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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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spectra of films deposited on CaF_2 plates (1-in. diameter, Harshaw) were run in a vacuum-tight holder with NaCl windows. The sample was loaded in the glovebox and evacuated before obtaining the spectrum. UV–vis spectra were obtained on a Cary Model 17D spectrometer. Mass spectra were obtained on a Hewlett-Packard Model 5970 mass-selective detector. Crystalline solid phases were identified by X-ray diffraction of powder samples using a Scintag PAD V X-ray diffractometer. Combustion analyses for carbon, hydrogen, and nitrogen were determined by Galbraith Laboratories, Knoxville, TN. Carbon in refractory materials was determined by the Oak Ridge National Laboratory Analytical Chemistry Division using a LECO carbon analyzer. Vanadium was determined by Galbraith Laboratories using atomic absorption spectroscopy and by ICP spectroscopy or neutron activation analysis at Oak Ridge. The vanadium content of films on quartz or boron nitride substrates were determined by dissolving the film in hot 70% perchloric acid, and after cooling, the vanadium was determined spectrophotometrically as the yellow phosphotungstovanadate ion.[13]

Photochemical Experiments. Samples for preparative-scale photolyses were irradiated with the full output of a medium-pressure 150-W Hg arc lamp, filtered only by the Pyrex walls of the reaction vessel; the samples were continuously cooled with a stream of air. Spectroscopic-scale photolysis was carried out with an optical train consisting of a 450-W Xe arc lamp, a $^1/_4$-m monochromator, and the necessary lenses, filters, and shutter. The photon flux at 400 ± 20 nm was estimated with a Scientech Model 362 power meter with Model 38-0001 sensor head. The quartz cell for quantum yield estimation has a 2-cm path for irradiation and a side arm with a 0.5-cm path for spectroscopic observation.

Reactions in Liquid Ammonia. Heavy-walled Pyrex ampules were used to safely contain liquid ammonia.

Preparation of $V(Cp)(CO)_3(NH_3)$. A 1-mmol sample of $V(Cp)(CO)_4$ was loaded into an ampule in the inert-atmosphere glovebox, 10 g of ammonia was added by distillation, and the reaction mixture was sealed under vacuum. As the mixture warmed to room temperature, the vanadium compound dissolved, giving an orange solution. The reaction ampule was irradiated for 8–11 h, during which time the solution turned deep red. The ampule was then returned to the vacuum line, and the quantity of noncondensable gas generated during the reaction was measured. The ammonia was removed by vacuum transfer, the solid was pumped for several hours at room temperature, and the evacuated ampule was taken into the glovebox to isolate the solid. Mechanical losses due to the geometry of the ampule and due to the product sticking to the walls of the ampule were generally rather large, and a typical yield was 57%. Anal. Calcd for $C_8H_8NO_3V$: C, 44.26; H, 3.71; N, 6.45; V, 23.46. Found: C, 40.55; H, 3.71; N, 5.44; V, 21.53. A second independent analysis gave 23.94% vanadium.

Reaction of $V_2(Cp)_2(CO)_5$. A sample of the vanadium dimer was loaded into an ampule in the glovebox and then loaded with ammonia as described above. As the ammonia melted to a liquid, the solution color changed from the original green color of the dimer to yellow and finally to deep red. From the color changes the reaction appeared to be complete after 1 h at room temperature although the ampule was allowed to stand overnight. The noncondensable gas was measured and the solid was isolated as described above. As will be discussed below, this solid is formulated as a mixture of compounds.

Vacuum Pyrolysis and CVD Experiments. Vacuum pyrolyses were generally done in 100 °C stages starting at 200 °C and progressing up to 800 °C, and the apparatus consisted of a quartz tube within a tube fitted with a stopcock. The inner tube was preweighed to allow easy determination of weight loss following pyrolysis. Condensable products were collected in a liquid nitrogen cooled U-trap for identification and quantification. The pyrolysis of $V(Cp)(CO)_4$ was carried out with a tube that allowed a substrate to be supported in the center of the furnace at a controlled temperature. Vapor of the reactant was generated by heating the solid to 60–80 °C, and the vapor was forced to impinge upon the substrate with a base pressure of 5×10^{-3} Torr. Following the initial deposition reaction, the substrate could be removed for spectroscopic examination or further reacted at higher temperature.

Results and Discussion

Reaction of $V(Cp)(CO)_4$. Norman and Whaley[6b] reported the use of cyclopentadienylvanadium compounds such as $V(Cp)(CO)_4$ and $V(Cp)_2Cl_2$ as reagents for the vapor deposition of vanadium coatings. This reference did not describe the analytical methods but stated that the films contained vanadium and carbon. In the work reported here, the pyrolysis of $V(Cp)(CO)_4$ has been repeated. The vapor of this compound was allowed to impinge upon a quartz disk heated to 350 °C. After all of the compound had reacted (or passed through the apparatus unreacted), the temperature of the disk was raised to 700 °C and allowed to stand at this temperature under vacuum for about $^1/_2$ h. This procedure produced a shiny, metallic-looking dark film on the disk and walls of the quartz tube. The circumstances of the deposition made it difficult to quantify the extent of reaction or the volatiles evolved. Nonetheless, very little HCp was evolved, and a major product was vanadocene, $V(Cp)_2$. The presence of this vanadium compound was confirmed by its IR spectrum,[14] and the quantity evolved was determined from visible spectroscopy[15] in toluene. The quantitative determination was achieved by trapping the product and removing the trap to the glovebox, where the solid was dissolved in a measured volume of oxygen-free toluene for spectroscopy. This analysis indicates 33% of the starting $V(Cp)(CO)_4$ was recovered as $V(Cp)_2$. The IR spectrum of the noncondensable gas evolved during the reaction showed the presence of CO.

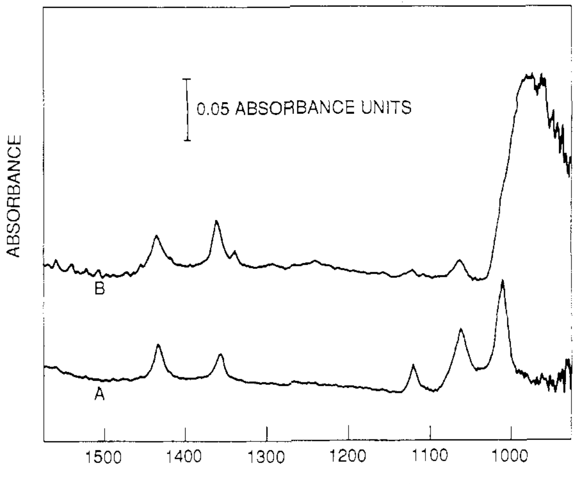

Figure 1. Infrared spectra of the deposit formed by the reaction of V(Cp)(CO) vapor at a CaF_2 substrate: (A) spectrum of the initial deposit formed at 280 °C; (B) spectrum following air oxidation.

Glancing-angle diffraction of the film on this quartz plate indicated it was amorphous. However, some of the film was removed from the surface of the quartz with dilute HF, and XRD of this material indicated the presence of V_4C_3. Analysis of the film for vanadium content was achieved by carrying out the deposition on a preweighed quartz disk and subsequently dissolving the film. This analysis indicated the vanadium content was 54 ± 1%, a value far lower than the theoretical value of 84.97% for V_4C_3. The atom ratio of carbon to vanadium was determined in a separate experiment. A boron nitride disk was coated under the same conditions as the quartz substrate. The disk was divided to analyze for carbon and vanadium, finding that the atomic ratio of C to V was 2.75. Given this result and assuming the same composition on quartz and boron nitride, it is found that the vanadium and carbon analyses account for 89% of the deposit. The difference from 100% not only reflects the experimental limitations of the procedure but also would suggest the presence of oxygen as an additional component.

The infrared spectrum of the initial deposit formed by the reaction of $V(Cp)(CO)_4$ at 280 °C is shown in Figure 1A. Calcium fluoride is transparent to infrared radiation above 900 cm^{-1}, and with this material as the substrate the spectrum of the initially formed product could be obtained. Sharp bands occur at frequencies characteristic of C–C stretching and C–H bending vibrations, and these are assigned to bound cyclopentadiene.[16]

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There were no bands in the region characteristic of CO stretching vibrations. This is evidence that all of the CO bound to vanadium in the starting compound was either lost or converted to a solid vanadium–oxygen species. The film on the CaF_2 substrate was exposed to air for various periods of time, and the IR spectrum was again recorded after each exposure. Large bands appear at 979 and 958 cm^{-1}, as shown in Figure 1B. These bands are at frequencies characteristic of a vanadium–oxygen stretching vibration.[17] The absence of the 979- and 958-cm^{-1} bands in the initial deposit is indicative of total loss of CO rather than the formation of a vanadium–oxygen species. However, the presence of a low-valent vanadium–oxygen species or the presence of lattice or interstitial oxygen cannot be excluded by this experiment.

When the initial deposit on CaF_2 was further heated to 570 °C, the weight loss was only ~3%, and this result is consistent with the loss of hydrogen from cyclopentadiene. The IR spectrum became featureless as expected for a lattice structure such as V_4C_3. After exposure to air overnight, weak peaks appeared at 1007 and 990 cm^{-1} in the IR spectrum, and they were assumed to be vanadium–oxygen stretching vibrations.

The patent literature[6b] suggested that vanadium metal was deposited at the temperature at which our reaction was carried out but that vanadium carbide was the product if the deposition was carried out at 700 °C. We have demonstrated that V_4C_3 is indeed formed after heating to 700 °C, but the initial low-temperature deposition product appears to be a polymeric cyclopentadienyl complex of vanadium. The infrared spectrum shows the presence of cyclopentadiene in the initial deposit, and the weight loss and spectrum following the 570 °C heat treatment suggest the vanadium cyclopentadiene deposit is dehydrogenated to a lattice structure.

Preparation and Reactions of $V(Cp)(CO)_3(NH_3)$. Cyclopentadienylvanadium tetracarbonyl is known to readily photosubstitute phosphines, alkanedienes, or alkynes for CO.[18] If CO could be substituted by ammonia, it may be possible to create a precursor to vanadium nitride. Although this postulation was not demonstrated, the chemistry of cyclopentadienylvanadium was changed by bonding NH_3 to V. In the absence of light, $V(Cp)(CO)_4$ reacts neither with liquid NH_3 nor with NH_3 when dissolved in THF. However, the photosubstitution of $V(Cp)(CO)_4$ by NH_3 occurs readily in liquid NH_3 and in THF solution under 1-atm pressure of NH_3.

A solid product was isolated following the photoreaction of the vanadium carbonyl compound in liquid ammonia. This product proved to be unstable in the solid state, and unfortunately a satisfactory analysis was never obtained. Nonetheless, the atom ratios from elemental analysis suggested the formulation $V(Cp)(CO)_3(NH_3)$. Further support for this formulation comes from the quantity of CO evolved in the photoreaction. In the average of three separate experiments, 1.04 ± 0.03 mol of CO/mol of $V(Cp)(CO)_4$ was evolved. A spectroscopic-scale experiment in THF solution indicated the quantum yield for photosubstitution was near unity. Furthermore, four isosbestic points were observed in the conversion of the starting material to the product, indicating there were no appreciable concentrations of other species in solution. The IR spectrum of the photoproduct generated in situ in THF shows bands at 1956 and 1845 cm^{-1}. This spectrum is analogous to that observed for monosubstituted vanadium cyclopentadienyl compounds, $V(Cp)(CO)_3L$.[19] The visible spectrum and the IR spectrum in the ν_{CO} stretch region of the solid product isolated from liquid ammonia, when dissolved in THF, are identical with those of the primary photoproducts generated in THF solution. The solid product loses weight slowly, and analysis indicates the solid is losing ammonia. Assuming the weight loss is entirely ammonia loss, the half-life is 60 days. The solid product remaining after NH_3 loss was not identified although sublimation experiments and the IR spectrum in THF solution suggest one of the products is $V(Cp)(CO)_4$.

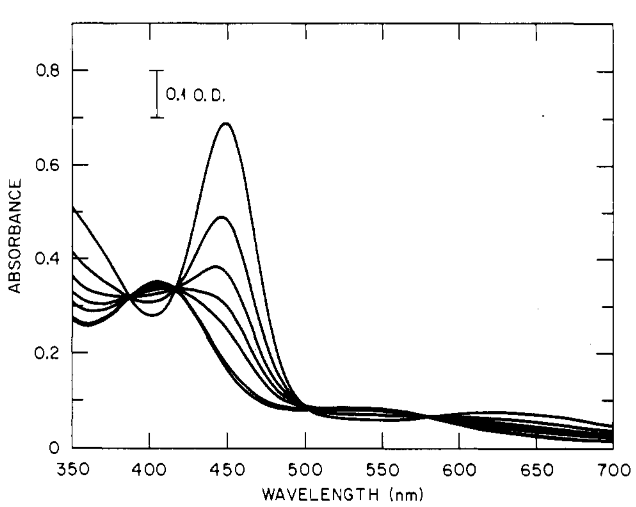

Figure 2. Visible spectra at various times during the reaction of $V_2(Cp)_2(CO)_5$ with NH_3. The absorption maxima at 630 and 488 nm decrease as the maxima due to the product $V(Cp)(CO)_3(NH_3)$ appear at 540 and 406 nm.

Sublimation of $V(Cp)(CO)_3(NH_3)$ at 200 °C results in loss of ammonia; 0.97 mol of ammonia/mol of vanadium is lost. The weight of the residue plus the weight of condensable gases subtracted from the weight of starting compound indicates approximately 2 mol of CO/mol of vanadium is also lost. The IR spectrum of the sublimation residue shows bands at 2020, 1948, and 1912 cm^{-1}. The solid may contain an oligomer of V(Cp)(CO), although the IR spectra are not consistent with any previously reported compounds. The tetrameric cluster compound $V_4(Cp)_4(CO)_4$ and the trinuclear compound $V_3(Cp)_3(CO)_9$ have been reported in the literature.[20] None of the bands noted above are in agreement with those reported for these cluster compounds. Pyrolysis of the residue of the sublimation of the monoammine compound to 800 °C results in the evolution of some C_5H_6. X-ray diffraction shows the solid contains V_4C_3, although chemical analysis indicates the sample contains 29.3% carbon, an excess over the stoichiometric amount.

Pyrolysis to 800 °C of a sample of $V(Cp)(CO)_3(NH_3)$ that had been allowed to age for about $1^1/_2$ half-lives in the glovebox produced a metallic-looking mirror on the walls of the quartz reaction tube. The residue was identified by XRD as V_4C_3 although analysis of the solid for vanadium gave a relatively low value (56.8%), indicating the probable contamination by excess carbon. The mirror was removed with dilute HF, and it was identified as V_4C_3 by XRD.

Reactions of $V_2(Cp)_2(CO)_5$. The chemistry of dicyclopentadienyldivanadium pentacarbonyl with ammonia was investigated as a possible way to substitute more than one ammonia at the vanadium center of cyclopentadienylvanadium compounds. The photolysis of $V(Cp)(CO)_4$ in THF with a stream of inert gas to remove CO from solution results in the formation of the divanadium species. Since the photochemistry of the mononuclear vanadium carbonyl complex is limited to the substitution of a single CO ligand, it was hoped that this prephotolysis dimer formation would allow substitution of more than one CO per V to occur. This divanadium compound reacts thermally with ammonia either in liquid ammonia at room temperature or in THF solution in the presence of an atmosphere of NH_3. Measurement of the quantity of gas evolved indicates 1 mol of CO/mol of dimer was evolved. A solid product was obtained by evaporation of the ammonia. The IR spectrum of this solid in THF solution indicated the only CO-containing species was $V(Cp)(CO)_3(NH_3)$, and the ratio was approximately 1 mol of ammine complex/mol of dimer. Elemental analysis of the solid isolated from liquid ammonia

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indicates the approximate composition is a mixture of 1 mol of $V(Cp)(CO)_3(NH_3)$ and 1 mol of $V(Cp)(NH_3)$.

The reaction of $V_2(Cp)_2(CO)_5$ with NH_3 in THF solution takes an unusual course. More than 1 mol of ammine complex/mol of dimer reacted is produced. A spectroscopic-scale experiment (see Figure 2) indicates the stoichiometry

$$3V_2(Cp)_2(CO)_5 + 5NH_3 \rightarrow 5VCp(CO)_3(NH_3) + \text{“}V(Cp)\text{”}$$

As shown in Figure 2, four isosbestic points were maintained for over 90% of the reaction, indicating that intermediates do not build up to a significant level in solution. The isosbestic point at 500 nm shows a slight deviation after the fourth half-life. The one part in six of vanadium that does not end up incorporated as a monoammine complex apparently does not have a strong chromophore for visible spectroscopy. A plot of log $(A_t - A_\infty)$ vs time, where A_t and A_∞ are the 488-nm absorbances at time t and time infinity, respectively, was linear for over 4 half-lives, indicating the reaction is first order in the concentration of the dimer. The observed rate constant is 1.0×10^{-3} s^{-1} at ambient room temperature. Infrared spectroscopy in the ν_{CO} stretch region also indicates that $V(Cp)(CO)_3(NH_3)$ is the only CO-containing product of reaction of the vanadium dimer with NH_3 in THF.

Pyrolysis of the solid produced from reaction of the dimer with liquid ammonia was carried out to 800 °C. A 1-mol amount of NH_3/mol of vanadium along with some C_5H_6 was condensed in a liquid-nitrogen trap. The quantity of NH_3 evolved is in good agreement with the combustion analysis of the solid. The residue contains V_4C_3, as shown by XRD; however, analysis shows the solid contains 50.5% vanadium. This value is indicative of an excess of carbon over the stoichiometric amount.

Pyrolysis Pathway for Cyclopentadienylvanadium Compounds. The monoammine-substituted cyclopentadienylvanadium carbonyl loses ammonia and some CO at a relatively low temperature (<200 °C). This intermediate is probably an oligomeric $V(Cp)(CO)_x$ species whose composition is dependent on reaction conditions. At higher temperatures some of the cyclopentadiene is evolved from this intermediate, but none of the vanadium is lost as $V(Cp)_2$. The pyrolysis of $V(Cp)(CO)_4$ also leads to the loss of some Cp although it is in the form of $V(Cp)_2$ rather than CpH. In both cases an intermediate with less than one Cp per V is achieved. This is the species that is converted to V_4C_3 by pyrolysis to 800 °C. As will be discussed below, the intermediate contains more carbon than the stoichiometric amount required for V_4C_3, and this excess carbon remains in the solid in the form of amorphous carbon.

The thermal decomposition of several cyclopentadienylvanadium compounds has been reported in the literature. The decomposition of dicyclopentadienylvanadium compounds of the type $V(Cp)_2R_2$ or $V(Cp)_2R$, where R is an alkyl or aryl group, were studied in the solid state,[8-10] and the thermolysis of vanadocene was studied in the gas phase.[11] The latter study showed that methane and hydrogen were decomposition products of the cyclopentadiene ring at 500 °C and the solid decomposition products were catalysts for the decomposition reaction. The solid products were noted to be composed of pyrolytic vanadium that contained carbon and hydrogen. The work cited in ref 8–10 showed that decomposition of dicyclopentadienylvanadium compounds in the solid state occurs with evolution of hydrocarbons in which a bound cyclopentadienyl group is dehydrogenated. These reactions occurred by both intermolecular and intramolecular pathways depending on the R group. The residue from the decomposition reaction of $V(Cp)_2(C_6H_5)$ contained 12.8 carbon atoms per vanadium, a large excess of carbon over that required for stoichiometric vanadium carbide.

A process in which a bound cyclopentadienyl group is dehydrogenated to serve as a source of hydrogen for the evolution of C_5H_6 is probably occurring in the reactions studied in this work. This dehydrogenation reaction could be occurring via solid-state $(C_5H_{5-n})VH_n$ intermediates. After a Cp ring has been dehydrogenated, these carbon atoms are retained in the solid. Chemical analysis of the solid formed by reaction to 800 °C indicates a carbon retention corresponding to about 3.5 carbons per vanadium. This carbon to vanadium ratio is an excess over that required for the formation of stoichiometric V_4C_3. This excess carbon is assumed to be in the form of amorphous carbon. The vanadium is assumed to be in the form of V_4C_3, since this was the only form indicated by XRD. However the XRD analysis does not rule out the presence of an amorphous vanadium species.

Conclusion

The pyrolysis of cyclopentadienylvanadium tetracarbonyl produces vanadium carbide coatings in a reaction in which one-third of the vanadium is lost as $V(Cp)_2$. Infrared spectroscopy shows that an intermediate in the pyrolysis is a species containing vanadium bound to cyclopentadiene. By the bonding of NH_3 to V via a photochemical reaction, a nonvolatile precursor is produced. This substitution of NH_3 for CO changes the pyrolytic chemistry so that none of the vanadium is lost as vanadocene. These pyrolytic reactions proceed through an intermediate in which a bound Cp ring is dehydrogenated. Unfortunately this reaction leads to the incorporation of an excess of carbon over the stoichiometric amount. However these materials remain as useful precursors to metal carbides.

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Registry No. $V(Cp)(CO)_4$, 12108-04-2; $V(Cp)(CO)_3(NH_3)$, 119820-24-5; $V_2(Cp)_2(CO)_5$, 41699-43-8; $V(Cp)_2$, 1277-47-0; V_4C_3, 12076-63-0; $[V(Cp)(NH_3)]$, 119820-25-6.