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13. ABSTRACT *(Maximum 200 words)*

The synthesis and chemistry of compounds in which two transition metal centers are bridged by a single nitrogen atom, the bridging nitride ligand, has been investigated. These studies have focused on understanding the chemical and physical properties of the M(N)M unit in order to explore its use as a building block for new transition metal-containing polymers. The approach to this chemistry has involved parallel exploration of molecular nitride-bridged species, which serve as model systems for developing the chemistry of these compounds, and of extended structures incorporating metal-nitrogen-metal linkages. Supporting studies on the reactivity and spectroscopy of silylimido precursor compounds, which are used in the synthetic route to nitride-bridged structures, have been performed. Extension of this chemistry to phosphide-bridged species has been explored.

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SYNTHESIS AND STUDY OF METALLONITRIDE COMPLEXES AND POLYMERS

Final Report for AFOSR-91-0179

For Period: May 1, 1991 – November 30, 1991

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INTRODUCTION

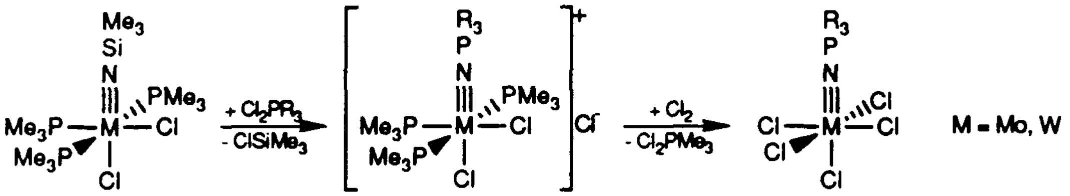
We have been investigating the synthesis and chemistry of compounds in which two transition metal centers are bridged by a single nitrogen atom, the bridging nitride ligand. This research is directed at understanding the chemistry of the M(N)M unit in order to use it as a building block for new transition metal-containing polymers. Inorganic polymers which have transition metal atoms incorporated into the backbone are anticipated to be important new materials with a variety of desirable properties, however study of these systems is severely limited by the scarcity of methods available for their synthesis. Our work has emphasized developing synthetic routes to such systems and has involved parallel exploration of molecular nitride-bridged model compounds and extended structures incorporating metal-nitrogen-metal linkages.

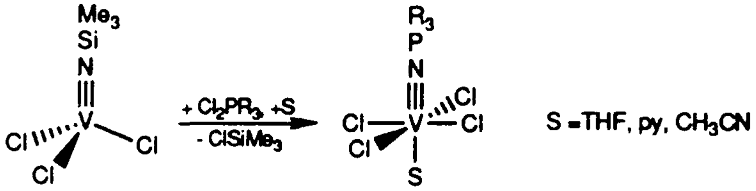
RESEARCH ACCOMPLISHMENTS

In our previous AFOSR-supported work, we discovered and developed a simple condensation reaction between silylimido and halide ligands for the preparation of metallonitride complexes and polymers. Using this chemistry, we synthesized a series of heterobimetallic nitride-bridged complexes, examples of homobimetallic nitride-bridged complexes, and new linear chain metallonitride polymers. We additionally used spectroscopic and reactivity studies to explore the nature of the nitride bridge in these compounds.

During the grant period which is the subject of this report, our research has moved in four new directions: (a) the formation of phosphiniminato complexes from silylimido precursors, (b) the synthesis of silylphosphido transition-metal compounds as potential precursors to phosphide-bridged compounds, (c) the mechanism of formation of linear chain metallonitride polymers from silylimido precursors, and (d) correlations between reactivity and ^{29}Si NMR spectra of silylimido compounds. Our most significant results in these areas are summarized below.

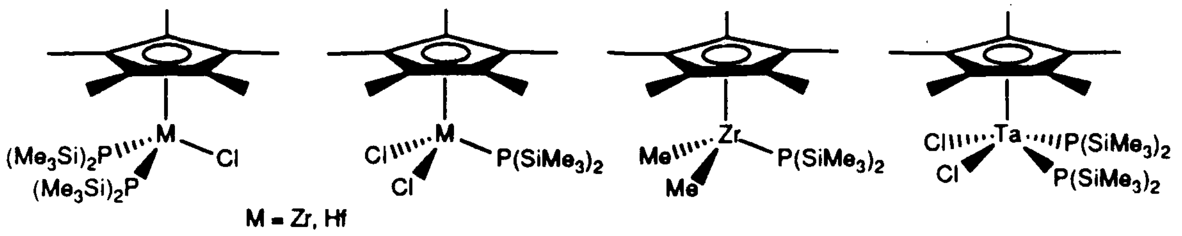
Formation of phosphiniminato complexes from silylimido precursors. In order to obtain a more general understanding of the reactivity of silylimido ligands, we have been examining the reactions of vanadium(V), molybdenum(IV), and tungsten(IV) silylimido compounds with simple halogen-containing reagents capable of attacking the nitrogen-silicon bond. Of particular interest are the clean reactions of these compounds with phosphine dichlorides (and with chlorine) to yield phosphiniminato compounds.





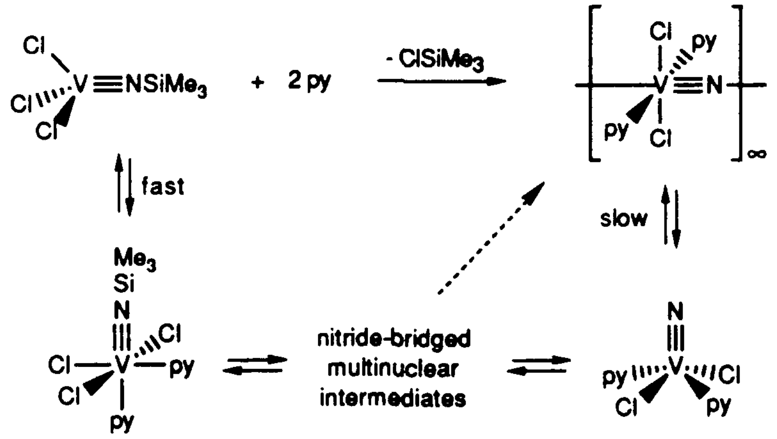
These remarkable transformations involve main-group analogues of our route to nitride-bridged transition metal complexes. This chemistry also provides us with reactive nitrogen-phosphorus bonds in phosphiniminato compounds which we are examining as precursors to nitride-bridged systems. Furthermore, this reactivity suggests a new and potentially extremely useful route to metallophosphazenes—addition of metal silylimido compounds to chlorophosphazenes—which we are currently exploring.

Silylphosphido transition-metal compounds as potential precursors to phosphide-bridged compounds. The marked preference of phosphorus to form single rather than multiple bonds suggests that the phosphide ion (P^{3-}) would be well-suited to bridge metal centers and more likely to form strong symmetric bridges than the nitride ion. We have begun experiments aimed at extending our studies to phosphide-bridged transition-metal systems. These have focused on using silylphosphido ligands as possible precursors to phosphide-bridged compounds. We have prepared examples of zirconium(IV), hafnium(IV), and tantalum(V) complexes containing the disilylphosphido ligand and have started exploring the potential for reactivity at the phosphorus-silicon bonds in these compounds.

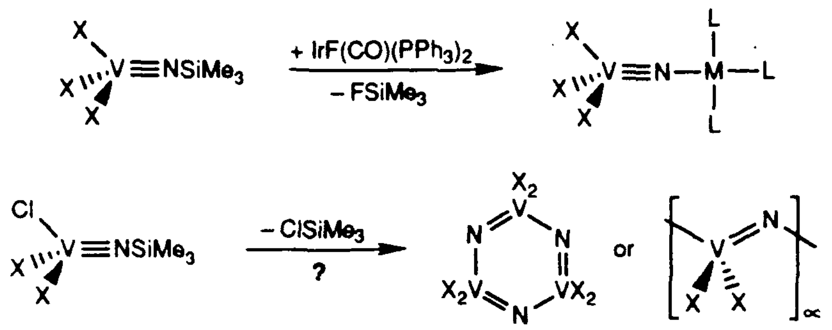


Mechanism of formation of linear chain metallonitride polymers from silylimido precursors. A key feature of the condensation reaction is its potential for the preparation of polymeric metallonitrides from starting materials having the silylimido and halide ligands on the same metal center. Using this reaction, we had previously prepared new linear chain polymers based on a vanadium-nitride backbone. The rapid self-assembly of this highly ordered polymeric structure in quantitative yield is striking. In order to understand the factors making this chemistry possible, we have used reactivity and kinetic studies to address the mechanism of the condensation/polymerization reaction.

We have shown that a highly reactive silylimido intermediate can be isolated and observed spectroscopically at low temperatures and is the major vanadium-containing species present during the condensation reactions. This intermediate reacts to produce either polymeric or monomeric vanadium nitrides, depending on the reaction conditions. Mechanistic modelling has demonstrated that both intermolecular condensation of silylimido and chloride ligands and oligomerization of vanadium nitride monomers are involved in producing the nitride-bridged linear chain complex.



Correlations between reactivity and ^{29}Si NMR spectra of silylimido compounds. We have prepared a variety of new transition-metal silylimido derivatives and examined their reactivity toward transition-metal halides. Formation of nitride-bridged products occurs readily and in extremely high yield for some silylimido complexes, but not at all for others. In order to further develop our understanding of the reactivity of silylimido complexes, we set out to explore whether a correlation exists between reactivity of the nitrogen-silicon bond and the ^{29}Si NMR spectrum of the silyl group. We decided to initially focus on vanadium(V) silylimido compounds exploring the effects of modification of the vanadium center on the reactivity and on the ^{29}Si NMR spectrum.



X = $OSiMe_3$, O-*t*-Bu, OPh, O-*p*-tol, CH_2SiMe_3, etc.

For the series of compounds we have studied thus far, we observe a downfield shift and sharpening of the ^{29}Si NMR signal as the reactivity of the silylimdo ligand toward formation of nitride-bridge compounds increases. We hope to develop this methodology into a predictive tool for future synthesis of nitride-bridged compounds. We are also examining whether the modified vanadium silylimido complexes can function as precursors to new vanadium nitrides oligomers and polymers.

Summary. We have continued our studies of the chemistry of transition-metal silylimido complexes, the nitrogen-containing building blocks for our synthesis of nitride-bridged compounds and polymers, and have begun extending this work to silylphosphido complexes, potential precursors for phosphide-bridged compounds. This research is aimed at the preparation of inorganic materials using techniques usually applied to molecular species and, consequently, offers tremendous potential for the discovery of new materials. Our goals are to develop general routes for the synthesis of transition-metal-containing materials, to understand the pathways for their formation, and, ultimately, to relate their properties to composition, structure, and bonding. Our efforts in nitride-bridged transition-metal chemistry have progressed well and have allowed a detailed picture of the nitride bridge, including its potential for use as a building block for new transition metal-containing polymers, to emerge.

PUBLICATIONS ACKNOWLEDGING AFOSR SUPPORT (1988-PRESENT)

1. "Vanadium Nitride Linear Chain Polymers and Monomers. Synthesis and Structures of $[V(\mu\text{-}N)Cl_2(py)_2]_\infty$ and $V(N)Cl_2(quin)_2$," S. C. Critchlow, M. E. Lerchen, R. C. Smith, and N. M. Doherty, *J. Am. Chem. Soc.*, **1988**, *110*, 8071. (AFOSR-87-0362)
2. "Synthesis of Molybdenum and Tungsten Silylimido Complexes. Structure of a Five-Coordinate Bis(silylimido) Complex," J. D. Lichtenhan, S. C. Critchlow, and N. M. Doherty, *Inorg. Chem.*, **1990**, *29*, 439. (AFOSR-87-0362)
3. "Synthesis of Vanadium, Niobium, and Tantalum Silylimido Complexes and Reactivity of Their Nitrogen-Silicon Bonds," C. M. Jones, M. E. Lerchen, C. J. Church, B. M. Schomber, and N. M. Doherty, *Inorg. Chem.*, **1990**, *29*, 1679. (AFOSR-87-0362)

4. "Transition-Metal Fluoro Complexes Containing Carbonyl, Phosphine, Arsine, or Stibine Ligands," N. M. Doherty and N. W. Hoffman, accepted for publication in *Chem. Rev.*, **1991**. (AFOSR-87-0362)
5. "Synthesis and Reactivity of *trans*-$ReF(CO)_3(PPh_3)_2$ and *trans*-$(Me_3SiO)_3V{\equiv}N{-}Re(CO)_3(PPh_3)_2$," N. W. Hoffman, N. Prokopuk, M. J. Robbins, C. M. Jones, and N. M. Doherty, *Inorg. Chem.* **1991**, *30*, 4177-4181. (AFOSR-87-0362)
6. "Reactions at Metal-Bound Nitrogen Atoms. Synthesis and Structure of $V(NPMePh_2)Cl_4(NCMe){\cdot}NCMe$," B.M. Schomber, J.W. Ziller, and N.M. Doherty, *Inorg. Chem.* **1991**, *30*, 4488-4490. (AFOSR-87-0362)
7. "Mixed-Valence Nitride-Bridged Vanadium Compounds. Synthesis and Structure of $V_2(N)Cl_5(TMEDA)_2$," K.L. Sorensen, M.E. Lerchen, J.W. Ziller, and N.M. Doherty, submitted to *J. Am. Chem. Soc.* (AFOSR-87-0362)
8. "The Nature of the Nitride Bridge. Synthesis and Reactivity of Early-Late Heterobimetallic Nitride-Bridged Complexes," C. M. Jones, D. M.-T. Chan, J. C. Calabrese, and N.M. Doherty, in preparation. (AFOSR-87-0362)
9. "Synthesis and Structures of Electron-Rich Iridium Silylimido and Nitrido-Bridged Complexes," N.M. Doherty, C. M. Jones, J. D. Lichtenhan, S. C. Critchlow, D. S. Glueck, F. J. Hollander, and R. G. Bergman, in preparation. (AFOSR-87-0362)
10. "Reactions at Metal-Bound Nitrogen Atoms. Formation of Molybdenum and Tungsten Phosphiniminato Complexes from Silylimido Compounds and Synthesis of a Nitride-Bridged Tungsten Derivative," J. D. Lichtenhan, J. W. Ziller, and N. M. Doherty, submitted to *Inorg. Chem.* (AFOSR-87-0362 & AFOSR-91-0179)
11. "The Synthesis of Group IV Transition-Metal Pentamethylcyclopentadienyl Complexes Containing the Bis(trimethylsilyl)phosphido Ligand," M. B. O'Regan and N. M. Doherty, in preparation. (AFOSR-91-0179)
12. "Mechanism of the Condensation-Polymerization Reaction Forming a Vanadium Nitride Linear Chain Compound," B.M. Schomber, J. M. Farrier, and N.M. Doherty, in preparation. (AFOSR-91-0179)

STUDENTS AND POSTDOCTORALS INVOLVED IN WORK

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Jeffrey M. Farrier (B.S. expected 1993)
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