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The synthesis of siloxide and silamide complexes of tantalum has been carried out and their reactivity with respect to bond breaking and aggregation phenomena has been studied. Types of reactions include carbon monoxide cleavage to dicarbides and ketenylidene, carbon monoxide reduction, ketyl formation, ether cleavage, ligation of pyridine and related adducts, hydrocarbon activations, routes to early metal nitrides, and formation of cubic tantalum nitride.

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**Final Report:** Synthesis and Reactivity of Siloxide and Silamide Complexes Pertaining to Bond Breaking and Aggregation Phenomena

AFOSR-87-0103  
88 NC 223

November 1, 1991

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## I. Introduction

Transition metal complexes that are highly reactive toward small molecule substrates possess a degree of coordinative and electronic unsaturation that typically renders them susceptible to aggregation.<sup>1-6</sup> The catalytic and stoichiometric reactivity exhibited by these molecules continues to be at the forefront of both organometallic and inorganic chemistry. Recently, the interface between the latter fields and materials science has emerged<sup>7</sup> as a burgeoning area of interdisciplinary research with significant applications.<sup>8</sup> Refractory transition metal compounds that possess attractive physical characteristics,<sup>8-12</sup> complexes manifesting non-linear optical properties,<sup>13-15</sup> inorganic/organometallic polymers,<sup>16-19</sup> and solid state compounds<sup>20,21</sup> with inherent electronic, magnetic, optical and superconducting properties<sup>22-26</sup> are representative of materials generating excitement due to their potential applications.

In this interdisciplinary field, new methods of materials synthesis are of primary importance, since conventional preparations<sup>20,21</sup> typically rely on high temperatures and pressures to achieve desirable conversion rates. Molecular or oligomeric precursors to solid state compounds, species that may directly lead to a desired product via low temperature chemical or thermal processing,<sup>27-34</sup> provide an intriguing alternative. For example, the hydrolysis of main group and early transition metal alkoxides (e.g.,  $[M(OR)_4]_n$ ;  $M = Si, Ti, Zr, \text{ etc.}$ ), the sol-gel process, has been used to prepare amorphous  $[MO_2]_x$  ceramic precursors at low temperatures.<sup>9-12</sup> A mechanistic comprehension of the sol-gel process is gradually developing,<sup>35-39</sup> primarily through the pioneering efforts of Klemperer, who has begun to assess the aggregation phenomena associated with silica growth. In addition, the chemical vapor deposition (CVD) of binary refractory metal compounds processes has also benefited from the molecular precursor approach.<sup>40-43</sup>

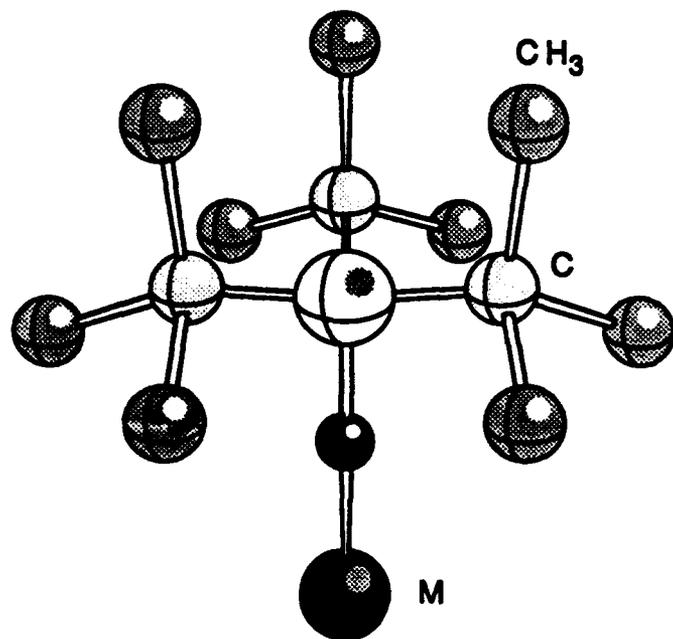
In order to design and understand the role of a molecular precursor, it is imperative to understand the chemistry of low-coordinate metal centers, for it is this characteristic that enables a molecular entity to aggregate. The chemistry in this proposal will lead to fundamental insights into the reactivity of coordinatively unsaturated metal centers, and will relate this information to the design of molecular precursors, and ultimately, new solid state compounds and materials. The specific area of investigation encompasses the chemistry of early transition metal-nitrogen bonds.

**A. Objectives.** This proposal consists of a blend of molecular and materials chemistry intended to further our understanding of metal-nitrogen bonds in both solid state and molecular compounds. The research encompasses the synthesis of compounds containing transition metal-nitrogen bonds, fundamental reactivity studies of molecular complexes, and investigations into the formation of solid state metal nitrides via molecular precursors.

Refractory metal nitrides serve as the solid state targets of this project. These materials are commonly prepared from the respective elements at high temperatures (e.g., cubic TiN, 1200°C; ZrN, 1200°C; HfN, 1400°C),<sup>21</sup> thereby representing a conspicuous challenge for alternative precursor methodologies. Furthermore, refractory metal nitrides are not as numerous as related oxides,<sup>20</sup> thus the probability of uncovering new kinetically stable materials is significant. The complementary nature of the materials/solid state and molecular chemistry will continue to serve as the foundation for the proposed research. The preparation of new molecular nitride complexes will necessarily precede their application as precursors toward the synthesis of solid state nitrides. Reactivity patterns and structures established for molecular imido, amido,<sup>44-46</sup> and nitride<sup>33,34</sup> complexes will lead to rational precursor methodologies. Furthermore, significant new insights into the mechanisms of nitride formation are anticipated. For example, the unusual carbon-hydrogen bond activations by molecular imides have provided a logical pathway by which carbide impurities are generated in solid state nitrides.<sup>21,42</sup> Herein the symbiotic relationship between the molecular and solid state chemistry programs will continue to be exploited for mutual benefit.

#### B. General Approach.

1. **Molecular Program.** The molecular program focuses on the synthesis and reactivity of complexes containing bulky alkoxide (tritox,  ${}^t\text{Bu}_3\text{CO}^-$ ),<sup>47-49</sup> siloxide (silox,  ${}^t\text{Bu}_3\text{SiO}^-$ ;<sup>50-59</sup>  $\text{Cy}_3\text{SiO}^-$ ,<sup>60</sup> Cy = cyclohexyl), silamide ( ${}^t\text{Bu}_3\text{SiNH}^-$ ), and silimide ( ${}^t\text{Bu}_3\text{SiN}^{2-}$ )<sup>44-46,61</sup> ligands. As shown by the illustration of tritox, silox, and  ${}^t\text{Bu}_3\text{SiNH}^-$ , these groups impose substantial steric constraints on a metal center, enabling the preparation of low-coordinate, highly



(tritox)M ( ${}^t\text{Bu}_3\text{COM}$ )

○ = C      ● = O

(silox)M ( ${}^t\text{Bu}_3\text{SiOM}$ )

○ = Si      ● = O

( ${}^t\text{Bu}_3\text{SiNH}$ )M

○ = Si      ● = NH

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reactive species. Since three-coordinate complexes and transients have provided examples of dramatic reactivity,<sup>44,54</sup> the synthesis of similar *new* derivatives is expected to also generate important advances. In addition, the final mechanistic details of C-H bond activation by M=N groups<sup>44-46</sup> will be addressed, and further reactivity studies of this functionality and related alkyl and silamides<sup>62-65</sup> are targeted.

A new emphasis will be placed on the construction of early transition metal nitrides analogous to polyoxoanions.<sup>66-68</sup> A new class of molecules, "polyamidoimidonitrides", will be prepared by controlled ammonolysis<sup>32-34,42</sup> of metal alkoxide/siloxide alkyls and the subsequent sterically directed clusterification of transient amides. The first examples of these complexes have just recently been prepared in these laboratories, and early reactivity studies indicate that a wealth of chemistry awaits exploration, including the application of these complexes as precursors to solid metal nitrides.

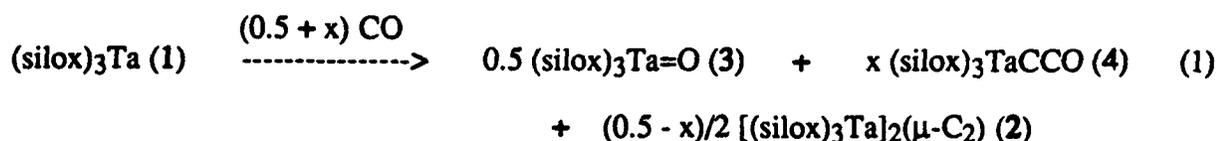
**2. Solid State Program.** The solid state chemistry of metal nitrides is being pursued in a three-pronged approach with an emphasis on the designed synthesis and mechanistic understanding of oligomeric and solid state materials prepared via ammonolysis,<sup>32-34,42</sup> the nitrogen equivalent of the hydrolytic sol-gel process:<sup>9-12</sup> 1) It has been shown that ammonolysis of  $\text{Np}_3\text{Ta}=\text{CH}^t\text{Bu}$  ( $\text{Np} = \text{CH}_2^t\text{Bu}$ )<sup>69</sup> results in metastable cubic TaN (*Fm3m*)<sup>70</sup> via a molecular pentamer,  $[\text{Np}_2\text{TaN}]_5$ .<sup>33,34</sup> The structural motif of cubic TaN is a three-dimensional extension of the  $\text{Ta}_2\text{N}_2$  squares in the pentamer, in contrast to the tantalum environments in hexagonal TaN (*P62m*),<sup>71</sup> the expected thermodynamic product.<sup>72</sup> Through appropriate <sup>15</sup>N labeling studies and solid state NMR monitoring,<sup>73</sup> spin echo experiments<sup>73-75</sup> designed to prove a direct relationship between the pentamer and cubic TaN will be conducted; 2) Designed oligomerizations of the aforementioned polyamidoimidonitrides will lead to new solid state and polymeric nitrides. Inorganic nitride clusters will be linked via organic and metallic spacers<sup>16-19</sup> to generate the new materials; 3) Using a unique melt technique,  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}$  ( $\text{Ln} = \text{lanthanide}$ )<sup>64,76</sup> has been subjected to ammonolysis to yield LnN. The properties of the LnN prepared in this fashion differ substantially from those synthesized via conventional high temperature techniques,<sup>77,78</sup> reflecting a greater purity. Variations of this technique promise to yield new phases of rare earth binary, ternary and rare earth/transition metal ternary nitrides. For example, heterobimetallic amidoimido complexes<sup>62-65</sup> will be prepared as stoichiometric "single stage" precursors for the synthesis of ternary nitrides.

**II. Summary of Results from Current AFOSR Support: Synthesis and Reactivity of Siloxide and Silamide Complexes Pertaining to Bond Breaking and Aggregation Phenomena (11/1/88-10/31/91; AFOSR-87-0103; 88 NC 223)**

For references pertaining to completed projects, consult the indicated publication.

**A. Carbon Monoxide Cleavage** - "Carbon Monoxide Cleavage by (silox)<sub>3</sub>Ta (silox = *t*-Bu<sub>3</sub>SiO<sup>-</sup>): Physical, Theoretical and Mechanistic Investigations." Neithamer, D.R.; LaPointe, R.E.; Wheeler, R.A.; Richeson, D.S.; Van Duyne, G.D.; Wolczanski, P.T. *J. Am. Chem. Soc.* 1989, 111, 9056-9072. Project completed 3/89.

The most widely accepted initial step of the Fischer-Tropsch (F-T) reaction, the conversion of synthesis gas (CO + H<sub>2</sub>) to hydrocarbons, is believed to be the dissociative adsorption of carbon monoxide to give a surface carbide (C<sub>s</sub>) and oxide (O<sub>s</sub>), a process modeled by the carbonylation of (silox)<sub>3</sub>Ta (1). An extensive investigation into the mechanism of CO cleavage by 1 (eq 1) to afford the dicarbide [(silox)<sub>3</sub>Ta]<sub>2</sub>(μ-C<sub>2</sub>) (2), oxo (silox)<sub>3</sub>Ta=O (3), and ketenylidene

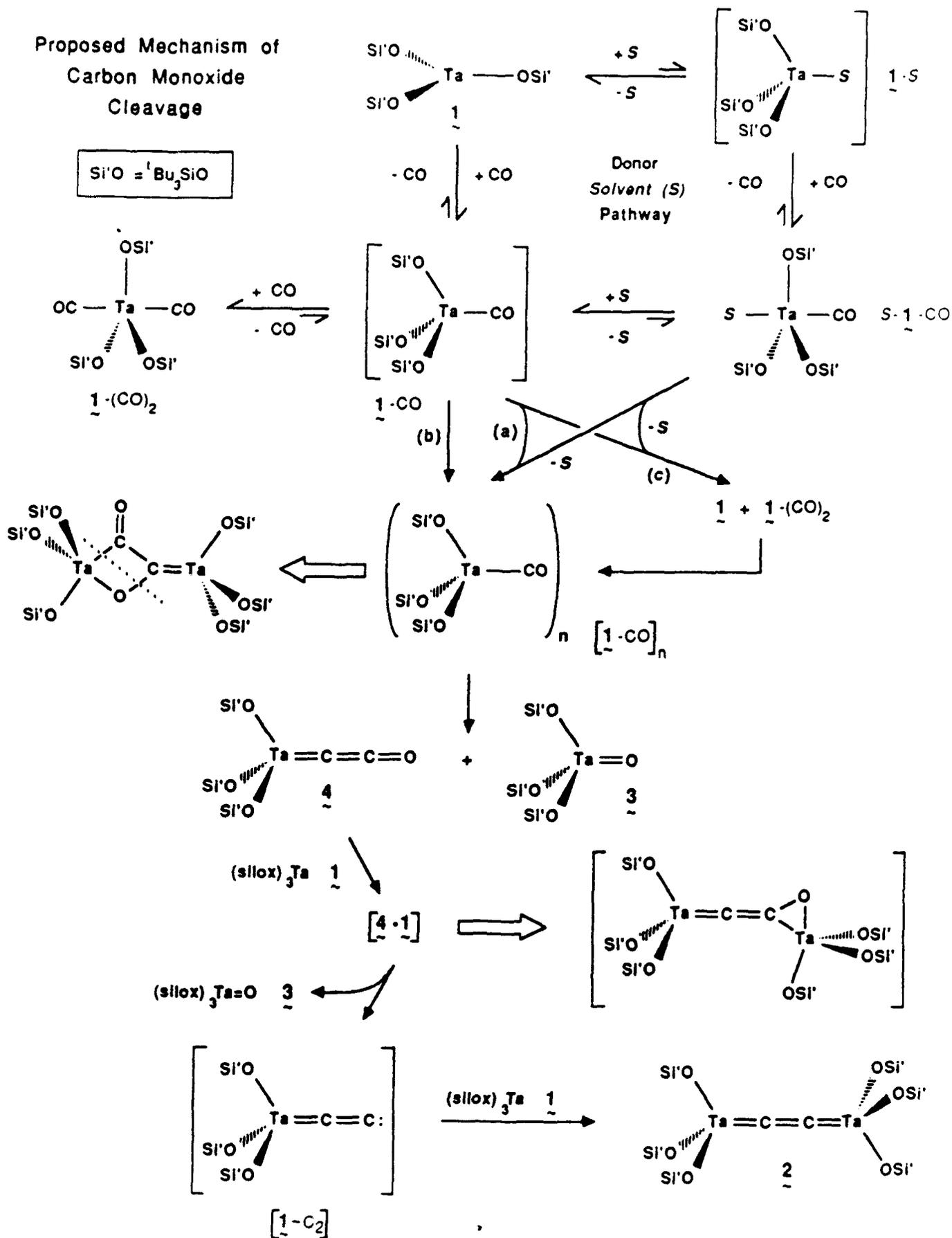
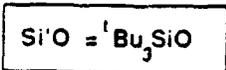


(silox)<sub>3</sub>TaCCO (4) has been completed. X-ray structural, IR and Raman studies of dicarbide 2 manifested a near-linear μ-C<sub>2</sub> bridge ( $\angle\text{TaCC} = 173 (3)^\circ$ ), a C=C double bond (1.37 (4) Å,  $\nu(\text{C}=\text{C}) = 1617 \text{ cm}^{-1}$ ) and typical TaC double bonds (1.95 (2) Å,  $\nu(\text{Ta}=\text{C}) = 709 \text{ cm}^{-1}$ ), respectively. EHMO calculations of a linear μ-C<sub>2</sub>-bridged *D*<sub>3d</sub> 2 indicated that the e<sub>g</sub><sup>2</sup> HOMO (<sup>3</sup>A<sub>2g</sub>, <sup>1</sup>E<sub>g</sub>, <sup>1</sup>A<sub>1g</sub>) is ~80% Ta (d<sub>xz</sub>, d<sub>yz</sub>) and ~20% C (p<sub>x</sub>, p<sub>y</sub>) while magnetic susceptibility measurements (2-300 K) were consistent with a large temperature independent susceptibility (25°C, μ<sub>eff</sub> = 1.93 BM) and a singlet ground state, either <sup>1</sup>E<sub>g</sub>, <sup>1</sup>A<sub>1g</sub> (*D*<sub>3d</sub>), or one arising from a Jahn-Teller distortion of the <sup>1</sup>E<sub>g</sub> level.

The most plausible overall mechanism for the formation of dicarbide (2), compiled from numerous labeling, kinetic and modeling studies, is shown in **Scheme I**. Critical steps in the sequence are as follows: 1) (silox)<sub>3</sub>Ta (1) binds CO to form an unstable, pseudo-tetrahedral, paramagnetic adduct, (silox)<sub>3</sub>TaCO (1-CO); 2) In donor solvents (*S*), 1-CO is trapped and stabilized by solvent (-78°C) as (silox)<sub>3</sub>STaCO (*S*-1-CO); 3) Either dimerization of 1-CO (b), aggregation of *S*-1-CO and equilibrium amounts of 1-CO (a), or a disproportionation of 1-CO to 1 and 1-(CO)<sub>2</sub>, which then quickly recombine (c), generates a red precipitate (-78°-(-50°C)), designated as [(silox)<sub>3</sub>TaCO]<sub>n</sub> ([1-CO]<sub>n</sub>, n = 2); 4) Either (b) or (c) leads to [1-CO]<sub>n</sub> in non-donor solvents; 5) Degradation of [1-CO]<sub>n</sub>, possibly through cleavage of the four-membered ring shown

**Scheme 1**

**Proposed Mechanism of Carbon Monoxide Cleavage**



( $-5^{\circ}\text{C}$ ), produces the ketenylidene,  $(\text{silox})_3\text{Ta}=\text{C}=\text{C}=\text{O}$  (4) and the oxo,  $(\text{silox})_3\text{Ta}=\text{O}$  (3); 6) Another  $(\text{silox})_3\text{Ta}$  (1) then deoxygenates ketenylidene 4 ( $-5^{\circ}\text{C}$ ), probably via intermediate adduct  $(\text{silox})_3\text{Ta}=\text{C}=\text{C}-\text{O}-\text{Ta}(\text{silox})_3$  (4·1), to afford oxo 3 and a transient vinylidene,  $(\text{silox})_3\text{Ta}=\text{C}=\text{C}:(1-\text{C}_2)$ , that electronically resembles CO; 7) In the dicarbide-forming last step, a final  $(\text{silox})_3\text{Ta}$  (1) unit scavenges the vinylidene ( $1-\text{C}_2$ ), resulting in  $[(\text{silox})_3\text{Ta}]_2(\mu-\text{C}_2)$  (2). The original observation that only dicarbide (2) was formed upon carbonylation of 1 in benzene was a consequence of the reaction conditions. At  $25^{\circ}\text{C}$ , formation of the red precipitate,  $[1-\text{CO}]_n$ , is swift, but the complex quickly decomposes to give ketenylidene, 4. Under conditions of variable CO pressure (0.1 - 1.0 atm), 1 deoxygenates 4 and caps the resulting vinylidene,  $(\text{silox})_3\text{Ta}=\text{C}=\text{C}:(1-\text{C}_2)$ , faster than it is scavenged by CO. It is likely that the rate of CO dissolution at  $25^{\circ}\text{C}$  is slow relative to this sequence of reactions.

If one accepts the premise that early metal complexes exhibit reactivity commensurate with late transition metal/metal oxide F-T systems (e.g.,  $\text{Fe}_2\text{O}_3$  or  $\text{Co}_2\text{O}_3$  on  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$ ) that operate at substantially higher temperatures and pressures, some important conclusions may be drawn from the unusual chemistry portrayed herein. It is evident that only two metal centers are necessary for the cleavage of 1 equiv of CO, since only two tantalums are involved in the formation of ketenylidene  $(\text{silox})_3\text{Ta}=\text{C}=\text{C}=\text{O}$  (4) and oxo  $(\text{silox})_3\text{Ta}=\text{O}$  (3); an additional two tantalums are involved in deoxygenation of 4. The  $d^2$  Ta(III) metal center is an extremely effective reductant, since the formation of carbide ( $\text{C}^{4-}$ ) or dicarbide ( $1/2 \text{C}_2^{4-}$ ) and oxide ( $\text{O}^{2-}$ ) from CO requires 6 or 4  $e^-$ . Furthermore, 1 can also act as a potent electrophile, enabling attack of a bound CO molecule at both ends.

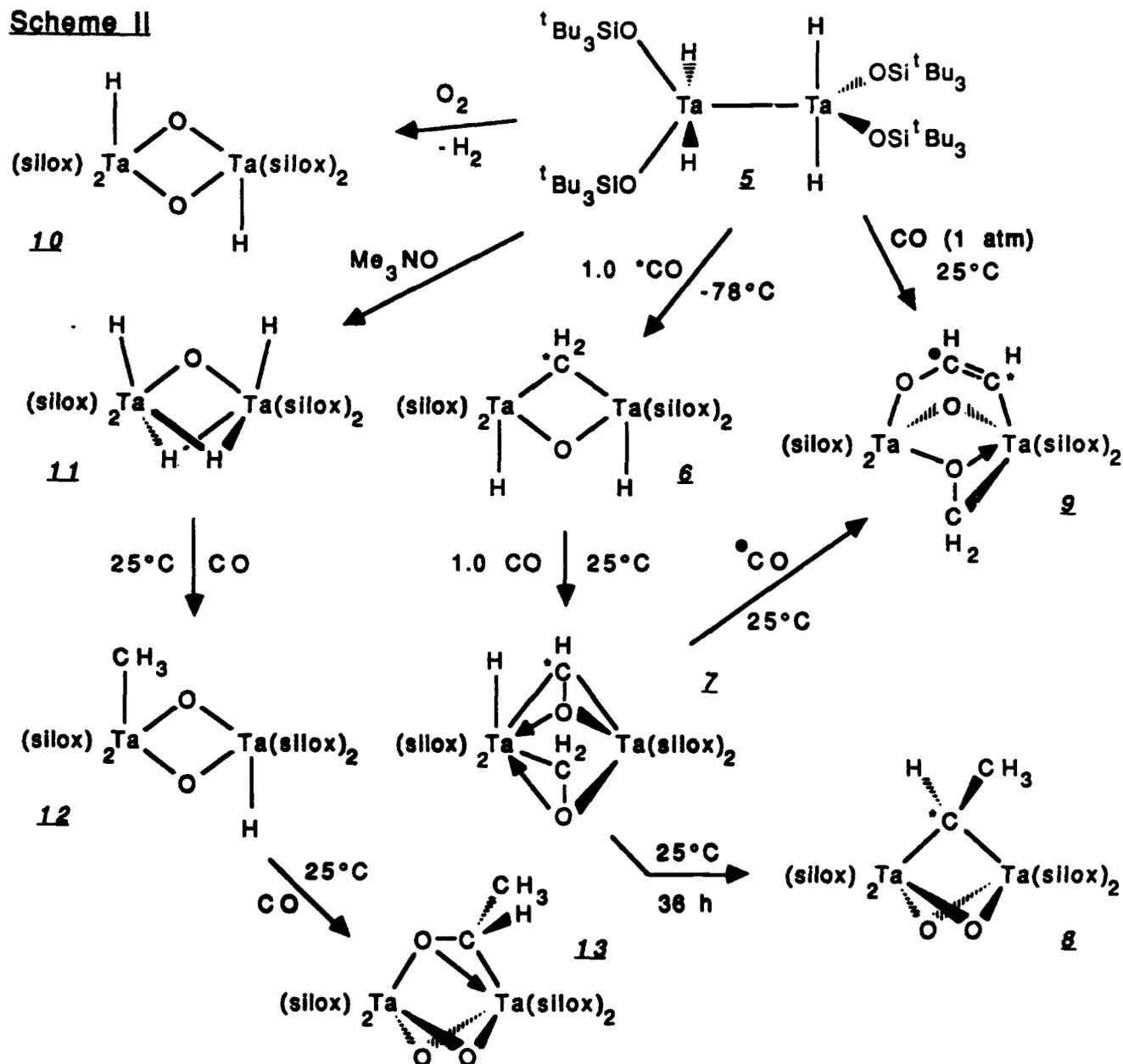
The relevance to heterogeneous systems is apparent. Although an ensemble of about five atoms is depicted in a typical portrayal of the dissociative adsorption of CO on surfaces, the only requirement is either 6 (to  $\text{C}^{4-}$  and  $\text{O}^{2-}$ ) or 4 electrons (to  $1/2 \text{C}_2^{4-}$  and  $\text{O}^{2-}$ ), and whatever number of metals are needed to supply this quantity. The chemistry illustrated in **Scheme I** also suggests that CO bond-breaking pathways involving the interactions of more than one carbonyl are plausible. In conclusion, while the dissociative adsorption of carbon monoxide is an experimentally verified occurrence, intriguing questions regarding the mechanism(s) by which adsorbed CO cleaves to give surface carbide and oxide remain.

**B. CO Reduction Mediated by Dinuclear Tantalum Hydrides** - Project will be completed by 6/1/91.<sup>79</sup>

The standard mechanism for the Fischer-Tropsch (F-T) process,<sup>80-84</sup> essentially the same as that postulated by Fischer and Tropsch in 1926,<sup>84</sup> incorporates three critical steps for the conversion of synthesis gas ( $\text{CO}/\text{H}_2$ ) to hydrocarbons: (1) CO is deoxygenated, presumably via

dissociative adsorption (*vide supra*); (2) H-transfer to surface carbides or  $\text{CO}_{\text{ads}}$  produces surface methylene groups; and (3) C-C bond formation occurs through oligomerization of  $(\text{CH}_2)_{\text{ads}}$ . Various organometallic species have been shown to model each individual step, including some that mimic the sequence with the aid of exogenous reagents. As **Scheme II** depicts, for the first time a homogeneous system, utilizing only M-H's and CO, has been shown to incorporate each of these crucial transformations.

**Scheme II**



As the sequence illustrates,  $[(\text{silox})_2\text{TaH}_2]_2$  (5) severed the C-O bond of carbon monoxide while transferring two hydrides to form the resultant  $\mu\text{-CH}_2$  species,  $[(\text{silox})_2\text{HTa}]_2(\mu\text{-O})(\mu\text{-CH}_2)$

(6), thus modeling  $(\text{CH}_2)_{\text{ads}}$ . In an unusual and important transformation, the C-O bond was reformed upon addition of another equiv of CO, generating a  $\mu$ -formyl/ $\mu$ -formaldehyde complex  $[(\text{silox})_2\text{HTa}](\mu\text{-CHO})(\mu\text{-CH}_2\text{O})[\text{Ta}(\text{silox})_2]$  (7), with the originally labeled carbonyl carbon residing in the  $\mu$ -CHO. Mild, thermal deoxygenation of both bridging groups results in C-C bond formation, affording the  $\mu$ -ethylidene,  $[(\text{silox})_2\text{Ta}]_2(\mu\text{-O})_2(\mu\text{-CHMe})$  (8), with the labeled carbon residing in the bridge.<sup>53</sup> When tetrahydride 5 or formyl-formaldehyde 7 was exposed to 1 atm CO, a third carbonyl was reduced to provide  $[(\text{silox})_2\text{Ta}]_2(\mu\text{-O})(\mu\text{-CH}_2\text{O})(\mu\text{-OCH=CH})$  (9). Labeling studies indicated that the last  $^{13}\text{C}$  has undergone reduction by the remaining hydride in coupling to the formyl group that has again been deoxygenated.

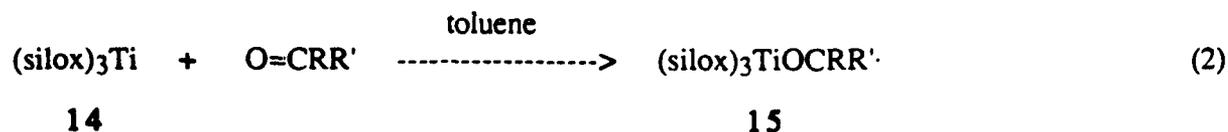
Two other dinuclear hydrides have been prepared via oxidation of  $[(\text{silox})_2\text{TaH}_2]_2$  (5); exposure to dioxygen resulted in the *bis*-( $\mu$ -oxo)dihydride species,  $[(\text{silox})_2\text{TaH}]_2(\mu\text{-O})_2$  (10) and treatment with  $\text{Me}_3\text{NO}$  afforded the  $\mu$ -oxotetrahydride,  $[(\text{silox})_2\text{TaH}_2]_2(\mu\text{-O})$  (11). While carbonylation of the former proved to be complicated, exposure of the latter to CO initially generated *bis*-( $\mu$ -oxo)methylhydride,  $[(\text{silox})_2\text{TaMe}](\mu\text{-O})_2[\text{HTa}(\text{silox})_2]$  (12) followed by the acetaldehyde-bridged binuclear,  $[(\text{silox})_2\text{Ta}]_2(\mu\text{-O})_2(\mu\text{-OCHMe})$  (13).

When protonated, the carbonylation products produced a full series of  $\text{C}_1$  and  $\text{C}_2$  hydrocarbons and oxygenates. Methane was released from  $\mu$ -methylene 6 and *bis*-( $\mu$ -oxo)methylhydride 12, while ethane was generated from  $\mu$ -ethylidene 8. Methanol was discharged from formyl-formaldehyde 7 and enolate-formaldehyde 9, which also released acetaldehyde. Finally, protonation of  $[(\text{silox})_2\text{Ta}]_2(\mu\text{-O})_2(\mu\text{-OCHMe})$  (13) liberated ethanol. The hydrolyses clearly generate typical F-T products that are produced under hydrogenation conditions in the heterogeneous systems.

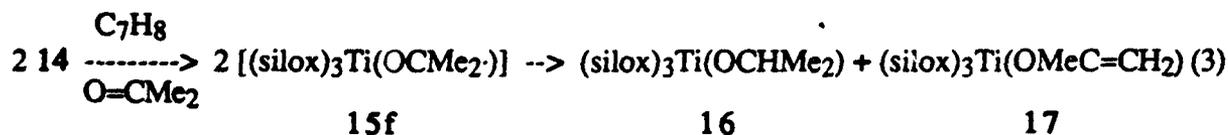
In addition to successfully modeling the transformations critical to the F-T sequence, two important alternative views of the heterogeneous process may be proffered. Since 6 is formed directly, the generation of  $(\text{CH}_2)_{\text{ads}}$  via H-transfer concomitant with or prior to C-O bond scission must still be considered; the dissociative adsorption of CO may not be necessary.<sup>85</sup> Noting that a C-O bond has been broken, reformed and broken again in the conversion of 6 to 8, heterogeneous oxygenated surfaces may serve as reservoirs for CH,  $\text{CH}_2$  and, presumably,  $\text{CH}_3$  functionalities via  $(\text{OCH})_{\text{ads}}$ ,  $(\text{OCH}_2)_{\text{ads}}$  and  $(\text{OCH}_3)_{\text{ads}}$  etc.<sup>86</sup> Hydrocarbon units on actual F-T surfaces should not be considered constrained to be metal-bound.

**C. Ketyl Formation and Ether Cleavage by  $(\text{silox})_3\text{Ti}$ .** "Reversible Dimerization of a Titanium Ketyl:  $(\text{silox})_3\text{TiOCPh}_2$ . ( $\text{silox} = {}^t\text{Bu}_3\text{SiO}^-$ )." Covert, K.J.; Wolczanski, P.T. *Inorg. Chem.* **1989**, *28*, 4565-4567. "Ketyl Complexes of  $(\text{silox})_3\text{Ti}$  ( $\text{silox} = {}^t\text{Bu}_3\text{SiO}^-$ )." Covert, K.J.; Wolczanski, P.T.; Hill, S.A.; Krusic, P.J. *Inorg. Chem.* **1992**, *31*, 66-78. Project completed 9/90.

A critical, but unseen, intermediate in the pinacol<sup>87-92</sup> and related reactions<sup>88,93-94</sup> is a transition metal based ketyl species. Numerous donor-adducts of (silox)<sub>3</sub>Ti (14) have been prepared, including ink-blue ketyl complexes, (silox)<sub>3</sub>TiOCRR' (R,R' = *p*-Me-Ph, 15a; 'Bu, 15b; R = 'Bu, R' = H, 15c; R = 'Bu, R' = Me, 15d; R,R' = O=CRR = 3,3,5,5-Me<sub>4</sub>-cyclohexanone, 15e) that form upon exposure to various bulky organic carbonyls (eq 2).

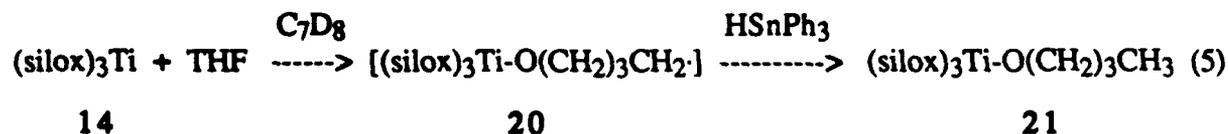
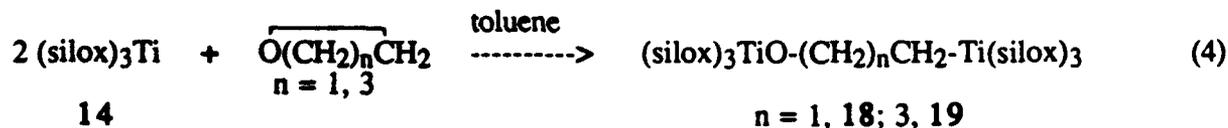


Characterization of 14 and the ketyl adducts (15) was obtained via epr spectroscopy.<sup>95-99</sup> Spectra of the latter were consistent with transposition of the electron from Ti to the carbonyl carbon. Smaller carbonyl substrates underwent subsequent reactivity. Acetone reacted with 14 to give isopropoxide and 2-propenoxide species, (silox)<sub>3</sub>Ti-(OCHMe<sub>2</sub>) (16) and (silox)<sub>3</sub>Ti(OMeC=CH<sub>2</sub>)



(17), respectively, resulting from hydrogen atom transfer between two acetone ketyl complexes, (silox)<sub>3</sub>Ti(OCMe<sub>2</sub>) (15f, eq 3). The ability of the Ti(III) center in 14 to serve as a potent reductant, while the *tris*-(silox) coordination sphere shields the carbon-based radical, enables this 1-e<sup>-</sup> chemistry to be exploited.

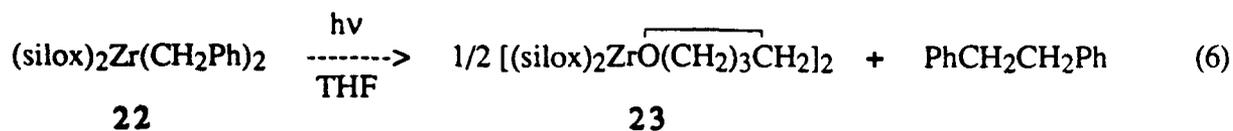
Ether carbon-oxygen bond cleavages were also effected by the d<sup>1</sup> center of (silox)<sub>3</sub>Ti (14). Both THF<sup>100-102</sup> and ethylene oxide<sup>103</sup> may be opened to produce alkoxy-alkyl bridged dititanium



complexes, (silox)<sub>3</sub>TiO-(CH<sub>2</sub>)<sub>n</sub>CH<sub>2</sub>-Ti(silox)<sub>3</sub> (n = 1, 18; 3, 19; eq 4). These C-O scission reactions proceed via radical opening of the ether linkage. Addition of HSnPh<sub>3</sub><sup>104</sup> and THF to 14

resulted in the formation of **19** and  $(\text{silox})_3\text{TiO}(\text{CH}_2)_3\text{CH}_3$  (**21**), implicating the intermediacy of  $(\text{silox})_3\text{TiO}(\text{CH}_2)_3\text{CH}_2\cdot$  (**20**, eq 5). A series of  $\text{HSnPh}_3$  concentration studies placed the rate of radical **20** attack on **6** at  $>10^7 \text{ M}^{-1}\text{s}^{-1}$ .

During the course of examining the thermal reactivity of  $(\text{silox})_2\text{Zr}(\text{CH}_2\text{Ph})_2$  (**22**), a pronounced photosensitivity was discovered.<sup>105</sup> When photolyzed in THF, **22** loses dibenzyl and

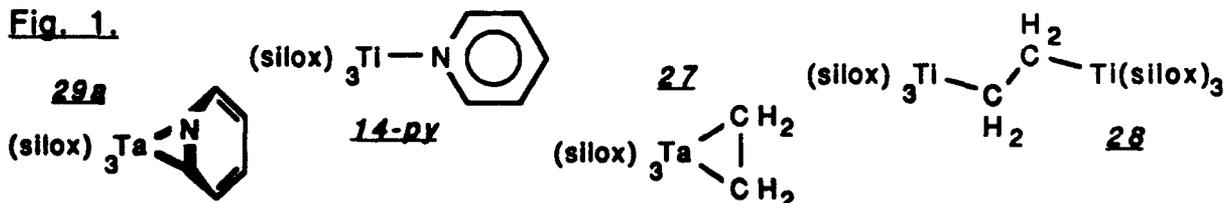


oxidatively adds the C-O bond of THF to form  $[(\text{silox})_2\text{ZrO}(\overline{\text{CH}_2)_3\text{CH}_2}]_2$  (**23**, eq 6). Crossover experiments indicated that benzyl radicals are formed during photolysis and the zirconium(III) "metallaradical",  $(\text{silox})_2\text{ZrCH}_2\text{Ph}$  (**24**), is a plausible intermediate. The subsequent reactivity is apparently related to the above Ti(III) chemistry. In both systems, the powerful reducing capabilities of the early metal siloxides are showcased in uncovering unusual chemistry.

**D.  $\eta^1\text{-N}$  vs.  $\eta^2\text{-(N,C)}$ -Pyridine Ligation.** "Pyridine and Related Adducts,  $(\text{silox})_3\text{ML}$  ( $\text{M} = \text{Sc, Ti, V, Ta}$ ):  $\eta^1\text{-N}$  vs.  $\eta^2\text{-(N,C)}$ -Pyridine Ligation." Covert, K.J.; Neithamer, D.R.; Zonneville, M.C.; LaPointe, R.E.; Schaller, C.P.; Wolczanski, P.T. *Inorg. Chem.* 1991, 30, 2494-2508. Project completed 10/90.

Adducts of  $(\text{silox})_3\text{M}$  ( $\text{M} = \text{Ta, 1; Ti, 14; Sc, 25; V, 26}$ ) have been prepared in order to assess the various electronic factors responsible for  $\eta^1\text{-N}$  vs.  $\eta^2\text{-(N,C)}$  pyridine ligation (**Fig. 1**).<sup>56,57</sup> Treatment of  $\text{ScCl}_3(\text{THF})_3$  or  $\text{VCl}_3$  with 3  $\text{Na}(\text{silox})$  in THF yielded  $(\text{silox})_3\text{M}(\text{THF})$

**Fig. 1.**



( $\text{M} = \text{Sc, 25-THF; V, 26-THF}$ ), and exposure of  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Sc}$  to 5  $(\text{silox})\text{H}$  provided  $(\text{silox})_3\text{ScNH}_3$  (**25-NH<sub>3</sub>**), but the bases could not be removed. While ethylene forms a typical metallacyclopropane,  $(\text{silox})_3\text{Ta}(\eta\text{-C}_2\text{H}_4)$  (**27**), with **1**, it did not displace the THF and  $\text{NH}_3$  from **25-THF**, **25-NH<sub>3</sub>** and **26-THF**, and reacted with **14** to provide  $[(\text{silox})_3\text{Ti}]_2(\mu\text{-C}_2\text{H}_4)$  (**28**, **Fig. 1**). Treatment of **1** with pyridine, 2-picoline, 2,6-lutidine, pyridazine ( $1,2\text{-N}_2\text{C}_4\text{H}_4$ ) and

pyrimidine (1,3-N<sub>2</sub>C<sub>4</sub>H<sub>4</sub>) provided (silox)<sub>3</sub>Ta{η<sup>2</sup>(N,C)-NC<sub>5</sub>H<sub>5</sub>} (**29a**), (silox)<sub>3</sub>-Ta{η<sup>2</sup>(N,C)-6-NC<sub>5</sub>H<sub>4</sub>Me} (**29b**), (silox)<sub>3</sub>Ta{η<sup>2</sup>-(N,C)-2,6-NC<sub>5</sub>H<sub>3</sub>Me<sub>2</sub>} (**30b**), (silox)<sub>3</sub>Ta{η<sup>2</sup>-(N,N)-N<sub>2</sub>C<sub>4</sub>H<sub>4</sub>} (**31**) and (silox)<sub>3</sub>Ta{η<sup>2</sup>(1,6-N,C)-N<sub>2</sub>C<sub>4</sub>H<sub>4</sub>} (**32**), respectively. Formation of these η<sup>2</sup>-heterocyclic adducts is proposed to occur via nucleophilic attack by **1** at the LUMO (predominantly C=N π\*) of the substrate, a process consistent with the generation of pyridyl-hydride, (silox)<sub>3</sub>Ta(H)(C<sub>5</sub>H<sub>2</sub>Me<sub>2</sub>N) (**30a**), from 2,6-lutidine prior to equilibration with **30b**. Similar treatments of **14** yielded (silox)<sub>3</sub>Ti(η<sup>1</sup>-py) (**14-py**) and related η<sup>1</sup>-py derivatives of 3,5-lutidine, 4-picoline, and 4-NC<sub>5</sub>H<sub>4</sub><sup>t</sup>Bu.

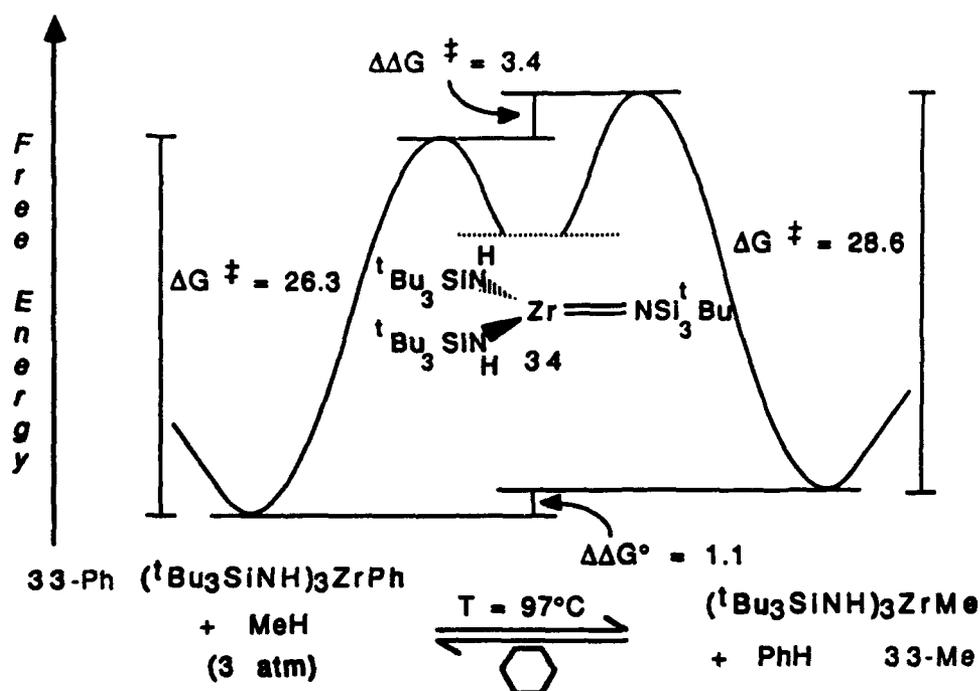
Interpretations of the uv-vis spectrum of **1**, and EHMO calculations of η<sup>1</sup> and η<sup>2</sup> forms of (silox)<sub>3</sub>Ta(py), provide a rationale for the variation in pyridine ligation. Of critical importance are the 4e<sup>-</sup> repulsion between the filled d<sub>z<sup>2</sup></sub> orbital of **1** and py N-donor orbital, and the capability of pyridine to function as a good π-acceptor in the η<sup>2</sup>-mode.

**E. Hydrocarbon Activations by Transient (<sup>t</sup>Bu<sub>3</sub>SiNH)<sub>2</sub>Zr=NSi<sup>t</sup>Bu<sub>3</sub>.** "Methane and Benzene Activation via Transient (<sup>t</sup>Bu<sub>3</sub>SiNH)<sub>2</sub>Zr=NSi<sup>t</sup>Bu<sub>3</sub>." Cummins, C.C.; Baxter, S.M.; Wolczanski, P.T. *J. Am. Chem. Soc.* **1988**, *110*, 8731-8733; "Carbonylation of [<sup>t</sup>Bu<sub>3</sub>SiNH]<sub>3</sub>ZrH and X-ray Structural Study of [<sup>t</sup>Bu<sub>3</sub>SiNH]<sub>3</sub>ZrCH<sub>3</sub>." Cummins, C.C.; Van Duyne, G.D.; Schaller, C.P.; Wolczanski, P.T. *Organometallics* **1991**, *10*, 164-170. Project ongoing.

Reactions of alkanes with multiply-bonded functionalities (e.g., L<sub>n</sub>M = X, X = O, NR, CR<sub>2</sub>, etc.)<sup>106-108</sup> constitute an important class of transformations related to the partial oxidation or functionalization of alkane C-H bonds.<sup>109-115</sup> As addressed in the previous proposal, (<sup>t</sup>Bu<sub>3</sub>SiNH)<sub>3</sub>ZrR (**33**) derivatives undergo a 1,2-elimination of RH, viewed as an abstraction of an amido proton by the alkyl, to form three-coordinate, transient [(<sup>t</sup>Bu<sub>3</sub>SiNH)<sub>2</sub>Zr=NSi<sup>t</sup>Bu<sub>3</sub>] (**34**), according to isotopic labeling and kinetic studies (e.g., k<sub>MeH</sub>/k<sub>MeD</sub> = 7.3(4)). The C-H bond or H<sub>2</sub> is "activated" via addition across the imido group to give **33-R** or (<sup>t</sup>Bu<sub>3</sub>SiNH)<sub>3</sub>ZrH (**35**).

In THF, intermediate **34** was trapped yield (<sup>t</sup>Bu<sub>3</sub>SiNH)<sub>2</sub>(THF)Zr=NSi<sup>t</sup>Bu<sub>3</sub> (**34-THF**), whose structure was determined by x-ray crystallography. The bond order of the Zr=N and Zr-NH groups is similar, since the imido linkage is 1.97 Å, only ~0.06 Å shorter than the amido-Zr bonds. Using this criterion, one view of the C-H bond activation by the imido group involves the use of the "lone pair" on nitrogen as internal base. Thus the extreme electrophilicity of the three-coordinate center draws the C-H bond into the coordination sphere where the internal imide base can remove the hydrogen.

Fig. 2.

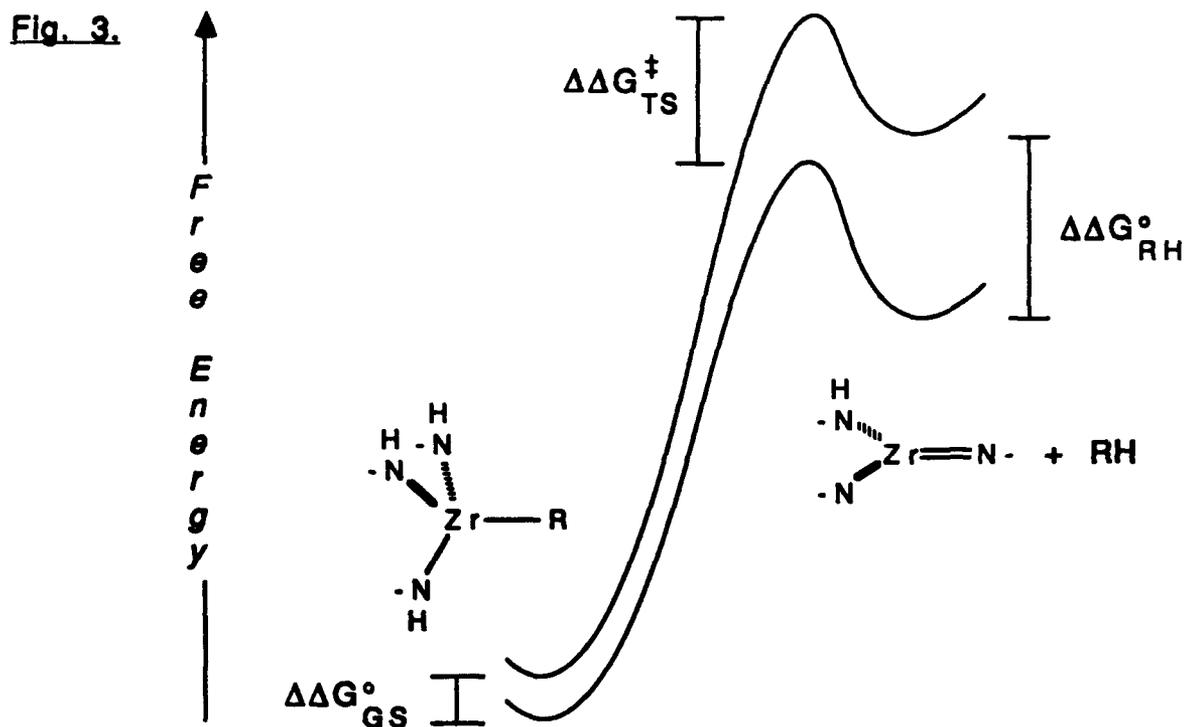


The free energy diagram shown in **Fig. 2.** was constructed by measuring the elimination rates of PhH and MeH from  $(\text{}^t\text{Bu}_3\text{SiNH})_3\text{ZrPh}$  (**33-Ph**) ( $\Delta G^\ddagger = 26.3$  kcal/mol) and  $(\text{}^t\text{Bu}_3\text{SiNH})_3\text{ZrMe}$  (**33-Me**) ( $\Delta G^\ddagger = 28.6$  kcal/mol), respectively, in combination with a competition experiment. Intermediate  $(\text{}^t\text{Bu}_3\text{SiNH})_2\text{Zr}=\text{NSi}^t\text{Bu}_3$  (**34**) exhibited a proclivity toward attacking benzene vs. methane C-H bonds ( $\Delta\Delta G^\ddagger = 3.4$  kcal/mol) in cyclohexane.

**Table I.** shows the elimination rates of several  $(\text{}^t\text{Bu}_3\text{SiNH})_3\text{ZrR}$  (**33**) derivatives at  $96.7^\circ\text{C}$  and the C-H bond strengths<sup>116</sup> of the released hydrocarbon. With the exception of MeH and CyH eliminations, the data reflect an inverse correlation between rate and C-H bond strength,

<b>Table I.</b> Complex ( <b>33-R</b> )	$k \times 10^4$ ( $\text{s}^{-1}$ ) 96.7°C	$\Delta G^\ddagger$ (kcal/mol)	D(R-H) (kcal/mol)
$(\text{}^t\text{Bu}_3\text{SiNH})_3\text{Zr-CH}_2\text{Ph}$	0.169(3)	29.9	88
$(\text{}^t\text{Bu}_3\text{SiNH})_3\text{Zr-Mes}$	0.34(2)	29.4	88
$(\text{}^t\text{Bu}_3\text{SiNH})_3\text{Zr-Me}$	1.06(2)	28.5	105
$(\text{}^t\text{Bu}_3\text{SiNH})_3\text{Zr-Et}$	3.21(6)	27.7	98
$(\text{}^t\text{Bu}_3\text{SiNH})_3\text{Zr-Cy}$	10.4(1)	26.9	94
$(\text{}^t\text{Bu}_3\text{SiNH})_3\text{Zr-CH}=\text{CH}_2$	13.2(4)	26.7	108
$(\text{}^t\text{Bu}_3\text{SiNH})_3\text{Zr-Ph}$	22.6(2)	26.3	112

implicating a late transition state<sup>117,118</sup> for 1,2-elimination. As **Fig. 3**, illustrates, the transition state for elimination reflects the free energy of the released hydrocarbon; in this situation, the ground state free energy differences are relatively small compared to the intermediate state of 34

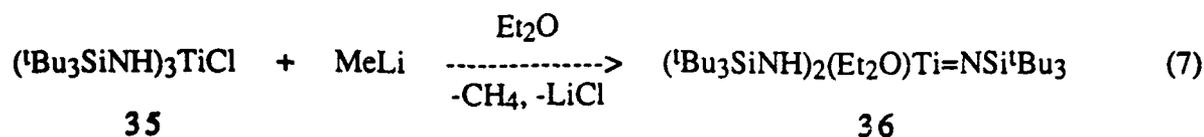


and RH, hence the weaker the C-H bond formed, the slower the rate of elimination. MeH and CyH eliminations deviate slightly from that expected because of subtle steric effects. Methyl derivative 33-Me possesses the least amount of <sup>t</sup>Bu<sub>3</sub>NH/Me interaction, reflected in a lower 1,2 elimination than predicted, while in 33-Cy the amide ligands interact strongly with the cyclohexyl group, since it has two substituents on the α-carbon, and thereby promotes a swifter CyH loss.

**F. Benzene and H<sub>2</sub> Activations by Tri-*tert*-butylsilylimido Complexes of Titanium.** "Tri-*tert*-butylsilylimido Complexes of Titanium: Benzene C-H Activation and Structure of [(<sup>t</sup>Bu<sub>3</sub>SiNH)Ti]<sub>2</sub>(μ-NSi<sup>t</sup>Bu<sub>3</sub>)<sub>2</sub>." Cummins, C.C.; Schaller, C.P.; Van Duyne, G.D.; Wolczanski, P.T.; Chan, E.A.-W.; Hoffmann, R. *J. Am. Chem. Soc.* 1991, 113, 2985-2994.

In an attempt to generate a stable *bis*-amidoimido complex analogous to (<sup>t</sup>Bu<sub>3</sub>SiNH)<sub>2</sub>-Zr=NSi<sup>t</sup>Bu<sub>3</sub> (34), the corresponding titanium derivative was sought in the hope that the smaller

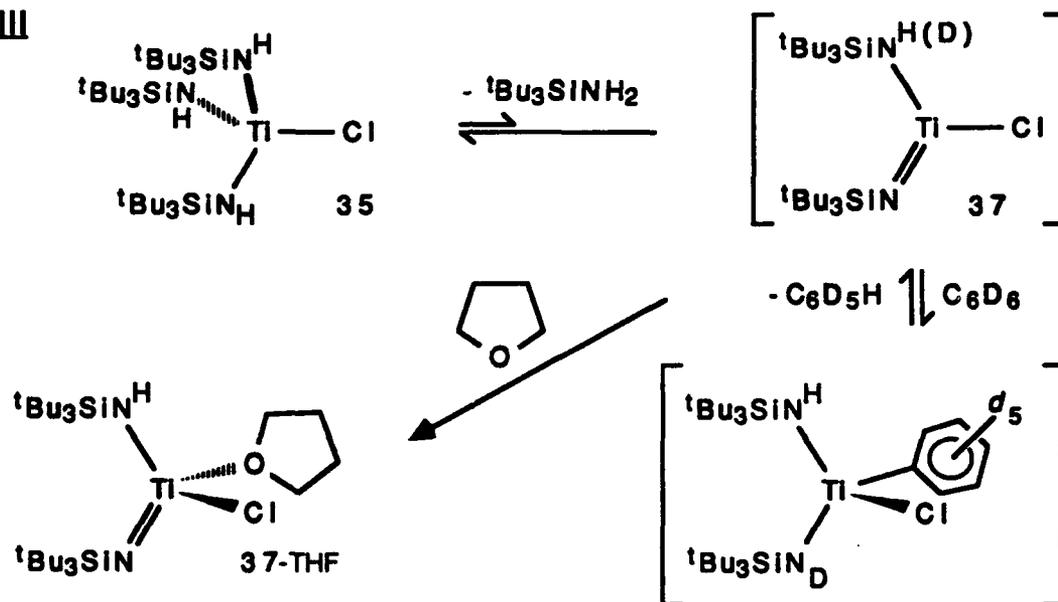
covalent radius of Ti would permit its isolation. Efforts to alkylate  $(^t\text{Bu}_3\text{SiNH})_3\text{TiCl}$  (**35**) failed, yet the product resulting from dehydrohalogenation,  $(^t\text{Bu}_3\text{SiNH})_2(\text{Et}_2\text{O})\text{Ti}=\text{NSi}^t\text{Bu}_3$  (**36**, eq 7),



exhibited deuteration of its amido protons, presumably via loss of  $\text{Et}_2\text{O}$  and addition/elimination of  $\text{C}_6\text{D}_6$  across the imido linkage.

Curiously, even the chloride derivative, **35**, underwent deuteration of its amido protons upon thermolysis. As **Scheme III** indicates, elimination of  $^t\text{Bu}_3\text{SiNH}_2$  occurred to give a another transient three-coordinate complex,  $(^t\text{Bu}_3\text{SiNH})\text{ClTi}=\text{NSi}^t\text{Bu}_3$  (**37**), that is capable

### Scheme III



of the addition/elimination of  $\text{C}_6\text{D}_6$ , thereby providing a deuteration pathway. Again, thermolysis in THF trapped the intermediate as the adduct,  $(^t\text{Bu}_3\text{SiNH})(\text{THF})\text{ClTi}=\text{NSi}^t\text{Bu}_3$  (**37-THF**). Kinetic experiments (**35**  $\rightarrow$  **37-THF**) portrayed the amine loss as an abstraction of an amido hydrogen by the leaving amide (e.g.,  $k(\text{RNH}_2) = 1.03(1) \times 10^{-4} \text{ s}^{-1}$  ( $80.5^\circ\text{C}$ );  $k_{\text{H}}/k_{\text{D}} = 5.9(6)$  at  $90.4^\circ\text{C}$ ;  $\Delta H^\ddagger = 23.3(8) \text{ kcal/mol}$ ;  $\Delta S^\ddagger = -11(2) \text{ eu}$ ) in concert with the previously observed alkane loss from  $(^t\text{Bu}_3\text{SiNH})_3\text{ZrR}$  (**33**).

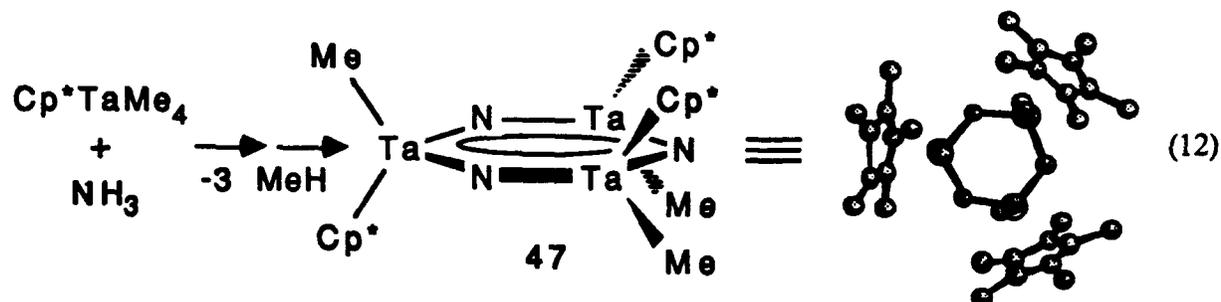
The THF adduct (**37-THF**) was smoothly alkylated with MeLi or  $^t\text{BuLi}$  to give the corresponding alkyl complexes,  $(^t\text{Bu}_3\text{SiNH})(\text{THF})\text{RTi}=\text{NSi}^t\text{Bu}_3$  ( $\text{R} = \text{Me}$ , **38**;  $^t\text{Bu}$ , **39**), and hydrogenation of either alkyl resulted in the formation of a Ti(III) dimer,  $[(^t\text{Bu}_3\text{SiNH})\text{Ti}]_2(\mu\text{-NSi}^t\text{Bu}_3)_2$  (**40**, eq 8); X-ray structural studies of **40** revealed a Ti-Ti bond length of 2.442 Å that





TaN and a Trimeric Nitride,  $[\text{Cp}^*\text{MeTaN}]_3$ ." Holl, M.M.B.; Kersting, M.; Pendley, B.D.; Wolczanski, P.T. *Inorg. Chem.* 1990, 29, 1518-1526. Project ongoing.

A metal-alkyl bond that is polarized  $\text{M}^{\delta+}\text{-R}^{\delta-}$  (e.g. refractory metal alkyl) is cleaved by polar reagents of the type  $\text{H}^{\delta+}\text{-X}^{\delta-}$ . As a test case,  $\text{Cp}^*\text{TaMe}_4$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ,  $\text{Me} = \text{CH}_3$ ) was treated with a stoichiometric amount of  $\text{NH}_3$  in benzene to produce a new nitride,  $[\text{Cp}^*\text{Ta}(\text{N})\text{Me}]_3$  (47, eq 12), whose structure (determined via X-ray crystallography) is shown. The product trimer is particularly exciting from two important standpoints: 1) It shows that the ammonolysis of Ta alkyls occurs under relatively mild conditions (100°C, 48 h); 2) The Ta-N bond lengths are equivalent (1.886(17) Å<sub>ave</sub>), indicative of *delocalized bonding akin to that found in solid nitrides*.

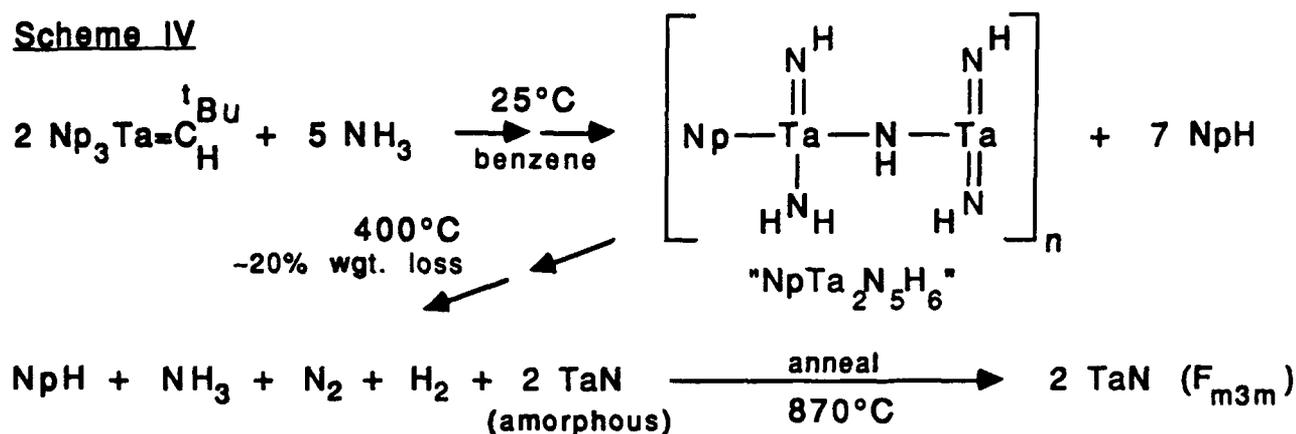


EHMO calculations of the trimer were also consistent with the delocalized description and revealed a non-bonding LUMO which suggested that the complex was reducible. The latter contention was confirmed via cyclic voltammetry ( $E^{\circ}_{\text{red}} = -2.06$  V vs. Ag wire). In addition, Na/K reduction of 47 led to the formation of the radical anion,  $[\text{K}\cdot n \text{Et}_2\text{O}]^+[\{\text{Cp}^*\text{MeTaN}\}_3]^-$  (48), a highly sensitive complex that degraded in both ethereal and hydrocarbon solvents. In accord with the EHMO calculations, the infrared TaN absorption of 48 ( $964 \text{ cm}^{-1}$ ) is virtually unchanged from that of the neutral trimer ( $960 \text{ cm}^{-1}$ ), presumably because a non-bonding molecular orbital is populated. These observations are interesting because the anion possesses features that model ternary nitrides.

**I. Ammonolysis of  $\text{Np}_3\text{Ta}=\text{CH}^t\text{Bu}$ : Formation of Cubic TaN via  $[(^t\text{BuCH}_2)_2\text{TaN}]_5$ .** "The Ladder Structure of  $[(^t\text{BuCH}_2)_2\text{TaN}]_5\cdot\text{NH}_3\cdot 2\text{C}_7\text{H}_8$  and Its Relationship to Cubic TaN." Holl, M.M.B.; Wolczanski, P.T.; Van Duyne, G.D. *J. Am. Chem. Soc.* 1990, 112, 7989-7994. Project ongoing.

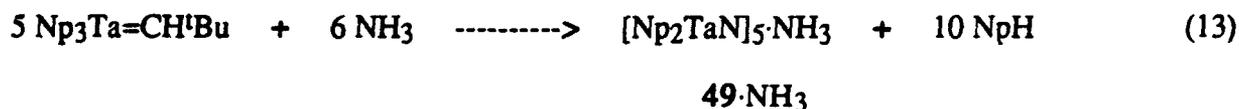
The preparation of cubic TaN ( $Fm\bar{3}m$ ) was affected via the ammonolysis of  $\text{Np}_3\text{Ta}=\text{CH}^t\text{Bu}$  ( $\text{Np} = \text{neopentyl}$ ) as described in **Scheme IV**. An oligomeric precipitate having the approximate stoichiometry " $\text{NpTa}_2\text{N}_5\text{H}_6$ " was initially formed. Thermolysis of this material at 400°C led to the

## Scheme IV



formation of amorphous TaN; annealing at 820°C provided crystalline cubic TaN ( $Fm\bar{3}m$ ). According to the Ta/N phase diagram, hexagonal tantalum nitride ( $P6/mmm$  or  $P62m$ ), is the expected thermodynamic product under the conditions employed. The diagram, which was compiled from various sources, suggests that rather extreme conditions are necessary to prepare cubic TaN from the elements (e.g., >1600°C, >3 atm  $\text{N}_2$ ); consequently, the solution and subsequent thermolytic methods delineated above comprise a low temperature route to a metastable product. Furthermore, it seemed plausible that structural elements critical to the formation of the cubic phase were established in the precipitate and its soluble precursors.

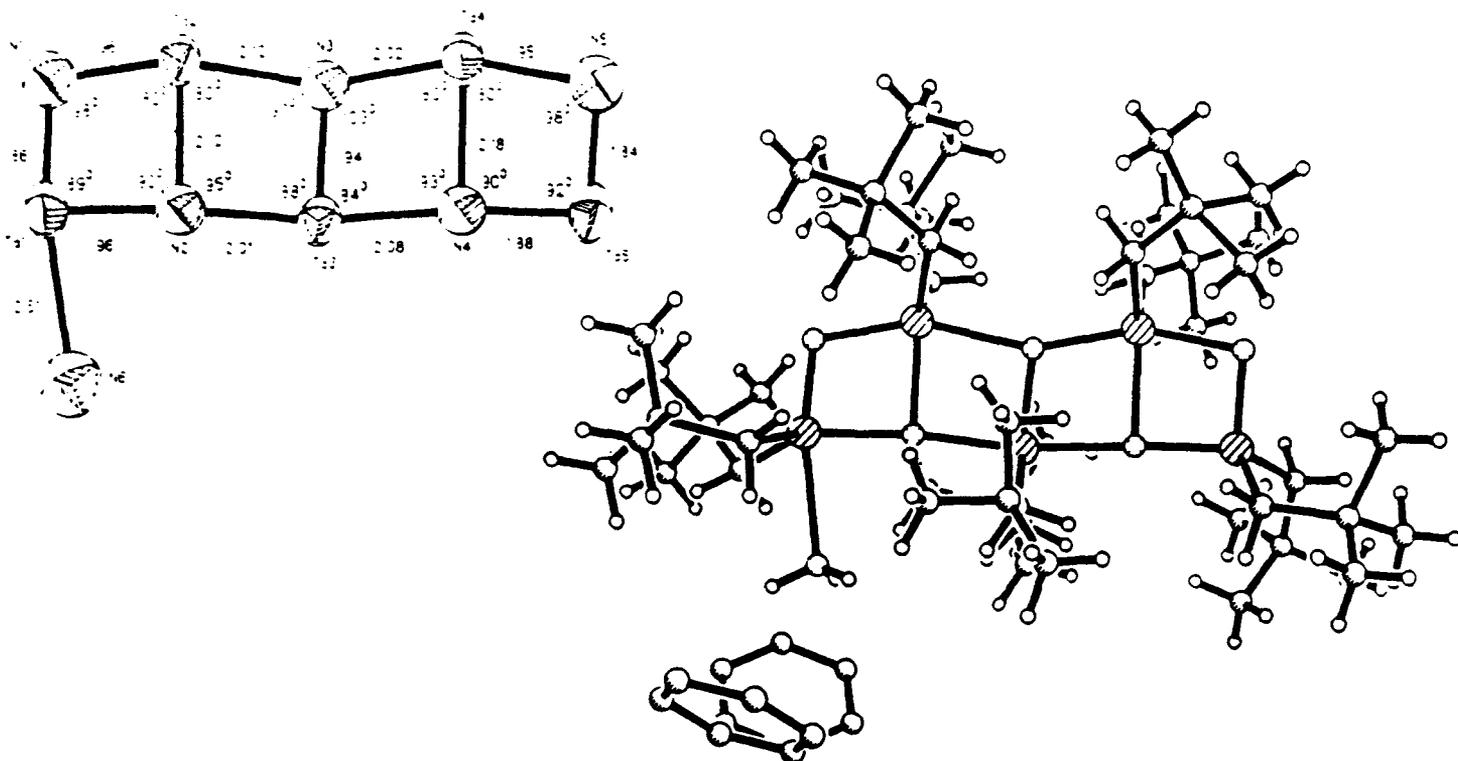
In an effort to better understand the structural character of the precipitate, attempts to isolate soluble species that led to " $\text{NpTa}_2\text{N}_5\text{H}_6$ " were initiated. By carefully monitoring the ammonolysis at 25°C in benzene, a possible soluble intermediate was discovered, later determined to be an



ammonia adduct of a light and temperature sensitive pentamer,  $[\text{Np}_2\text{TaN}]_5 \cdot \text{NH}_3$  ( $49 \cdot \text{NH}_3$ ), as indicated in eq 13.

X-ray structure determination via heavy atom methods revealed the pentameric structure indicated in Fig. 5. The complex possesses a ladder-type structure, with an alternating orientation of  $\text{Np}_2\text{TaN}$  units. Three of the Ta centers are *tbp* with axial nitrides, one corner tantalum is tetrahedrally coordinated and the third *tbp* with weak axial ligation by the bound ammonia, which is "solvated" by two toluene molecules. Examination of the structure reveals that the two Np groups attached to each Ta are relatively free to rotate with the exception of those bound to the middle tantalum. Each additional  $\text{Np}_2\text{TaN}$  unit would constrict another set of Np

Fig. 5.



groups. It is thus possible that the observed pentamer is stable to further oligomerization due to unfavorable entropic considerations brought about in adding steps to the ladder.

The four parallel, interior Ta-N bond lengths average 2.06(5) Å while the related exterior set averages 1.94(4) Å, indicative of greater  $\text{N}(\text{p}\pi) \rightarrow \text{Ta}(\text{d}\pi)$  bonding. In contrast, the perpendicular Ta-N "rungs" of the ladder alternate in distance; the middle Ta3-N3 length of 1.94(3) Å is significantly shorter than Ta2-N2 (2.12(2) Å) and Ta4-N4 (2.18(2) Å), whereas the outer nitride bonds reflect greater multiple bonding to four-coordinate Ta5 (1.84(3) Å) and Ta1 (1.86(3) Å), whose bond to  $\text{NH}_3$  is extremely long (2.51(3) Å). The dramatic differences in the interior perpendicular bonds cannot be so easily rationalized. Despite the sterically congested environment of Ta3, equatorial Ta3-N3 (1.94(3) Å) is significantly shorter than its axial partners, perhaps due to stronger  $\text{N}(\text{p}\pi) \rightarrow \text{Ta}(\text{d}\pi)$  bonding. In comparison, equatorial Ta2-N2 (2.12(2) Å) and Ta4-N4 (2.17(2) Å) are longer than the axial nitride bonds to Ta2 and Ta4, respectively.

As indicated by the sideways view of the molecular core at the bottom of Fig. 5, the ladder is virtually flat. Recall that the case was made for establishment of the cubic structural unit during the course of the " $\text{NpTa}_2\text{N}_5\text{H}_6$ " formation. The Ta-N distance in cubic tantalum nitride (rock-salt structure) is 2.165 Å, slightly longer than those in  $49 \cdot \text{NH}_3$ , since each tantalum in TaN

is six-coordinate. It is proposed that the square  $Ta_2N_2$  element in  $49-NH_3$  dictates the solid state structure of the  $TaN$  formed via the thermolytic procedure outlined in **Scheme IV**! This possibility has extremely important ramifications. If stable structural elements can be produced at low temperatures via solution chemistry, the structural type established may be used to "seed" the formation of unique solid state species that cannot be prepared with standard thermolytic methods. At the very least, this example manifests the use of solution chemistry in leading to the formation of a low temperature phase that cannot be produced conventionally.

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