REPORT DOCUMENTATION P

CTIONS
TING FORM

AD-A193 062

NUMBER

1. REPORT NUMBER	2	
AFOSR-TR. 88-0520		

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
The Chemistry of Precursors to Silicon Carbide	Final Report
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
M. A. Ring and H. E. O'Neal	AFOSR 83-0209

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Department of Chemistry San Diego State University San Diego, CA 92182	61102F 2303/B2

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Air Force Office of Scientific Research Building 410 Bolling AFB, DC 20332	3/25/88
	13. NUMBER OF PAGES

14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)	15. SECURITY CLASS. (of this report)
AFOSR/NC Bolling AFB DC 20332-6448 (Bldg 410)	UNCLASSIFIED
	15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release

Distribution Unlimited

DTIC
ELECTE
MAY 0 4 1988
D

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Silane, Organosubstituted Mono and Disilanes, Silylene, Organosubstituted Silylenes

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The research can be divided into 4 main areas:

1) Mechanisms and Kinetics of the Decompositions of Silane and Organosubstituted Monosilanes, and of Disilane and Organosubstituted Disilanes.

2) Relative Rate Kinetics of the Trapping Reactions of SiH_2 with Ethylene, Acetylene, Butadiene, Methanol, Silane and 1-butene.

Cont. (See Reverse Side)

DD FORM 1473
1 JAN 73

20. ABSTRACT (Cont.)

3) Mechanisms and Kinetics of the Isomerizations and Decompositions of
    Organosilylenes.

4) From the above studies, we were able to propose a general reaction
    mechanism for carbosilane production from the decomposition of
    dimethylsilane (paper #12).

FINAL PROJECT REPORT (AFOSR-83-0209)

1. SUMMARY OF WORK

Our AFOSR research has focused on three important areas of organosilicon chemistry as that chemistry relates to the formation and production of carbosilanes:
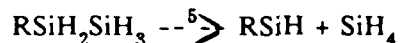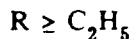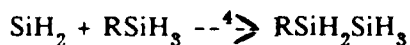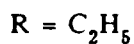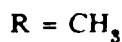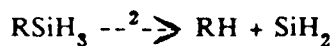
Area #1) Mechanisms and Kinetics of the Decompositions of Silane and Organosubstituted Monsilanes, and of Disilane and Organosubstituted Disilanes.

Systems investigated were n-propylsilane[1], ethylsilane[2], silane[3,4], dimethylsilane[5,12], ethynylsilane[6], butylsilane[7], chloromethyldimethylsilane[8], and 1,1,2,2-tetramethyldisilane[13], 1,1,2-trimethyldisilane[14] and 1,1-dimethyldisilane[15].

Results of area #1 studies: The main findings of these studies were:

1) The decomposition kinetics of monosubstituted silanes ($RSiH_3$), are independent of the nature of the R group, (A-factors $\approx 10^{15.2\pm0.2}$ sec^{-1} and $E_a \approx 64\pm1$ Kcal).

2) The primary dissociation reaction channel of $RSiH_3$ compounds is 1,1 H_2 elimination (rxn 1).

3) RH elimination (rxn 2) also occurs (when R = CH_3 and perhaps also C_2H_5 and phenyl) but does not compete with H_2 elimination

4) Decompositions of dialkylsilanes and monoalkylsilanes (R > CH_3) are accelerated by silylene induced chain reactions (e.g. rxns 3-6, for ethylsilane).

5) Free radical chain reactions, in addition to silylene chains, occur in the decompositions of dialkyl and higher alkylsubstituted monosilanes.

6) Alkyl substitution for H in monosilanes increases decomposition activation energies by about 4 ± 1 Kcal/R group up to R_2SiH_2 (i.e. the order of thermal stabilities in monosilanes is SiH_4 < $RSiH_3$ < $R_2SiH_2 \approx R_3SiH$).

7) Disilanes decompose mainly by 1,2 H shifts (e.g. rxn 7), but 1,1 H_2 eliminations become important at higher temperatures (e.g. rxn 8).

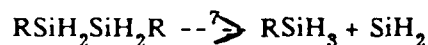8) Decompositions by 1,2 H_2 eliminations (e.g. rxn 9) do not occur.
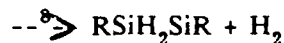
Alkylsilane Decompositions

$RSiH_3 \xrightarrow{1} RSiH + H_2$

$RSiH_3 \xrightarrow{2} RH + SiH_2$ $R = CH_3$

$RSiH_3 \xrightarrow{3} C_2H_4 + SiH_2$ $R = C_2H_5$

$SiH_2 + RSiH_3 \xrightarrow{4} RSiH_2SiH_3$ $R \geq C_2H_5$

$RSiH_2SiH_3 \xrightarrow{5} RSiH + SiH_4$ } CHAIN

$RSiH \xrightarrow{6} olefin + SiH_2$

Alkyldisilane Decompositions   Illustrated for a 1,1-alkyldisilane

$RSiH_2SiH_2R \xrightarrow{7} RSiH_3 + SiH_2$ 1,2 H-shift

$\xrightarrow{8} RSiH_2SiR + H_2$ 1,1 H_2 elimination

$X \xrightarrow{9} X$ $RSiH=SiHR + H_2$ does not occur

Area #2) Relative Rate Kinetics of the Trapping Reactions of SiH_2.

Systems studied were silylene reactions with ethylene and butadiene[10], silylene reactions with MeOH and butadiene[9], silylene reactions with acetylene and silane[4], and silylene reactions with 1-butene and silane[11]. Systems under investigation are SiH_2 with 1-pentene and cis-2-butene. Results of the area #2 relative rate studies were:

1) Silylene trapping by multiple bonded substrates are complex processes involving multiple reaction channels, some of which do not produce observable products. For example silylene trapping by acetylene and silane is non-quantitative and mass balances of the observable products, which are disilane, vinylsilane, ethynlsilane, ethylene, ethynlvinylsilane and ethynldivinyisilane, diverge increasingly from theoretical as the reaction proceeds. The mechanism, which involves silacyclopropane formations and subsequent isomerizations and decompositions, is shown in Scheme 1 below. [Observed products are underlined.]

Scheme I: Mechanism of the Silylene + Acetylene Reaction

$$SiH_2 + C_2H_2 \longrightarrow [HC\!=\!CH \rightleftharpoons HC\text{-}CH_2 \rightleftharpoons CH_2\text{-}CH_2]$$

$$\underset{SiH_2}{\qquad} \underset{SiH}{\qquad} \underset{Si}{\qquad}$$

$$\downarrow 16\% \qquad\qquad \downarrow 70\% \qquad\qquad \downarrow 14\%$$

$$\underline{HC\!\equiv\!CSiH_3} \qquad CH_2\!=\!CHSiH \qquad \underline{C_2H_4} + Si$$

$$CH_2\!=\!CHSiH + C_2H_2 \longrightarrow [\underset{VSiH}{CH\!=\!CH} \rightleftharpoons \underset{SiV}{HC\text{-}CH_2}] \qquad\qquad \text{where } V = (CH_2\!=\!CH)$$

$$\downarrow 14\% \qquad\qquad \downarrow 86\%$$

$$\underline{V_2SiH_2} \qquad\qquad V_2Si$$

$$V_2Si + C_2H_2 \longrightarrow [\underset{VSiV}{HC\!=\!CH}] \longrightarrow \underline{HC\!\equiv\!CSiH(V_2)}$$

$$RSiR' + SiH_4 \rightleftharpoons RR'SiHSiH_3 \longrightarrow \underline{RR'SiH_2} + SiH_2 \qquad \text{Where R and R' are H or V}$$
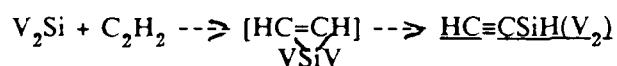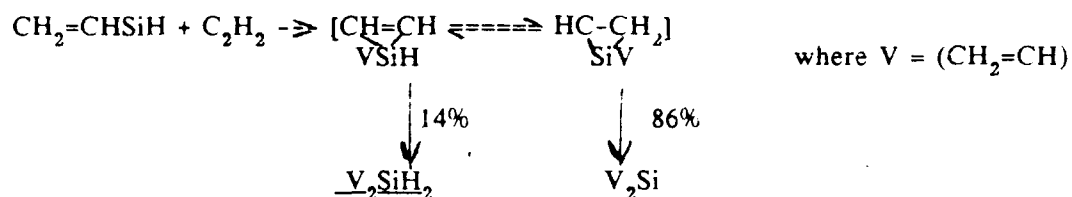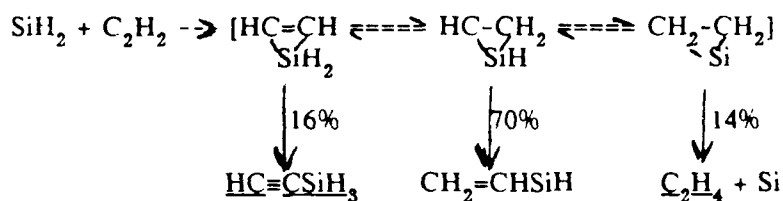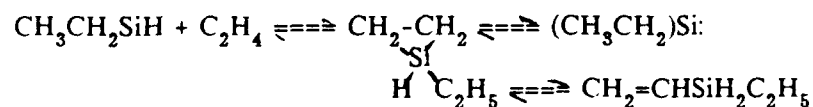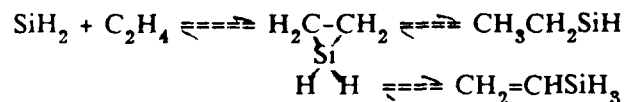
2) Trapping by ethylene and other olefins is similarly complex. The corresponding mechanism shown below in Scheme II:

Scheme II: Mechanism of the Silylene + Ethylene Reaction

$$SiH_2 + C_2H_4 \rightleftharpoons \underset{Si}{H_2C\text{-}CH_2} \rightleftharpoons CH_3CH_2SiH$$

$$\underset{H \quad H}{\qquad} \rightleftharpoons CH_2\!=\!CHSiH_3$$

$$CH_3CH_2SiH + C_2H_4 \rightleftharpoons \underset{Si}{CH_2\text{-}CH_2} \rightleftharpoons (CH_3CH_2)Si\!:$$

$$\underset{H \quad C_2H_5}{\qquad} \rightleftharpoons CH_2\!=\!CHSiH_2C_2H_5$$

The intermediate silylenes of the above reaction (SiH_2, C_2H_5SiH and $(C_2H_5)_2Si$) can be trapped by Si-H insertion trapping agents to eventually produce alkylated silanes. Also, on the basis of poor product mass balances, it is clear that continued trapping by ethylene leads not only to vinylsilane products but more importantly to polymeric materials. Solid deposits on the reaction cell walls and connecting inlet and outlet tubes are further evidence for polymer formation.

3) Relative rate constant determinations for silylene trapping reactions by various substrates have been determined, and the relevant reactions and their kinetics are shown below.

Competing Reactions	Relative Kinetics

$$SiH_2 + C_4H_6 \xrightarrow{10} SiH_2 \begin{array}{c} CH_2CH \\ | \\ CH_2CH \end{array}$$ $\ln(k_{10}/k_{11}) = 5.9 - 5846 \text{ cal}/RT$

$SiH_2 + MeOH \xrightarrow{11} MeOSiH_3$

$SiH_2 + C_2H_2 \xrightarrow{12} HC\equiv CSiH_3$ $\ln(k_{10}/k_{12}) = 1.5 - 712 \text{ cal}/RT$

$SiH_2 + 1\text{-butene} \xrightarrow{13} \text{all products}$
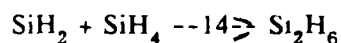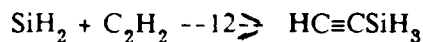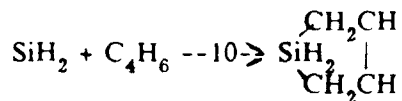
$SiH_2 + SiH_4 \xrightarrow{14} Si_2H_6$ $k_{13}/k_{14} = 2.1$ (643-689 K)

Area #3) Mechanisms and Kinetics of the Isomerizations and Decompositions of Organosilylenes.

Systems studied were the isomerization and decomposition kinetics of ethylsilylene[2], n-propylsilylene[1], ethynlsilylene[6], and most importantly, n-butylsilylene[7], and sec-butylsilylene[11].
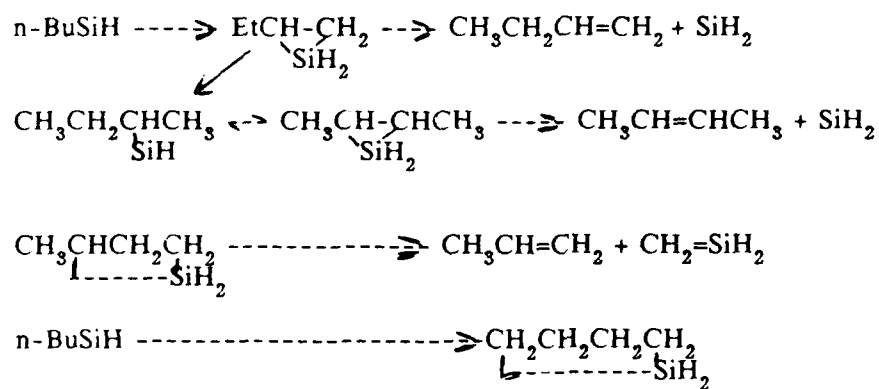
Results of the area #3 studies are:

1) Alkysilylenes (R > Me) decompose at SPST and static system reaction temperatures to SiH_2 and olefins.

2) The mechanism of decomposition involves silacyclopropane intermediates (or perhaps at SPST temperatures, silacyclobutanes).

3) Alkylsilylene decompositions have activation energies less than 30 Kcal.

4) The decomposition of sec-butylsilylene occurs with an activation energy significantly lower than its decomposition reaction enthalpy. This requires a very loose transition state for the decomposition reaction and also requires that the decomposition occur by a consecutive step process (e.g. a biradical mechanism).

5) Silylenes add very readily to pi bonds to form very labile silacyclopropanes. These addition reactions are high A-factor processes, probably consecutive step biradical processes, and cannot be, as formally believed, single step concerted processes.

6) Silacyclopropanes have three important and competing reaction pathways: decomposition to silylene and olefin, isomerization to a silylene via an H atom shift from silicon to carbon and

isomerization to a vinylsilane via an H atom shift from carbon to silicon.

7) Alkylsilylenes readily isomerize via intramolecular C–H insertion reactions. The 3-center insertions producing silacyclopropanes are the most facile and are the dominant reactions at 'low' temperatures. Higher center insertions, (e.g. four center to produce silacyclobutanes, and five center to produce silacyclopentanes) appear to occur only under 'high' temperature shock tube reaction conditions. Thus in the reactions of n-butylsilylene generated at shock tube temperatures (i.e. $T \approx 1200$ K), see Scheme III, the rate constant ratios for 3-center/4-center/5-center reactions were calculated on the basis of product yields to be $k_{3\text{-center}}/k_{4\text{-center}}/k_{5\text{-center}} =$ 1/0.3/1.[7]

Scheme III: n-Butylsilylene Isomerization and Decomposition Rxns

n-BuSiH $----\!>$ EtCH–CH$_2$ $--\!>$ CH$_3$CH$_2$CH=CH$_2$ + SiH$_2$
       \\SiH$_2$

CH$_3$CH$_2$CHCH$_3$ $\leftarrow\!\!\rightarrow$ CH$_3$CH–CHCH$_3$ $---\!>$ CH$_3$CH=CHCH$_3$ + SiH$_2$
    SiH   \\SiH$_2$

CH$_3$CHCH$_2$CH$_2$ $-----------\!>$ CH$_3$CH=CH$_2$ + CH$_2$=SiH$_2$
   L$------$SiH$_2$

n-BuSiH $-------------------\!>$CH$_2$CH$_2$CH$_2$CH$_2$
             L$--------$SiH$_2$

2. PROGRESS TOWARD UNDERSTANDING THE DETAILS OF THE MECHANISM FOR CARBOSILANE FORMATION FROM ALKYSILANE PYROLYSES.

From the above studies, we have managed to learn enough about the general reaction and kinetic behaviors of the important intermediates and reactive products produced in organosilicon pyrolysis reaction systems to be able to propose a general reaction mechanism for carbosilane production.[12] Thus a mechanism, shown in part in Scheme IV, has been presented relative to the dimethylsilane pyrolysis system. This mechanism explains both qualitatively and semiquantitative the complex of products formed in that system (including 4-membered, 6-membered and 6-membered polycyclic adamantane type carbosilane products). Thus modeling

predictions with regard to the nature and yield of products are in good agreement with the experimental data.

Scheme IV: Mechanism of the Dimethylsilane Pyrolysis

Me_2SiH_2 --45-> $Me_2Si + H_2$

$Me_2Si + Me_2SiH_2$ $\overset{46}{\rightleftharpoons}$ $Me_2HSiSiHMe_2$

$Me_2Si + Me_2HSiSiHMe_2$ ---47--> $Me_2Si=SiMe_2 + Me_2SiH_2$

$Me_2Si=SiMe_2$ $\overset{48}{\rightleftharpoons}$ $Me_3SiSiMe$

$Me_3SiSiMe$ --49-> $Me_2Si\text{-}SiMeH$ $\overset{50}{\underset{}{\rightleftharpoons}}$ Me_2SiHCH_2SiMe --51-> $MeHSi\overset{CH_2}{\underset{CH_2}{\diagdown}}SiHMe$
$\qquad\qquad\qquad\qquad \overset{|}{C}H_2$

$\qquad\qquad\qquad\qquad \uparrow$ 52
$\qquad\qquad\qquad\qquad \overset{}{\Longrightarrow}$ Me_3SiCH_2SiH --53-> $Me_2Si\overset{CH_2}{\underset{CH_2}{\diagdown}}SiH_2$

$Me_2SiHCH_2SiMe + Me_2SiH_2$ -----> rxns like 45-53 to trisilahexanes & tricyclohexanes

$Me_3SiCH_2SiH + Me_2SiH_2$ -----> rxns like 45-53 to trisilahexanes & tricyclohexanes
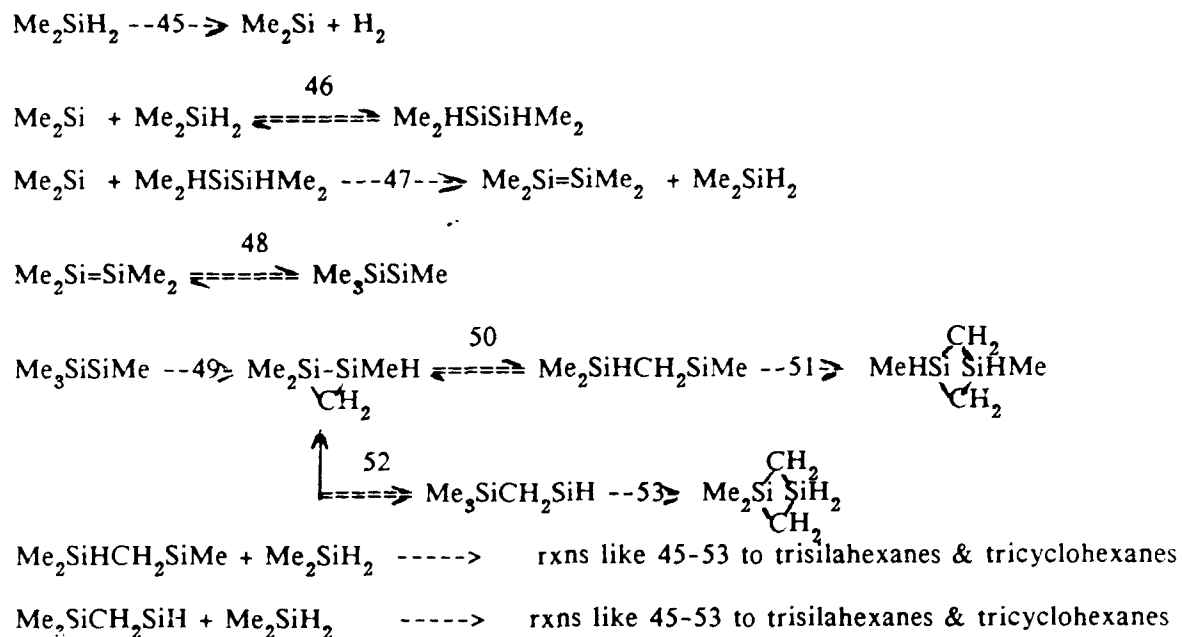
3. OTHER RECENTLY COMPLETED RESEARCH AND OTHER ONGOING RESEARCH

There are several projects still in progress which have been supported by AFOSR. These projects fall under the three research areas described previously and will produce results that are quite significant to those areas. Among these are the kinetic studies on 1,1,2-trimethyldisilane[14], 1,1-dimethyldisilane[15] and 1,1,2,2-tetramethyldisilane.[13] The data from these studies will be used to resolve long standing problems concerning the heats of formation of alkylated disilanes, and even more important, heats of formation of alkylated silylenes.[16] Preliminary calculations for the latter give $\Delta H°_f(MeSiH) \approx 48$ Kcal/mol and $\Delta H°_f(Me_2Si) \approx 34$ Kcal/mol. In addition, the heat of formation of hexamethyldisilane is calculated to be about -78 Kcal/mol, a value in agreement (within the experimental errors) of the -81 Kcal/mol value deduced from the decomposition kinetics of hexamethyldisilane as reported by Davidson et.al. This work[16], when coupled with other available and reliable literature data, will also result in a

revised additivity scheme for the accurate estimation of the thermodynamic properties of C,H,and Si containing compounds.[17]

Work continues on studies of the intramolecular rearrangements and decompositions of long chain alkylsilylenes, where the latter are generated via silylene additions to long chain olefins. The results of these studies will supplement our understanding of alkysilylene reactions and hopefully clarify the kinetics of their elementary reactions (i.2. their intramolecular insertions, ring openings and decompositions). Thus, for example, while reasonable estimates of the rate constants for intramolecular 3,4,5 and 6 membered ring formations can be made (i.e. such estimates have been used successfully in the various modeling studies mentioned in this report) no direct and unambiguous data have yet been gathered for these reactions. This has been, and will continue to be, one of the main focuses of our ongoing research with or without AFOSR support. A complete knowledge of carbosilane formation kinetics will not be possible until the kinetics of these kinds of reactions are fully understood.

PUBLICATIONS SUPPORTED BY THIS GRANT

1. B.A. Sawrey, H.E. O'Neal, M.A. Ring and D. Coffey Jr., Int. J. Chem. Kinet., 16, 801 (1984).

2. S.F. Rickborn, M.A. Ring and H.E. O'Neal, Int. J. Chem. Kinet., 16, 1371 (1984).

3. R.T. White, R.L. Espino-Rios, D.S. Rogers, M.A. Ring and H.E. O'Neal, Int. J. Chem. Kinet., 17, 1029 (1985).

4. J.W. Erwin, M.A. Ring and H.E.O'Neal, Int. J. Chem. Kinet., 17, 1067 (1985).

5. S.F. Rickborn, D.S. Rogers, M.A. Ring and H.E. O'Neal, J. Phys. Chem., 90, 408 (1986).

6. D.S. Rogers, M.A. Ring and H.E. O'Neal, Organometallics, 5, 1521 (1986).

7. B.A. Sawrey, H.E. O'Neal and M.A. Ring, Organometallics, 6, 720, (1987).

8. J.G. Martin, M.A. Ring and H.E. O'Neal, Organometallics, 5, 1228 (1986).

9. D.S. Rogers, H.E. O'Neal and M.A. Ring, Organometallics, 5, 1467 (1986).

10. D.S. Rogers, K.L. Walker, M.A. Ring and H.E. O'Neal, Organometallics, 6, 2313 (1987).

11. A.P. Dickenson, K.E. Nares, M.A. Ring and H. E. O'Neal, Organometallics, 6, 2596 (1987).

12. H.E. O'Neal and M.A. Ring, Organometallics, 7,0000 (1988), April.

13. K.A. Nares, M.A. Ring, H.E. O'Neal, in preparation.

14. K.A. Nares, M.A. Ring, H.E. O'Neal, to be published.

15. M. Harris, H.E. O'Neal and M.A. Ring, to be published.

16. H.E. O'Neal and M.A. Ring, in preparation.

17. G. Licciardi, H.E. O'Neal and M.A. Ring, to be published.

END

DATE

FILMED

DTIC

6-88