv of $TiCl_4$ in toluene solution quantitatively yields a single soluble Cp*-containing product according to ^1H NMR spectroscopy. This yellow material has been isolated, crystallized, and formulated as $(Cp^*Ti)_4O_5Cl_2$ (**2**) from analytical and mass spectral data. Mass balance considerations imply that $TiCl_4$ is converted to TiO_2:

$$2(Cp^*Ti)_4O_6 + TiCl_4 = 2(Cp^*Ti)_4O_5Cl_2 + TiO_2 \quad (6)$$

The $(Cp^*Ti)_4O_5Cl_2$ molecule displays two ^1H NMR methyl resonances at δ 2.08 and 1.99 having equal intensities and is assigned the structure shown in Figure 1. The upfield resonance is assigned to the central Cp^*TiO_3 methyl groups since the methyl resonance for the Cp^*TiO_3 methyl groups in $(Cp^*Ti)_4O_6$ have a similar chemical shift value, δ 1.97. The chemical shift of the resonance assigned to the peripheral Cp^*TiO_2Cl methyl groups is in good agreement with values observed for Cp^*TiO_2Cl groups in compound **4**, δ 2.12 and 2.10.

Reaction of $(Cp^*Ti)_4O_5Cl_2$ (2) with $TiCl_4$. When $(Cp^*Ti)_4O_5Cl_2$ reacts with $TiCl_4$ or $(Cp^*Ti)_4O_6$ reacts with >0.5 equiv of $TiCl_4$, five different compounds are observed in the reaction solution by ^1H NMR spectroscopy. Spectral assignments are based on data given in the Experimental Section. The structures and ^1H NMR spectra of two compounds, $(Cp^*Ti)_4O_5Cl_2$ (**2**) and $(Cp^*Ti)_3O_3Cl_3$ (**4**) are described in this paper (see above). The synthesis and characterization of a third compound, Cp^*TiCl_3 (**6**), have been reported in ref 5. The remaining two compounds have been isolated from the reaction mixture and characterized by ^1H NMR spectroscopy and mass spectroscopy. The first, $(Cp^*Ti)_2OCl_4$ (**5**), has been obtained in analytically pure, crystalline form and assigned the structure adopted by its cyclopentadienyl analogue, $[(C_5H_5)TiCl_2]_2O$:[14-16]



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The second, $(Cp^*Ti)_4O_4Cl_4$ (**3**), was not isolated in pure form but could be formulated from the mass spectrum of a sample containing both compounds **3** and **2**. It displays a single ^1H NMR resonance and is assigned the structure established for its cyclopentadienyl and methylcyclopentadienyl analogues[12,13] (see Figure 1).

The ^1H NMR spectrum shown in Figure 2 characterizes the type of product distributions obtained when $TiCl_4$ reacts with $(Cp^*Ti)_4O_5Cl_2$ or $(Cp^*Ti)_4O_6$. Here, $TiCl_4$ has reacted with 1 equiv of $(Cp^*Ti)_4O_6$ to yield compounds **2–5** in 39, 15, 16, and 30% yields, respectively. These percentages reflect complete incorporation, within experimental accuracy, of $TiCl_4$ chloride ligands into Cp*Ti complexes **2–5**.

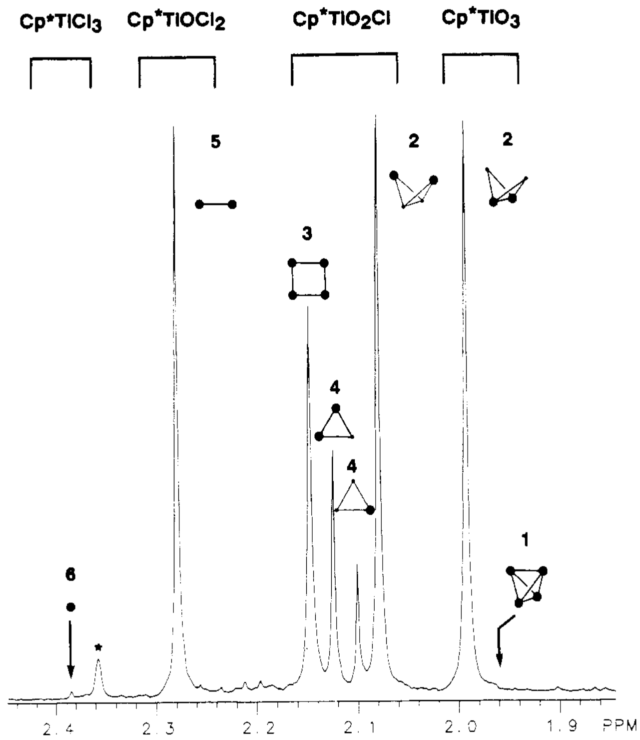

Figure 2. ^1H NMR spectrum of a mixture of compounds produced by the reaction of $(Cp^*Ti)_4O_6$ with 1 equiv of $TiCl_4$ as described in the Experimental Section. The principal resonances have been assigned to compounds **2–5** as described in the text. Simplified structural drawings are employed, where lines represent bridging oxo groups and dots represent the Cp^*TiCl_x group, x = 0–2. For compounds **2** and **4**, two nonequivalent types of Cp* groups are present in each case, and the specific Cp* groups assigned to each resonances are identified by the set of larger dots. The position of resonances observed for Cp^*TiCl_3 (**6**) and $(Cp^*Ti)_4O_6$ (**1**) are indicated by arrows; a residual toluene resonance is labeled with an asterisk. For numerical data, see the Experimental Section.

Discussion

The fact that hydrolysis/condensation of Cp^*TiCl_3 yields a completely condensed cage compound under basic conditions (see eq 4) and a less highly condensed ring compound under acidic conditions (see eq 5) is possibly of general interest. It is well-known that sol–gel polymerization under basic conditions promotes highly condensed oxide networks, whereas acidic conditions favor less highly cross-linked materials.[17] The hydrolysis/condensation of homoleptic chloride and alkoxide complexes yields, however, a vast number of reaction products, and molecular growth pathways are consequently difficult to delineate. Compounds such as Cp^*TiX_3, X = halide or alkoxide, contain inert substituents that simplify hydrolysis/condensation product distributions and may therefore serve as useful model compounds for understanding molecular growth pathways in sol–gel polymerization.

The degradation scheme shown in Figure 1 can be viewed as a specific example of a more general scheme where opposite edges of tetrahedral cages such as P_4, P_4S_{10} = $(SP)_4S_6$, and P_4O_{10} = $(OP)_4O_6$ are successively cleaved.[18] The case of $(OP)_4O_6$ hydrolysis has been studied in some detail.[19-21] Although the bicyclic

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species $H_2P_4O_{11}$ corresponding to **2** in Figure 1 is not observed, the cyclic species $H_4P_4O_{12}$ corresponding to **3** in Figure 1 is obtained in high yield, thus implicating the bicyclic acid as an intermediate. Breakdown of the $(Cp^*Ti)_4O_6$ cage proceeds in a similar manner: the bicyclic species **2** is produced in quantitative yields, but the cyclic species **3** has been produced only in low yields, even when lower temperatures or reagents such as $TiCl_4(CH_3CN)_2$[7] are employed.

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Cyclopentadienylvanadium Carbonyl Derivatives as Precursors to Vanadium Carbide

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The vapor of $V(Cp)(CO)_4$ (Cp is η^5-C_5H_5) reacted at a 280–350 °C substrate to produce a vanadium-containing deposit with the formation of volatile $V(Cp)_2$ as a byproduct. The IR spectrum of this deposit on a CaF_2 substrate showed bands characteristic of coordinated cyclopentadiene. When deposited on a quartz substrate, this vanadium-containing material by heating to 700 °C was converted to shiny, metallic-looking V_4C_3, which contains excess carbon. $V(Cp)(CO)_4$ reacted photochemically with NH_3 to produce the new compound $V(Cp)(CO)_3(NH_3)$. This nonvolatile compound lost NH_3 upon sublimation at 200 °C. The residue from this sublimation was thermally converted to V_4C_3 as the main constituent by heating to 800 °C. The vanadium dimer $V_2(Cp)_2(CO)_5$ reacted thermally with NH_3 to produce a solid product that appeared to be a mixture of $V(Cp)(CO)_3(NH_3)$ and $[V(Cp)(NH_3)]_x$. Pyrolysis of this solid resulted in the evolution of all of the NH_3 and produced V_4C_3. The thermal conversion of cyclopentadienylvanadium compounds to vanadium carbide is postulated to go through an intermediate in which bound cyclopentadiene is dehydrogenated, and this reaction results in the incorporation of an excess of carbon over the stoichiometric amount in the final product.

Introduction

The development of novel methods for the synthesis of the carbides, nitrides, borides, and silicides of groups 4–6 of the periodic table is an area of current interest. Of particular importance is the development of synthetic methods leading to these refractory materials in useful shapes or forms such as fibers, whiskers, or films. The metalloorganic compounds of these metals appear to be attractive precursors to these desirable materials, since they can be more readily processed than the traditional powdered metal or metal oxide starting materials. Some of these considerations have been discussed in a recent symposium on materials chemistry.[1,2]

The chemistry of cyclopentadienylvanadium compounds has been examined as a part of an effort[3–5] to develop general methods for the preparation of the important materials noted above. Pioneering work in this area includes that of Bulloff[6a] and Norman and Whaley,[6b] who were apparently the first to recognize the potential of organometallic compounds as precursors for the vapor deposition of vanadium-containing species. As late as the early 1980s, only a few reagents suitable for the chemical vapor deposition (CVD) of vanadium-containing species have been reported.[7] Several mechanistic studies of the thermal decomposition of dicyclopentadienylvanadium compounds have been described.[8–11] In one of these the residue was reported to contain only vanadium and carbon.

The present study was undertaken to elucidate and confirm the reports describing the production of coatings via the pyrolysis of $V(Cp)(CO)_4$ (Cp is η^5-C_5H_5). In addition, we wanted to examine the possibility of producing suitable precursors to vanadium nitride via photoassisted displacement of CO by NH_3 in $V(Cp)(CO)_4$.

Experimental Procedure

Chemicals and Methods. Experiments in liquid ammonia were carried out in electronic grade ammonia that was further purified by contact with metallic sodium. Tetrahydrofuran (THF) was dried and purified by refluxing over lithium aluminum hydride with triphenylmethane indicator and was freshly distilled before use. Hexane was dried over calcium sulfate and distilled immediately before use. Toluene was refluxed over Na/benzophenone and distilled immediately before use. Commercially available $V(Cp)(CO)_4$ (Alfa Inorganics) was purified by sublimation at 50 °C and 5×10^{-3} Torr. The purified material was protected from light and stored in an inert-atmosphere glovebox. $V_2(Cp)_2(CO)_5$ was prepared by the procedure described by Lewis et al.[12] and identified by the ν_{CO} stretch region of the IR spectrum. All other chemicals were of locally available reagent grade and were used without further purification. Boron nitride substrates were machined from 1 in. diameter, binderless, hot-pressed stock which was obtained from Atlantic Equipment Engineers. Glassware was oven-dried before use. All manipulations were conducted in the helium atmosphere of a Vacuum Atmospheres Co. glovebox (oxygen and water <1 ppm), on a vacuum line, or in sealed vessels sparged with an inert gas.

Instruments and Analyses. Infrared spectra were run on a Digilab Model 60 FTIR spectrometer. Spectra of solids were obtained as KBr pellets which were prepared in the glovebox. Solution spectra were run in 0.1 mm path length NaCl solution cells; gas-phase spectra were obtained in a conventional vacuum-tight gas cell having KBr windows. IR

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