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Synthesis of Tungsten Nitrene Complexes as Precursors to Tungsten Nitride

5. FUNDING NUMBERS

6. AUTHOR(S)
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The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
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13. ABSTRACT *(Maximum 200 words)*

Chemical vapor deposition using organometallic precursors (MOCVD) provides a method for the preparation of thin films. Low valent tungsten nitrene complexes were synthesized as potential precursors to tungsten nitride (WN_x), a material used in diffusion barriers for Si or GaAs semiconductor devices. The original target precursors for MOCVD of WN_x were the carbonyl-containing complexes $(CO)_{5-n}(PR_3)_nW{=}NR$, where R is an alkyl or aryl group. Later synthetic work involved the tungsten(IV) imido (or nitrene) complexes $(CO)_2I_2LW{\equiv}NPh$, which were prepared by oxidation of the zwitterionic species $(CO)_5WNPhNPhC(OMe)Ph$ with one equivalent of I_2 followed by addition of a coordinating species L [L= THF, pyridine, PMe_3, $P(OMe)_3$].

14. SUBJECT TERMS	15. NUMBER OF PAGES
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Final Report

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2. PERIOD COVERED BY REPORT: 15 May 1994 - 14 November 1994

3. TITLE OF PROPOSAL: Synthesis of Tungsten Nitrene Complexes as Precursors to Tungsten Nitride

4. GRANT NUMBER: DAAH04-94-G-0096

5. NAME OF INSTITUTION: University of Florida

6. AUTHOR OF REPORT: Lisa McElwee-White

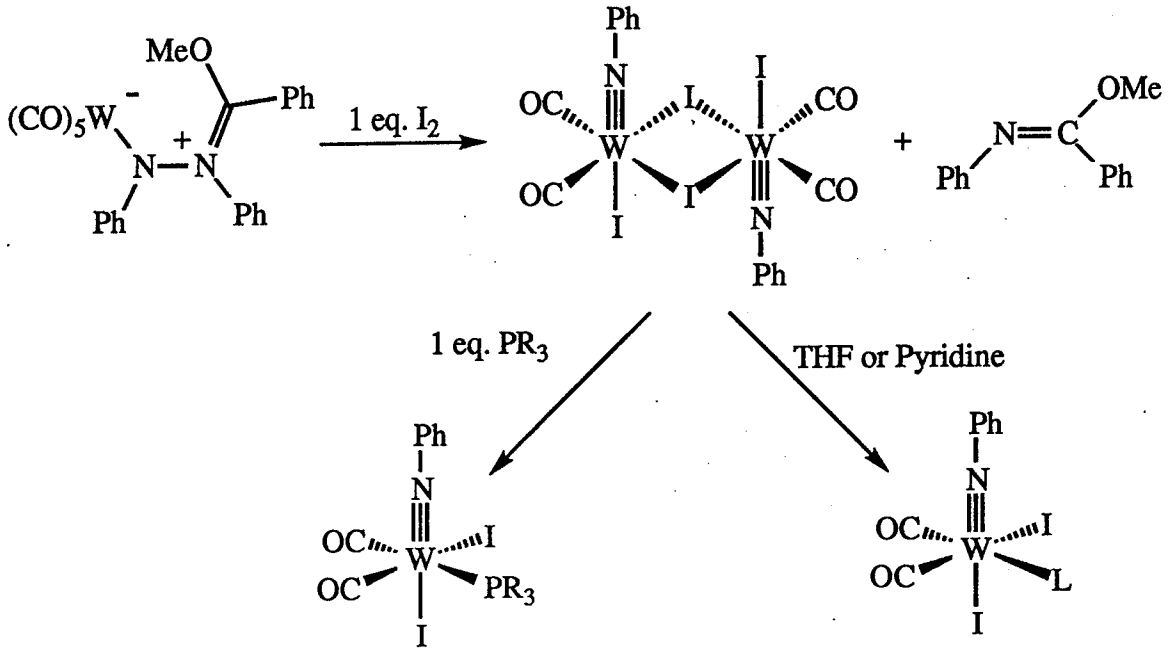
7. STATEMENT OF PROBLEM:

Chemical vapor deposition using organometallic precursors (MOCVD) provides a method for the preparation of thin films. We are developing syntheses of low valent tungsten nitrene complexes as precursors to tungsten nitride (WN_x), a material used in diffusion barriers for Si or GaAs semiconductor devices. Our target precursors for MOCVD of WN_x are the carbonyl-containing complexes $(CO)_{5-n}(PR_3)_nW{=}NR$, where R is an alkyl or aryl group. Upon heating at a surface, these compounds should lose the five ancillary ligands and undergo fragmentation of the NR group to deposit a film of WN_x.

8. SUMMARY OF MOST IMPORTANT RESULTS:

We have recently begun to explore the chemistry of tungsten (IV) imido complexes bearing CO ligands. The new target complexes were molecules of the type $(CO)_2I_2LW{\equiv}NPh$. These species maintain the CO ligands that should be good leaving groups during MOCVD of tungsten nitride but the higher oxidation state renders the metal nitrene (or imido) moiety much more stable than in the zero-valent nitrene complexes studied in the earlier stages of the project. We had previously reported that the zwitterionic complex $(CO)_5WNPhNPhC(OMe)Ph$ decomposes upon thermolysis or photolysis to yield $(CO)_5W{=}NPh$. We have now demonstrated that this species is also a precursor to the tungsten (IV) imido complexes since the zwitterion can serve as a protected imido functionality during oxidation of the metal center. Treatment of the zwitterionic complex $(CO)_5WNPhNPhC(OMe)Ph$ with one equivalent of I_2 leads to the formation of highly unusual iodo-bridged tungsten (IV) imido dimer $[(CO)_2I_2W{\equiv}NPh]_2$ and phonic(OMe)Ph (Scheme 1). Cleavage of the dimer with coordinating species leads to formation of the monomeric compounds $(CO)_2I_2LW{\equiv}NPh$ [L = pyridine, amines, phosphines, or phosphites] These complexes are now being explored as MOCVD precursors in collaboration with Professor Timothy J. Anderson, Department of Chemical Engineering, University of Florida.

Scheme 1



9. LIST OF PUBLICATIONS:

1. "Reactions of $(CO)_5W(THF)$ with Triphenylmethyl Azide and Triptycyl Azide," Massey, S.T.; Mansour, B.; McElwee-White, L. *J. Organomet. Chem.*, in press.

2. "Tungsten (IV) Imido Complexes From Oxidation of a Protected Zero-Valent Nitrene Precursor," McGowan, P.C.; Massey, S.T.; Abboud, K.A.; McElwee-White, L. *J. Am. Chem. Soc.*, **1994**, *116*, 7419-7420.

10. PARTICIPATING SCIENTIFIC PERSONNEL:

Graduate Students:	Scott T. Massey Man Lung Kwan
Undergraduates:	Kacy Gapinski Joel Weber
Postdoctorals:	Dr. Patrick C. McGowan Dr. Nicholas D.R. Barnett

Graduate Students and Postdoctorals received stipends, undergraduates received only research supplies.