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Final Techninal Report

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by the

Department of Chemistry

Kentucky State University

Synthesis of

"ORGANOSILOXY – TRANSITION METAL POLYMERS"

Gerald A. Marano, Principal Investigator   Date _____

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I. Introduction

"Synthesis of Organosiloxy-Transition Metal Polymers"

Synthetic polymeric materials that are thermally stable at high temperatures have many useful applications. Protective coatings, nose cones for missiles, electrical insulators, ablative heat shields for satellites, and lubricants are just a few of their many applications.

Consequently, scientists have continuously sought ways to increase the thermal stability of polymers. For example, the addition of an inorganic element into the backbone of an organosiloxy polymer significantly increases its thermal stability.[1,2]

e.g. polymer (B) is much more thermally stable than polymer (A),

[R representing certain organic groups].

$$\left\{ \begin{array}{c} R \qquad R \\ | \qquad | \\ -O-Si-O-Si-O- \\ | \qquad | \\ R \qquad R \end{array} \right\}_n \qquad (A)$$

$$\left\{ \begin{array}{c} R \qquad\quad R \\ | \qquad\quad | \\ -O-Si-O-Al-O-Si-O- \\ | \qquad | \qquad | \\ R \qquad R \qquad R \end{array} \right\}_n \qquad (B)$$
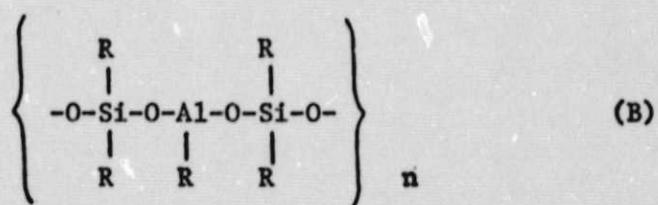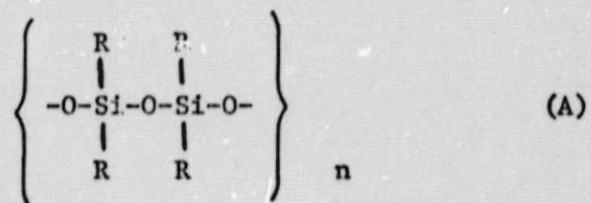
Scientists have extended this concept and synthesized several types of polymers containing -Si-O-M- bonds (where M represents certain transition elements, i.e. Co, Cr, Fe, and Ti[3,4,5,6] and other elements[7]).

Various approaches have been investigated. For example,

a. (-Si-O-Co-) polymers

$$n\ R_2Si(OC_2H_5)_2 + n\ Co(OCOCH_3)_2 \xrightarrow{200^\circ} [R_2SiOCoO]_n + n\ CH_3COOC_2H_5 \qquad (1)^{8,9}$$
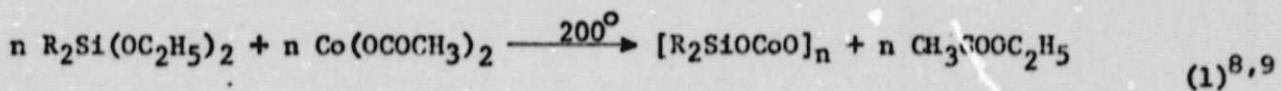
(where R represents various organic groups)

$$n\ R_2Si(ONa)_2 + n\ CoX_2 \xrightarrow[MCl_x]{THF} (R_2SiOCoO)_n + 2n\ NaX \qquad (2)^{9,10}$$
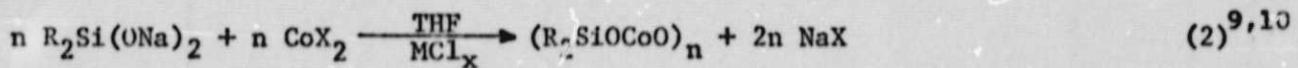
(where X represents certain halogens and M represents various metals)

b. (-Si-O-Cr-) polymers

$$n\ RSiCl_3 + Cr(NO_3)_3 + H_2O \xrightarrow{NaOH} [(RSiO_{1.5})_n\ CrO_{1.5}]_x + 3n\ NaCl + 3\ NaNO_3 \qquad (3)^{11}$$

c. (-Si-O-Fe-) polymers

$$RSi(OH)_2ONa + \left\{ \begin{array}{l} FeCl_3 \\ or \\ FeNH_4(SO_4)_2 \end{array} \right. \longrightarrow \left\langle [-RSi(OH)O-]_x [RSiO_{1.5}]_y FeO_{1.5} \right\rangle_n \qquad (4)^{12,13}$$
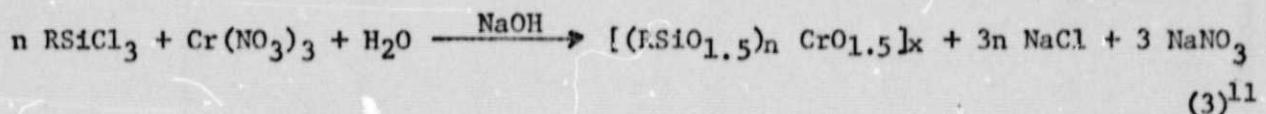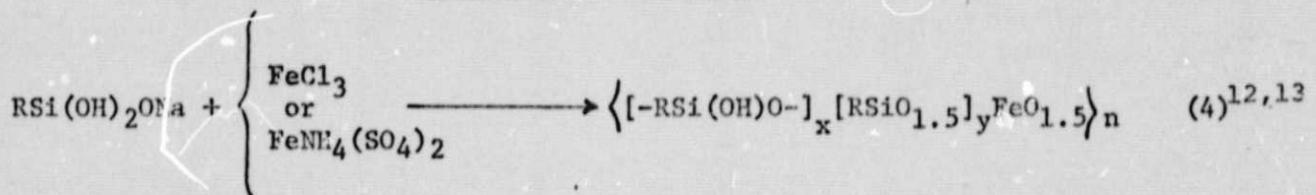
A balanced equation was not given in the literature for reactions (3) and (4), presumably due to the authors not knowing the exact stoicheometry of these reactions.

d. (-Si-O-Ti-) polymers

$$n\ (R_3SiO)_2Ti(OR')_2 + n\ R_2Si(OCOCH_3)_2 \longrightarrow R'O[Ti(OSiR_3)_2OSiR_2O]_nCOCH_3$$
$$+ (2n-1)\ CH_3COOR' \qquad (5)^{14}$$
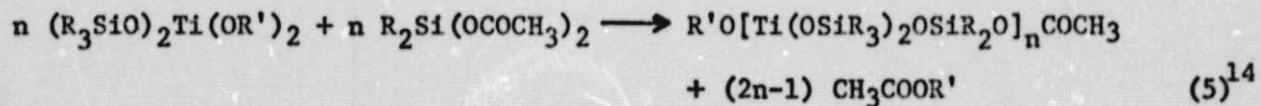
In summary, several conclusions may be drawn regarding known polymers containing a -Si-O-M- linkage, based upon a general survey of the literature

(1) Details regarding their synthesis are not extensive.

(2) The polymers that have been prepared are not representative of all transition elements.

(3) A majority of these polymers do not possess an ordered structure.

(4) Much work still remains to be done regarding general methods for synthesis, characterization and utility of these polymers.

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It is the intention of this project to study any novel synthetic approaches to the formation of polymers containing a -Si-O-M- linkage and to investigate the chemical and physical properties of these polymers. It is felt that because silicon-oxygen-transition metal bonds generally have high thermal stability, any polymers containing such a linkage should retain this property. In addition, the synthesis of an ordered, long chained, linear polymer containing alternating -Si-O-M-O- bonds could act as an electrical semi-conductor. This property, in theory, would result from the presence of a delocalized $(p \rightarrow d)_\pi$ bonding system involving empty silicon 3d orbitals, filled oxygen 2p orbitals and the (nd) orbitals of the transition metal. Discovering whether these properties exist should prove interesting.

Footnotes

1. Bruck, S. D., J. Chem. Ed., 42, 1 (January, 1965) 18.

2. Kirichenko, E. A., B. A. Markov, A. I. Ermakov and A. D. Damaeva. Zh. Fiz. Khim. 47 (11) 1973 p. 2809.

3. Borisov, S. N., M. G. Voronkov and E. Ya Lukevits. Organosilicon Heteropolymers and Heterocompounds. New-York: Plenum Press. 1970. See also references cited therein.

4. Schendler, F. and H. Schmidbaur. Angew. Chem. Internat. Edit. 6, 9(1967) 683.

5. Breed, L. W., R. L. Elliott, L. M. McDonough, W. H. Burton, M. E. Whitehead. "Synthesis and Evaluation of New High Temperature Polymers for Coating Applications." Tech. Summary Report June 26, 1964 to Sept 25, 1966. Cont. No. NAS8-11338. See also J. Org. Chem., 27 (1962) 257.

6. O'Connell, J. J., S. C Kwan, et al. "Development of Improved Semi-organic Structural Adhesives for Elevated Temperatures Applications." Monsanto Research Corporation- Boston Laboratory. May 15, 1968. Contract No. NAS8-11371.

7. Schmidbaur, H. Angew. Chem. Internat. Edit. 4, 3(1965) 201.

8. Belgian Patent 583,614 (1959). C.A.: 54, (1960) 14777d.

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11. Korshak, V. V. Usp. Khim., 26(1957) 1295. C.A.: 52, (1958) 5C22i.

12. Andrianov, K. A., T. N. Ganina and N.N. Sokolov. Vysokmolekul. Soedin., 4(1962)678. C.A.: 58, (1963) 9239c.

13. British Patent 978,666 (1964). C.A.: 62, (1965) 6650.

14. Author's Certificate of USSR. 154,397(1963). Byull. Izobr. No. 9, (1963) 52.

II. Abstract

The new compound, $Mo(OSiPh_3)_4$ (where Ph is C_6H_5) has been synthesized. An overall chemical reaction which accounts for the observed products is given by the redox approach in equation (1), viz.

$$2MoO_2Cl_2 + 4MOSiPh_3 + xH_2O \xrightarrow{TiCl_4} O_2 + \text{"}MoO_2 \cdot xH_2O\text{"} + 4MCl + Mo(OSiPh_3)_4 \quad (1)$$
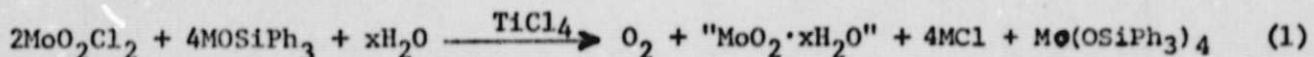
(where M is Na or K)

The reagents in equation (1) were synthesized by reactions (2) and (3)

$$2 MoO_3 + TiCl_4 \longrightarrow TiO_2 + 2 MoO_2Cl_2 \qquad (2)[1]$$

$$2M + 2 Ph_3SiOH \longrightarrow H_2 + 2MOSiPh_3 \qquad (3)[2,3]$$
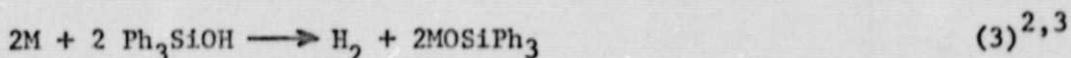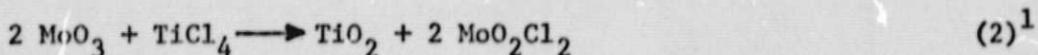
(where M = Na or K)

Results carried out during this study indicate that $Mo(OSiPh_3)_4$ is thermally stable up to $230^{\circ}C$ and relatively unreactive toward most common acids and bases even at elevated temperatures. Its behavior is not unlike that of $Ti(OSiPh_3)_4$.[4]

Whether a polymer of the type $(Ph_2Si-O-Mo-O)_x$ would retain these properties should be of considerable scientific interest. Polymers of this type could be synthesized according to reaction (4) which is a redox approach analogous to reaction (1).

$$xMoO_2Cl_2 + x(MO)_2SiPh_2 \xrightarrow{TiCl_4} xO_2 + 2 xMCl + (Ph_2Si-O-Mo-O)_x \qquad (4)$$
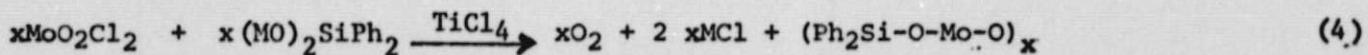
Footnotes

1. United States Patent 3,111,380 (1963).

2. Chugunov, V. S., _Zh. Obsch. Khim._, _28_ (1958) 336.

3. Schlenk, W. J. Renning and G. Racky. _Ber._, _44_ (1911) 1178. _C. A._: _5_
    (1911) 2839.

4. Zeither, Vernon A. and Charles A. Brown, _J. Am. Chem. Soc._ _79_ (1957) 4616.

A. Synthesis of tetrakis(triphenylsiloxy)molybdenum IV, Mo(OSiPh$_3$)$_4$.

$$2\ MoO_2Cl_2 + 4\ MOSiPh_3 + xH_2O \xrightarrow{TiCl_4} O_2 + \text{"}MoO_2 \cdot xH_2O\text{"} + 4MCl + Mo(OSiPh_3)_4 \qquad (1)$$

(where M is K or Na)
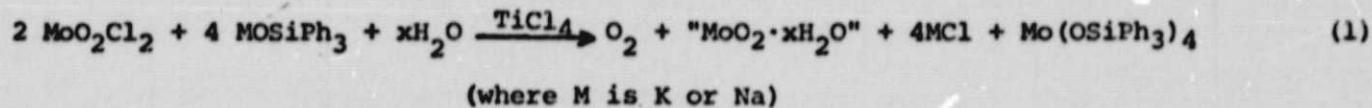
Reaction (1) is presently thought to best describe the experimental observations. This unique redox approach to the synthesis of Mo(OSiPh$_3$)$_4$ involves a reduction of molybdenum in the +6 oxidation state in MoO$_2$Cl$_2$ to the +5 state in "MoO$_2 \cdot$xH$_2$O"[#] and +4 state in Mo(OSiPh$_3$)$_4$ with the corresponding oxidation of oxygen in the -2 state in MoO$_2$Cl$_2$ to the zero state in molecular oxygen. Thus, MoO$_2$Cl$_2$ serves as both the oxidant and reductant in reaction (1).

One possible reaction mechanism which could account for the observed products is given as follows:

$$2\ MoO_2Cl_2 + 4MOSiPh_3 \longrightarrow 4MCl + 2[O_2Mo(OSiPh_3)_2] \qquad (2)$$

$$2\ [O_2Mo(OSiPh_3)_2] + xH_2O \longrightarrow O_2 + \text{"}MoO_2 \cdot xH_2O\text{"} + Mo(OSiPh_3)_4 \qquad (3)$$
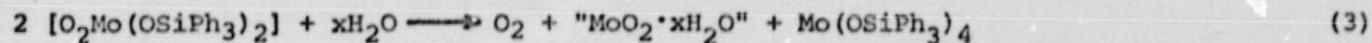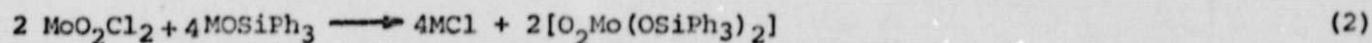
The intermediate [O$_2$Mo(OSiPh$_3$)$_2$] represents only one of several possible (and as yet) unidentified intermediates in this reaction. Support for reaction (2) is given in the literature by the analogous reaction (4) viz.,

$$2\ CrO_2Cl_2 + NaCSiPh_3 \longrightarrow 4\ NaCl + 2\ O_2Cr(OSiR_3)_2 \qquad (4)[2]$$
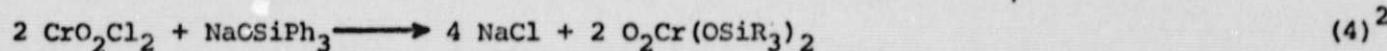
The presence of TiCl$_4$ (or one of its hydrolysis products) as a possible reaction catalyst in this system needs further investigation. Titanium tetrachloride does react vigorously with the reaction solvent, THF, according to the following reaction:

[#]   The product, "MoO$_2 \cdot$xH$_2$O" was written to balance reaction (1). Actually, "MoO$_2 \cdot$xH$_2$O" is meant to stand for a series of compounds collectively labeled as "molybdenum blue" whose composition varies from MoO$_{2.88} \cdot$xH$_2$O to MoO$_2$(OH) and whose oxidation state varies form 5.76 to 5.00, respectively. [1]
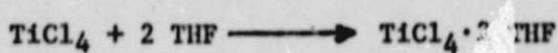
$$TiCl_4 + 2\ THF \longrightarrow TiCl_4 \cdot 2\ THF \qquad (4a)[3]$$

It also has the capacity to coordinate with molybendenum and analogous compounds (e.g.)
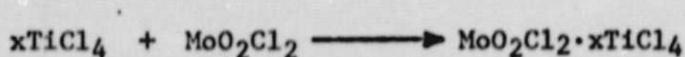
$$xTiCl_4 + MoO_2Cl_2 \longrightarrow MoO_2Cl_2 \cdot xTiCl_4 \qquad (5)[4,5,6]$$

or react with $MOSiPh_3$ (e.g.)
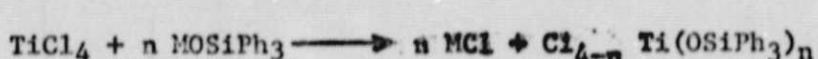
$$TiCl_4 + n\ MOSiPh_3 \longrightarrow n\ MCl + Cl_{4-n}\ Ti(OSiPh_3)_n \qquad (6)[7]$$

where (M is Na or K)

In addition, it is presently felt that the presence of small amounts of water are essential for the formation of good yields of $Mo(OSiPh_3)_4$. The presence of water ensures the formation of the insoluble blue precipitate of "$MoO_2 \cdot xH_2O$" and thus is the driving force for reaction (3). When attempts were made to remove all traces of water vapor from the reaction system by use of high vacuum drying techniques, extremely dry glove box techniques and solvents, the formation of the blue precipitate "$MoO_2 \cdot xH_2O$" was not observed and the yields of $Mo(OSiPh_3)_4$ were very poor (see experimental section, page 35).

It should be noted that the amount of water necessary to cause reaction (1) to go to completion may be calculated as only $6.0 \times 18 = 108$ mg based upon an initial concentration of 2.444 g of MoO_2Cl_2 (as described in the experimental section, page 31) and a product of "molybdenum blue" containing one water molecule. (i.e.)

$$2\ MoO_2Cl_2 + 4\ MOSiPh_3 + H_2O \longrightarrow O_2 + "MoO_2 \cdot H_2O" + 4\ MCl + Mo(OSiPh_3)_4 \qquad (7)$$
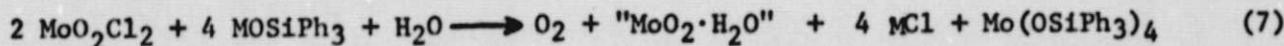
mg	2.444×10^3	(108)	(875.7)	(7.185×10^3)
mw	198.84	18	145.95	1197.56
mm	12	1/2(12)=6	(6)	(6)

It is entirely possible that this small amount of water is always present when

the synthesis of $Mo(OSiPh_3)_4$ is attempted using the bench top techniques and the "relatively wet" solvents used in the preparation of $Mo(OSiPh_3)_4$ as described in the experimental section on page 31.

An alternate mechanism which could account for the observed products is given by the following reactions:

$$2\ MoO_2Cl_2 + 2\ HOH \longrightarrow 2\ [MoO(OH)_2Cl_2] \tag{8}$$

$$2\ [MoO(OH)_2Cl_2] + 4\ MOSiPh_3 \longrightarrow 4\ MCl + 2\ [MoO(OH)_2(OSiPh_3)_2] \tag{9}$$

$$2\ [MoO(OH)_2(OSiPh_3)_2] \longrightarrow O_2 + \text{"}MoO_2 \cdot H_2O\text{"} + H_2O + Mo(OSiPh_3)_4 \tag{10}$$
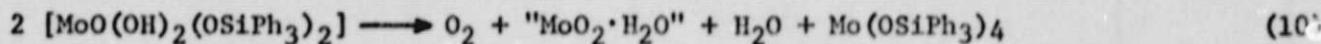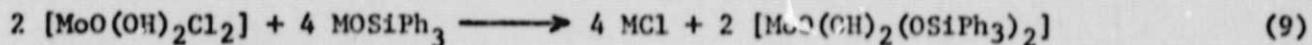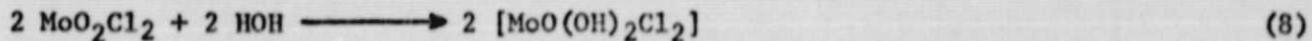
to give reaction (11) which is completely analogous to reaction (1).

$$2MoO_2Cl_2 + 4MOSiPh_3 + H_2O \longrightarrow O_2 + \text{"}MoO_2 \cdot H_2O\text{"} + 4\ MCl + Mo(OSiPh_3)_4 \tag{11}$$
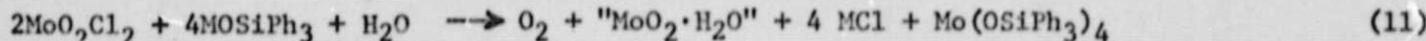
Reactions (8) and (9) of this mechanism would be supported by the work of Chamberlain et al.[8]

B. Identification of Tetrakis(triphenyl siloxy)molybdenum IV

1. By Infrared Analysis

Synthesis of $Ti(OSiPh_3)_4$, and $V(OSiPh_3)_4$ were carried out by Cohen and others according to reaction (12), viz.
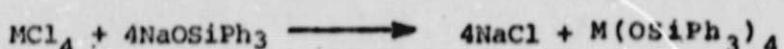
$$MCl_4 + 4NaOSiPh_3 \longrightarrow 4NaCl + M(OSiPh_3)_4 \qquad (12)^{7,9,10}$$

(where M is Ti or V)

The synthesis of $Ti(OSiPh_3)_4$ via reaction (12) was also confirmed during the course of the study. Infrared absorption spectra for $Ti(OSiPh_3)_4$, $V(OSiPh_3)_4$ and the new compound, $Mo(OSiPh_3)_4$ are presented in figures 1 to 5.

The only difference in these spectra is the position of the transition metal - oxygen - silicon stretching frequency (i.e. M-O-Si) as given in Table I.

Table I

Stretch	Absorption (μ)	Reference
Ti-O-Si	10.85 (vs broad)	a, 9,11
V-O-Si	11.2 (vs broad)	b, 9
Mo-O-Si	10.92 (vs broad)	c

Other metal - oxygen - silicon stretching frequencies correspond to those listed above, e.g.

Hg-O-Si	11 (11.5)	11, 12
As-O-Si	10.8 (11.3)	13, 14

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a   see enclosed infrared spectrum of $Ti(OSiPh_3)_4$

b   see enclosed infrared spectrum of $V(OSiPh_3)_4$

c   see enclosed infrared spectrum of $Mo(OSiPh_3)_4$

$V[OS_r(C_6H_5)_3]_4$

$Tr[OS_r(C_6H_5)_3]_4$
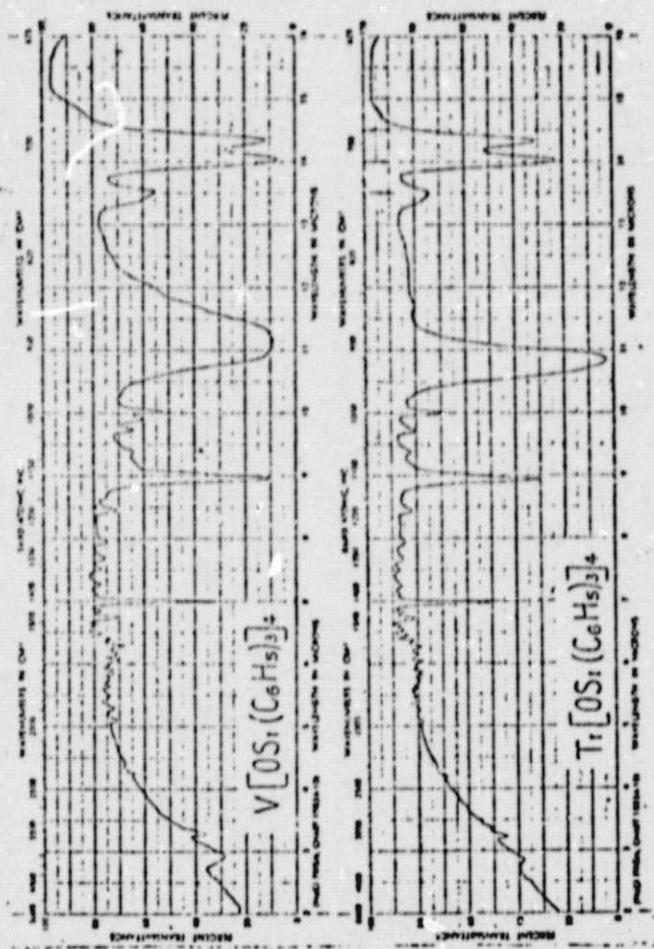
0.5% KBr pellet

Figure 1
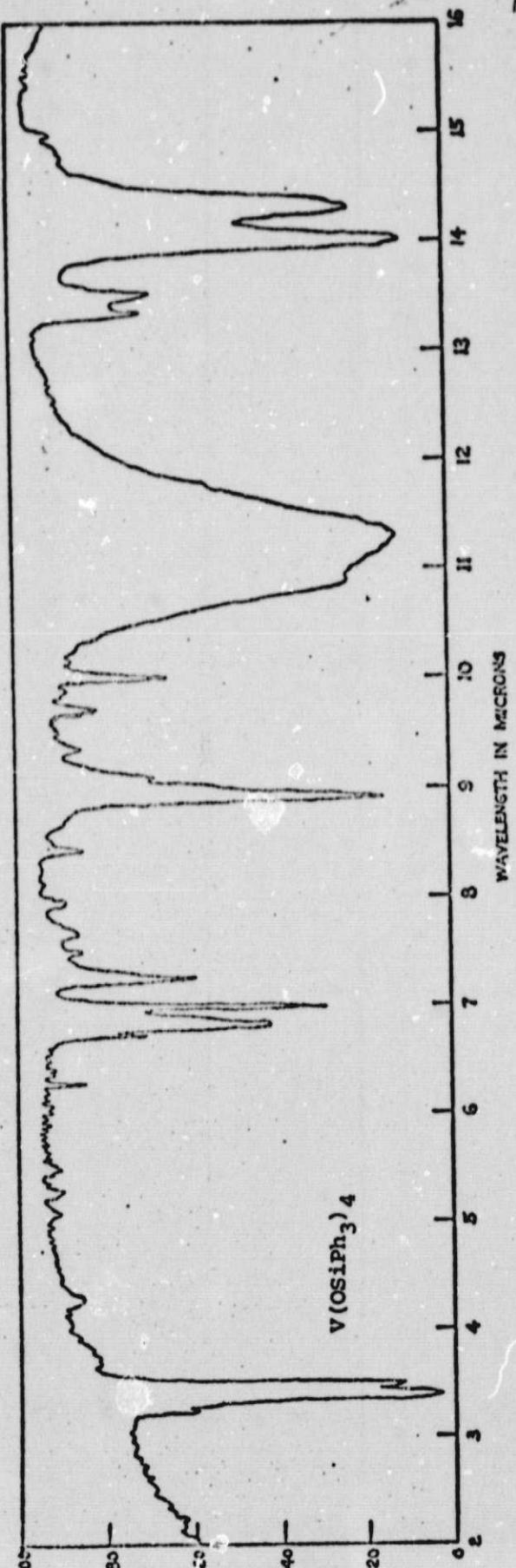
V(OSiPh₃)₄

Ti(OSiPh₃)₄

WAVELENGTH IN MICRONS

Nujol Mull
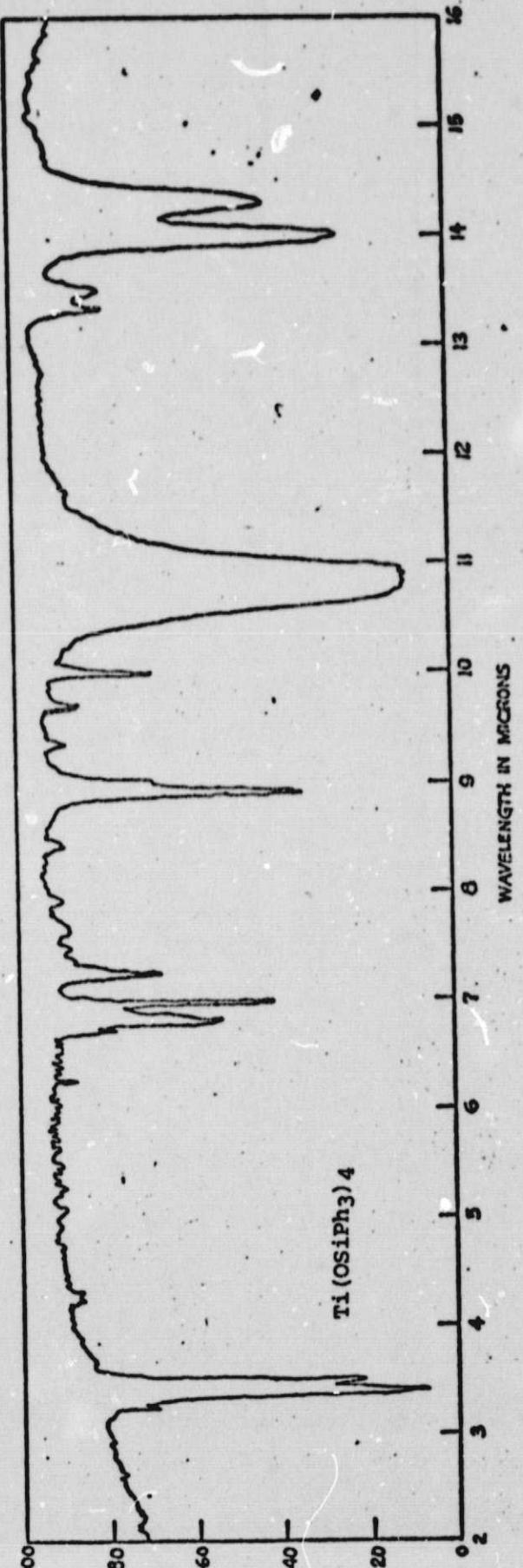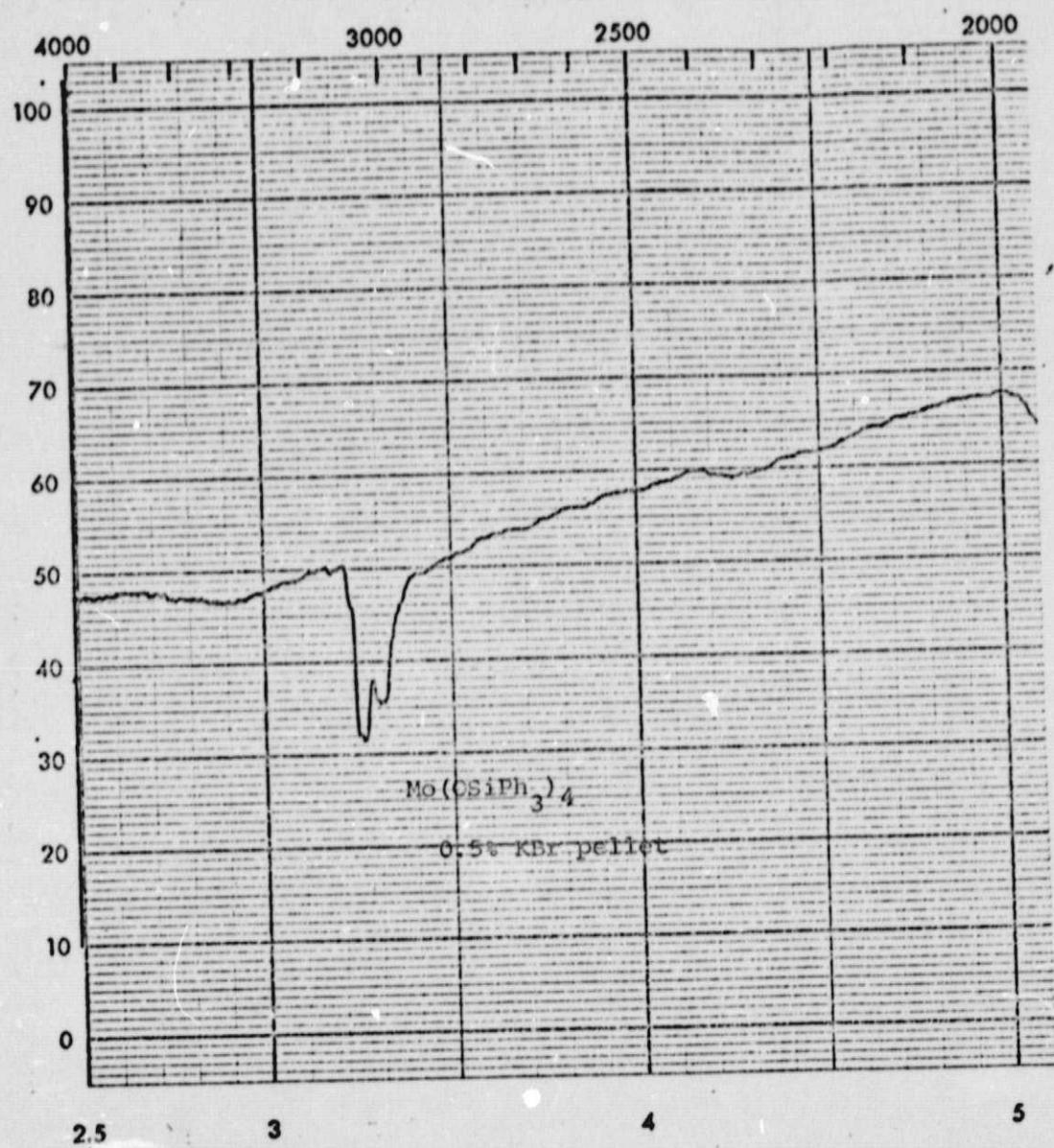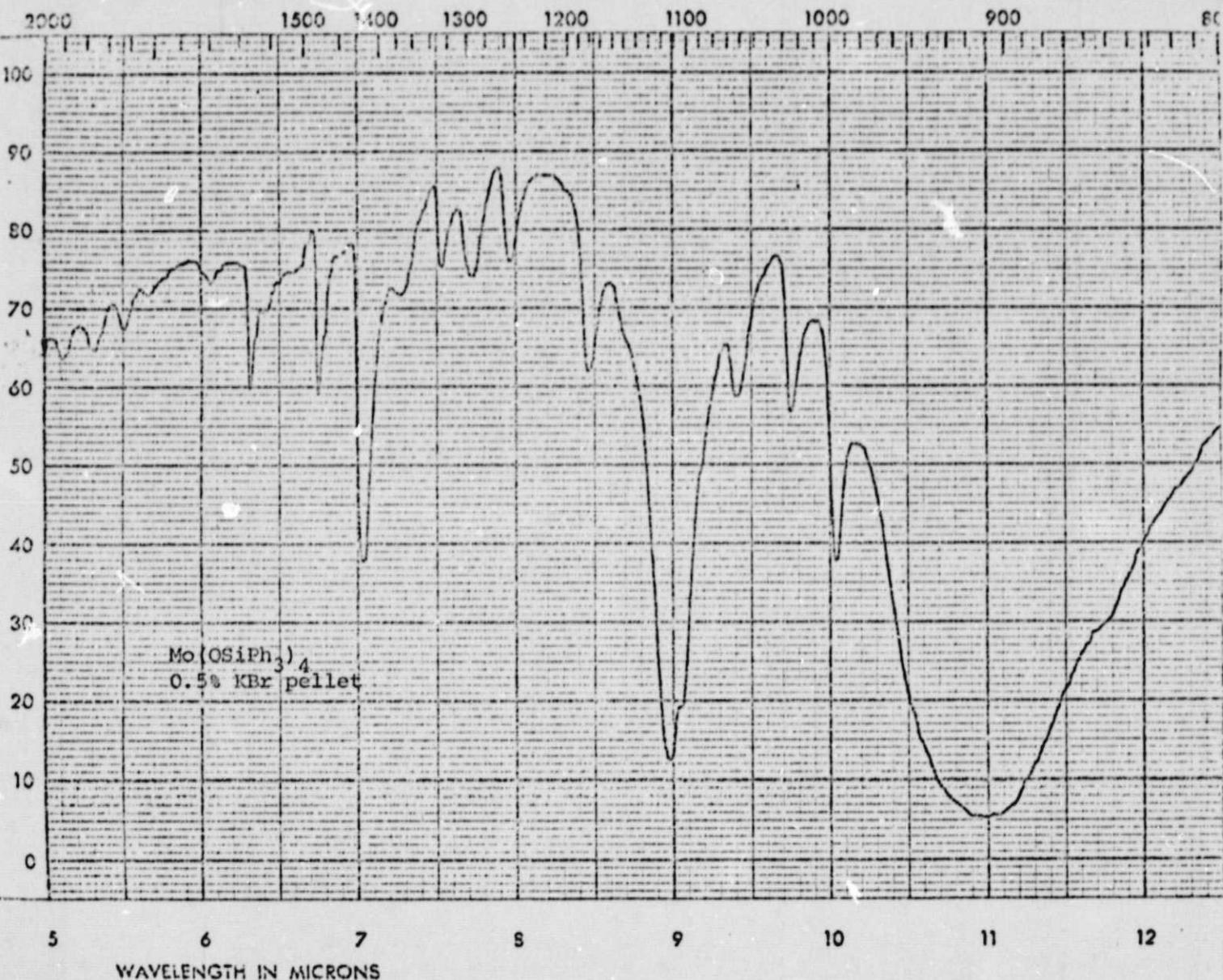
Figure 2

Figure 3

Figure 4

SPECTRUM NO. _IR-II_ - 57ρ
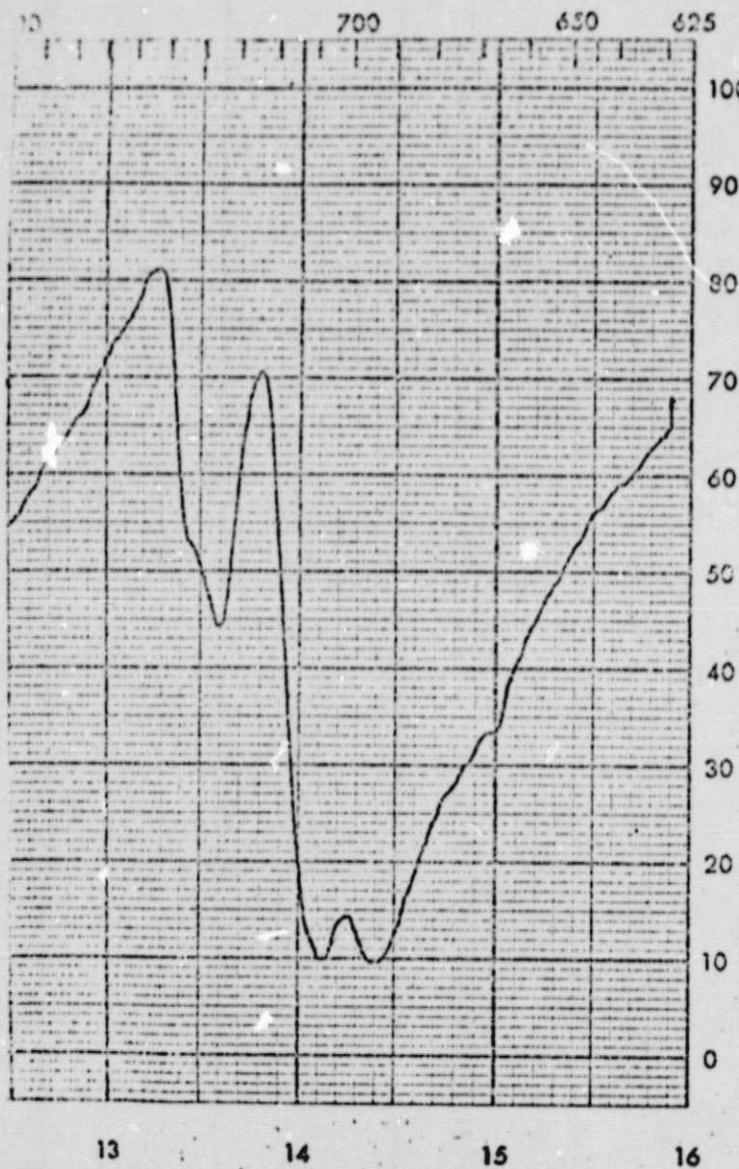
DATE _3-15-75_

SAMPLE Mo(OSiPh₃)₄   —

—tetrakis (triphenylsiloxy) molyb. IV.

SOURCE MoO₂Cl₂ + NaOSiPh₃ →
                              Oxy

STRUCTURE _____

PATH _____ mm
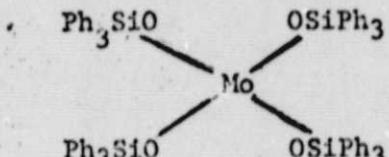
SOLVENT neat

CONCENTRATION _____

PHASE 0.5% KBr wafer

COMMENTS completely analogous
to IR of Ti(OSiPh₃)₄
and V(OSiPh₃)₄

ANALYST _____ ᴶˢ

Beckman®

INFRARED
SPECTROPHOTOMETER

Figure 5

A complete interpretation of the infrared absorptions for $Mo(OSiPh_3)_4$ is given in Table II.

Table II

INFRARED ABSORPTION SPECTRUM OF $Mo(OSiPh_3)_4$

Absorption (μ)	Intensity[a]	Assignment	Reference
3.25	V W	C-H aromatic stretching	11
3.30	V W		11
6.29	V W	phenyl - Si;b;c	11, 15
6.72	V W	phenyl - Si;b;c	11, 15
7.01	W	phenyl - Si;b	11, 15
7.50	V W	----------	-----
7.69	V W	phenyl - Si;c	11
7.94	V W	phenyl - Si;c	11
8.44	V W	phenyl - Si	15
8.96	S	phenyl Si;c planar ring vibration and some Si - C stretching	11, 15
9.39	V W	-----------	--------
9.72	V W	phenyl - Si	15
10.00	V W	phenyl -Si;c	11, 15
10.92	V S	Mo-O-Si asym stretch	--------
13.60	V W	Monosubstituted benzene ring	15
14.10	M	out of plane	
14.37	M	hydrogen deformation	

a) V = very; W = weak; S = strong; M = medium

b) C-C ring stretching

c) C-H and C=C vibration with ring deformation

2. By H^1 Nuclear Magnetic Resonance Analysis

Figure 6 is the H^1 n.m.r. spectrum for Mo$(OSiPh_3)_4$ dissolved in $TiCl_4$ (5% by weight) using TMS as an internal standard.

Figure 7 is the H^1 n.m.r. spectrum for Ti$(OSiPh_3)_4$ dissolved in $TiCl_4$ (7% by weight) using TMS as an internal standard.

As can be seen, these spectra are analogous and give the expected second order pattern for a mono-substituted benzene ring as supported by the literature.[16]
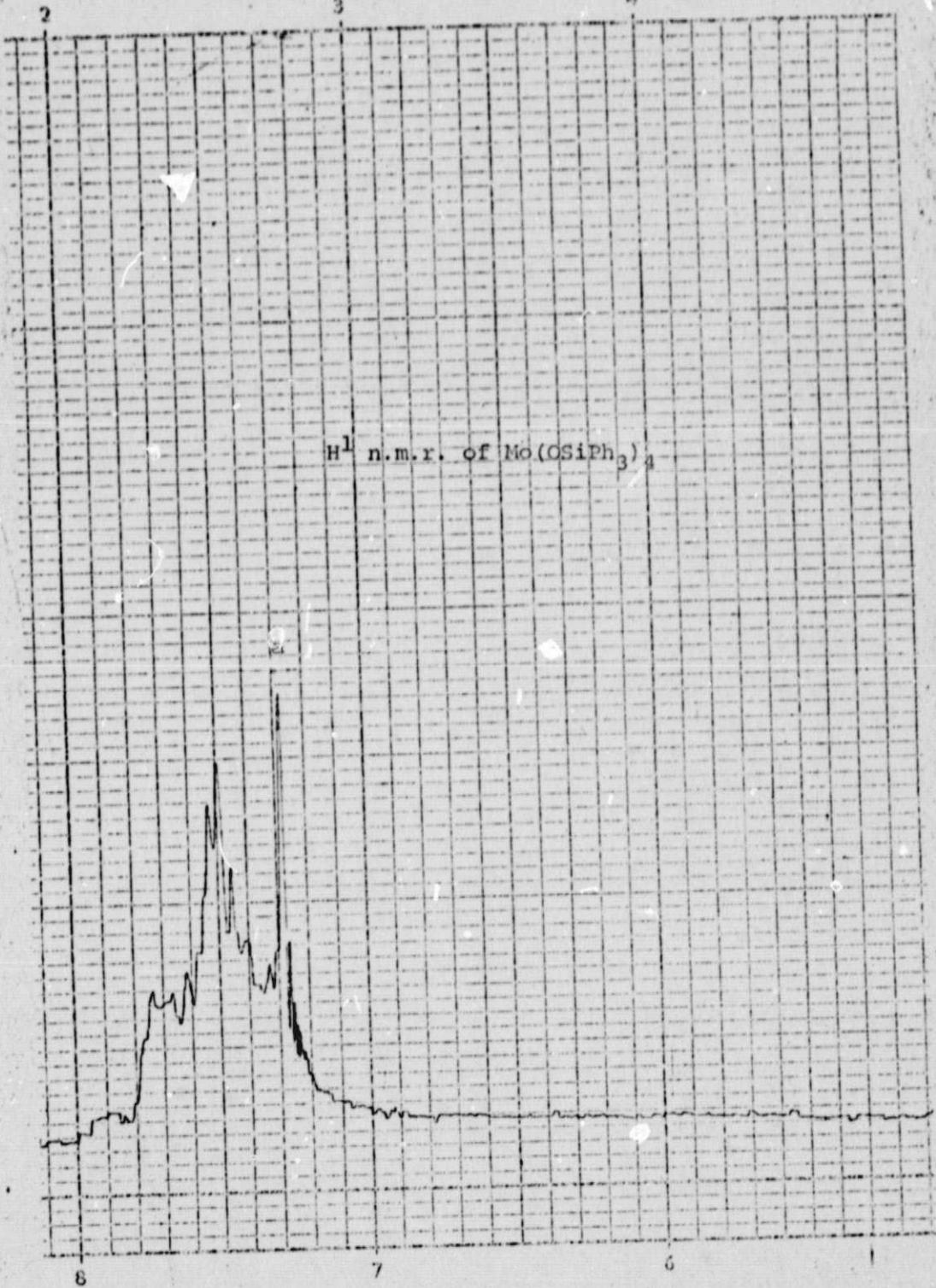
Figure 6

a. singlet due to trace of C_6H_6 in $TiCl_4$ solvent

H^1 n.m.r. of $Ti(OSiPh_3)_4$
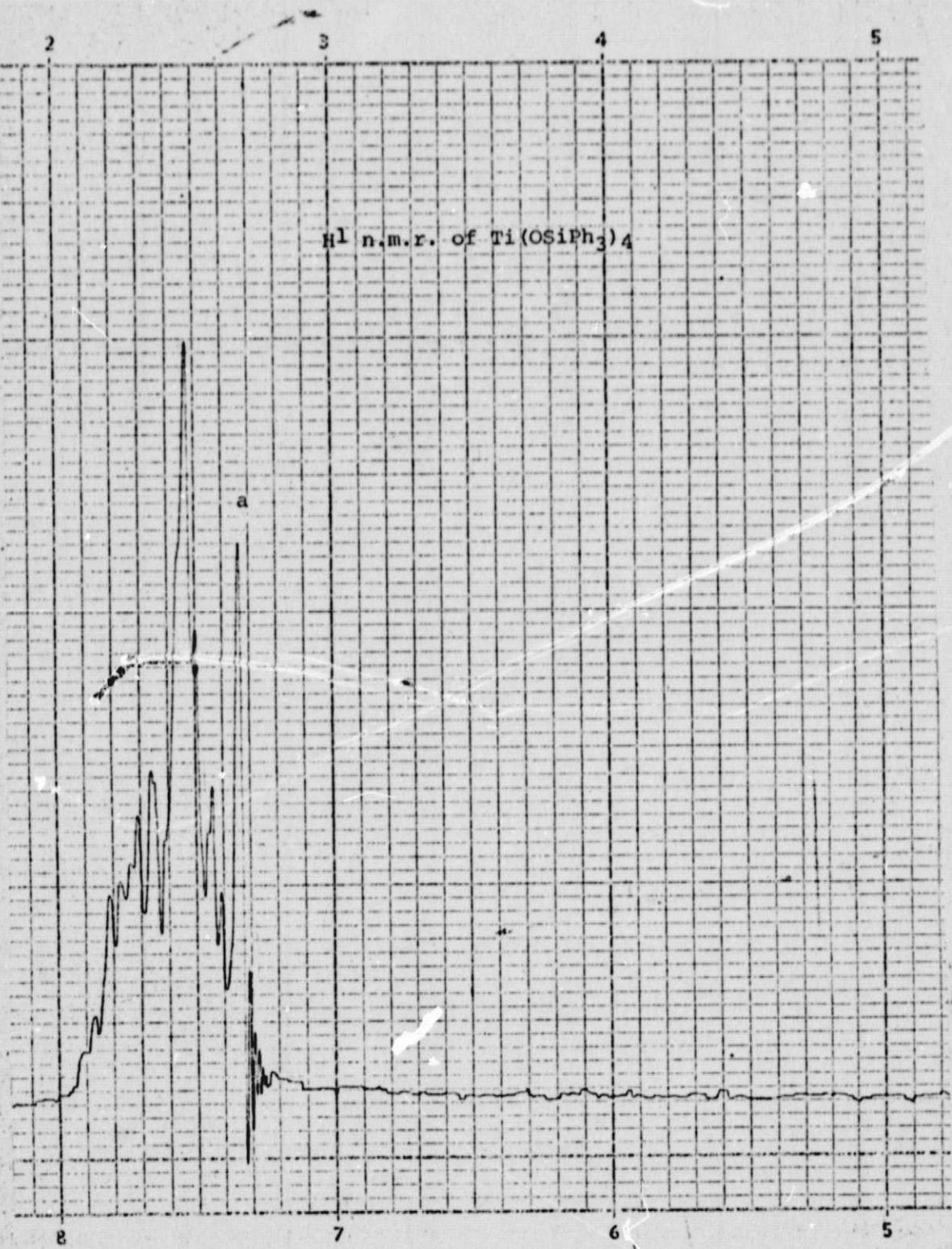
Figure 7

a.   singlet due to trace of C_6H_6 in $TiCl_4$ solvent

c.   A Study of the Chemical Properties of
Tetrakis (triphenylsiloxy) molybdenum IV

This study indicates that $Mo(OSiPh_3)_4$ is thermally stable up to $230^{\circ}C$ and does not react with water or on exposure to air. This compound has very limited solubility in common laboratory solvents at room temperature (see Table III).

Table III
Solubility of $Mo(OSiPh_3)_4$ in common solvents

Solvent	Solubility at 25° (mg/ml)
C_6H_6	insoluble
H_2O	insoluble
$SiCl_4$	insoluble
diethyl ether	0.5
Acetone	0.5
THF	1.0
Dioxane	2.5
CCl_4	3.0
Pyridine	4.0
$HCCl_3$	6.0
CS_2	7.0

However, it is appreciably soluble in $TiCl_4$ (200 mg/ml at $25^{\circ}C$) at room temperature. Branched crystals of $Mo(OSiPh_3)_4$ may be recovered from a solution of $TiCl_4$ by evaporating the solvent in vacuo.

The chemical reactivity of $Mo(OSiPh_3)_4$ with various reagents at their boiling point is summarized in Table IV.

Table IV

REACTION OF $Mo(OSiPh_3)_4$ WITH VARIOUS COMMON LABORATORY REAGENTS.

Common Reagent*	Approximate % $Mo(OSiPh_3)_4$ recovered unreacted	Conclusion
1. Concentrated HCl (12M)	95%	slight reaction
2. Concentrated H_3PO_4 (15M)	95%	slight reaction
3. Concentrated CH_3COOH (17M)	65%	moderate reaction
4. Concentrated HNO_3 (16M)	0%	complete reaction
5. Concentrated H_2SO_4 (18M)	87%	some reaction
6. Concentrated NaOH (19M)	85%	some reaction
7. Concentrated NH_3 (15M)	86%	some reaction

Common Reagent*	Approximate % $Mo(OSiPh_3)_4$ recovered unreacted	Conclusion
1. Dilute HCL (4M)	95%	slight reaction
2. Dilute H_3PO_4 (4M)	85%	some reaction
3. Dilute CH_3COOH (4M)	90%	some reaction
4. Dilute HNO_3 (4M)	95%	slight reaction
5. Dilute H_2SO_4 (4M)	98%	essentially no reaction
6. Dilute NaOH (4% by wgt.)	95%	slight reaction
7. Dilute NH_3 (4M)	87%	some reaction

* In excess and at its boiling point for at least one minute.

In summary, $Mo(OSiPh_3)_4$ showed little, if any, tendency to react with any of these reagents at room temperature (with the possible exception of concentrated HNO_3). The tendency of $Mo(OSiPh_3)_4$ to show little, if any, reaction toward dilute aqueous acids and bases can be explained by its insolubility in aqueous media. In addition, $Mo(OSiPh_3)_4$ appears to be thermally stable and relatively unreactive toward most common acids and bases even at elevated temperatures ($\sim230^o$). Its behavior is not unlike that of $Ti(OSiPh_3)_4$.[17]

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D. A Summary of Projected Areas of Research

Studies carried out by Cohen and Dessy[10,18] indicated that the following reaction possibly occurred:

$$2\ MoO_2Cl_2 + 2\ TiCl_4 + 6\ Ph_3SiONa \longrightarrow Mo_2(OSiPh_3)_6 + 3\ Cl_2 + 2\ TiO_2 + 6\ NaCl \qquad (13)$$
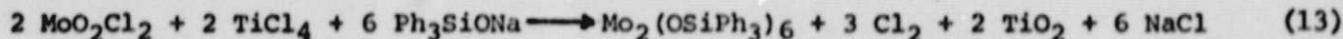
Work done by Chamberlain indicated that reaction did occur between $MoO(OH)_2Cl_2$ and Ph_3SiONa in DMF solvent to give a product containing a Mo-O-Si linkage(s). However, these products(s) were never characterized.[2,8,19]

It is proposed that the following areas should be further explored:

1. A determination of the exact chemical reaction by which $Mo(OSiPh_3)_4$ has been successfully and repeatedly synthesized in this laboratory.

2. A study of the mechanism by which Cohen & Dessey synthesized $Mo_2(OSiPh_3)_6$

3. A rationale as to the difference (if any) in the mechanisms operating in Cohen's reaction and that observed during the course of this study.

4. A comparison to the work of Chamberlain and that done during this study.

5. Further determinations as to the chemical and physical properties of $Mo(OSiPh_3)_4$ and any related compounds which may be synthesized in the future.

6. Polymerization of the monomer [i.e. $Mo(OSiPh_3)_4$] into $(Ph_2Si-O-Mo-O)_x$ polymer and a study of the chemical and physical properties of said polymer.

****

In summary, it is felt that a basic understanding of the synthesis and properties of the $Mo(OSiPh_3)_4$ and $(Ph_2Si-O-Mo-O)_x$ systems will provide a model for the better understanding of other less complex $(R_2Si-OMO)_x$ systems (where M represents a transition metal). The continuation of this work affords a unique opportunity for study in the following areas:

A. The stability of compounds containing molybdenum in various low oxidation states.

B. The utility of an oxidation-reduction synthetic approach to polymers of the type $(R_2Si-O-M-O)_x$.

C. The utility of such polymers in space age applications (e.g. semi-conductors, lubricants, heat shields, etc.).

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Footnotes

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IV. EXPERIMENTAL

A. Synthesis of the Reagents Molybdenum Dioxydichloride (MoO_2Cl_2) and Group IA (metal) triphenylsilonate (i.e. $MOSiPh_3$ where M is Na or K).

1. Synthesis of MoO_2Cl_2

$$2 \; MoO_3 + TiCl_4 \longrightarrow TiO_2 + 2 \; MoO_2Cl_2 \tag{1}$$

Solid MoO_3 (24.02g, 0.167 moles) was added to a 500 ml flask with an extended 35 cm neck. A silica gel or $CaCl_2$ drying tube was attached to the neck to prevent entrance of atmospheric moisture. An excess ($\sim$9%) of $TiCl_4$ (10.0 ml, 17.3 g, 0.091 moles) was added to the flask. This mixture was refluxed for four hours with magnetic stirring, during which time a red liquid formed. The refluxing occurred on the cooler sides of the extended neck in the region of the 500 ml flask.

Using a Bunsen burner flame, it was possible to sublime a yellow-red solid ($MoO_2Cl_2 \cdot xTiCl_4$) into the region of the extended neck. A white solid, TiO_2,[*] remained in the flask. The apparatus was then placed into a dry glove box containing an argon atmosphere and the neck (containing the sublimed $MoO_2Cl_2 \cdot xTiCl_4$) was severed from the flask. Good yields of $MoO_2Cl_2 \cdot xTiCl_4$ were routinely realized ($\sim$40% based upon deficit MoO_3). Note: $MoO_2Cl_2 \cdot xTiCl_4$ turns blue with fuming on exposure to air.

The method used during this study is a modification of the Cohen synthesis for $MoO_2Cl_2 \cdot xTiCl_4$.[1]

Identification of $MoO_2Cl_2 \cdot xTiCl_4$

A sample of $MoO_2Cl_2 \cdot xTiCl_4$ was placed into a 100 ml round bottom flask with attached 18/9 O-ring joint and teflon stopcock. (see figure 1).

---

[*] and some unreacted MoO_3

Teflon Stopcock for high vacuum →

← 18/9 O-ring joints
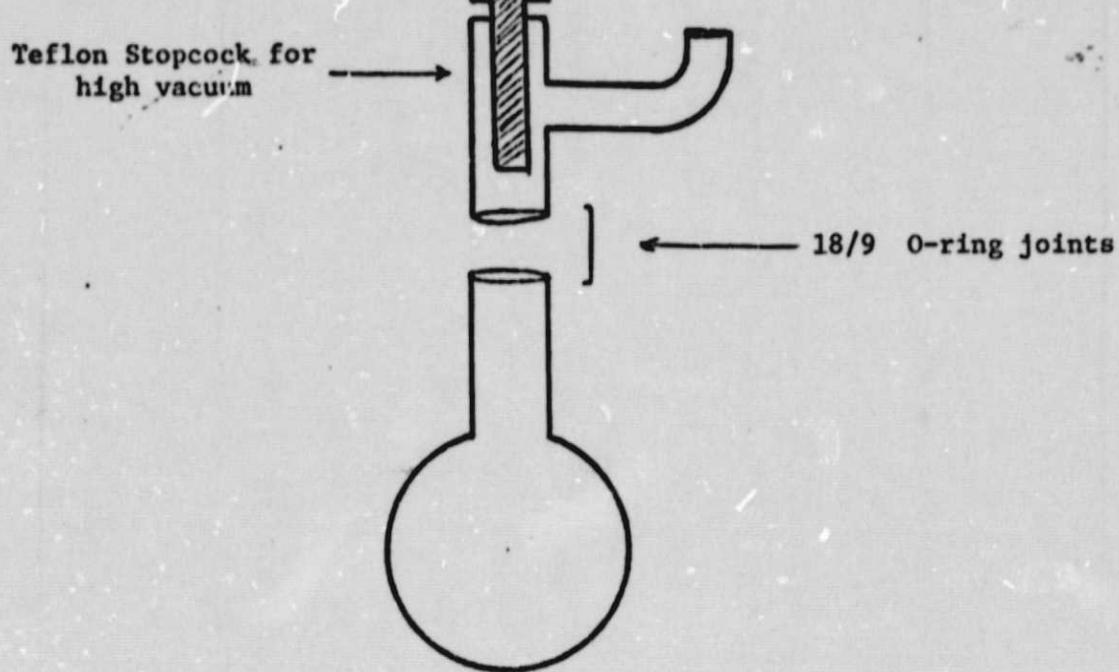
FIGURE 1

The sample was pumped on through two liquid nitrogen traps for one hour with heating at 100°C. At the end of this time period, a yellow crystalline solid (MoO_2Cl_2) had sublimed onto the extended neck of the apparatus and a volatile liquid $TiCl_4$,(as identified by infrared analysis[a] and hydrolysis properties) was collected in the first liquid nitrogen trap.

MoO_2Cl_2

ELEMENTAL ANALYSIS

	% Calculated	% Found	% Error
%Mo	48.25	48.05	0.4
%Cl	35.66	35.30	1.0

a

The liquid phase infrared absorption spectrum of the sample $TiCl_4$ was identical in every respect to the liquid phase infrared spectrum of a stock sample of $TiCl_4$ and the literature infrared absorption spectrum.[2]

Identified by infrared analysis

Major absorptions found

975 cm^{-1} (w); 905 cm^{-1} (w); 865 cm^{-1} (s); 830 cm^{-1} (sh); 785 cm^{-1} (s, broad)

Literature[3] absorptions

— 910 cm^{-1} (m); 864 cm^{-1} (s); 827 cm^{-1} (sh); 781 cm^{-1} (s, broad)

Identification by Sublimation Point

A sample of MoO_2Cl_2 as prepared during this study had an identical sublimation point (128 - 130°C, under one atmosphere pressure) to that of a stock solution of MoO_2Cl_2 as purchased from Alfa Inorganics, Beverly, Massachusetts.

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3. Barraclough, C. G. and J. Stals. Aust. J. Chem. 19 (1966) 741.

a. Synthesis of NaOSiPh₃

$$2 Na + 2 Ph_3Si OH \longrightarrow Ph_3SiONa + H_2 \qquad (2)$$
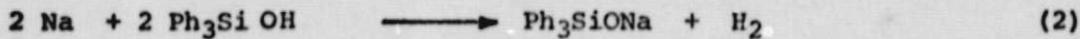
Into a three-neck, 250 ml flask equipped with magnetic stirrer, condensor, nitrogen inlet tube, dropping funnel and $CaCl_2$ drying tubes was added, 0.617g (0.027 moles) of sodium dispersed as small particles in 20 ml of toluene. This mixture was heated to reflux with rapid stirring, causing the sodium to melt and disperse itself as fine particles with exposed fresh metal surface area. On cooling, this mixture was diluted with 75 ml of benzene. A solution of Ph_3SiOH (6.908g, 0.025 moles) dissolved in 75 ml of benzene was slowly added dropwise. This mixture was refluxed for five hours. An essentially clear solution was present after this time period. Any significant amount of excess sodium should be removed by filtration prior to subsequent additions.

All solvents (C_6H_6 - THF) were freshly distilled after refluxing over sodium. This method is similar to those cited in the literature [4,5,6].

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b. Synthesis of KOSiPh$_3$.
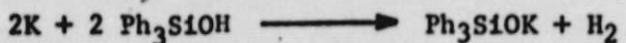
$$2K + 2 Ph_3SiOH \longrightarrow Ph_3SiOK + H_2 \qquad (3)$$

Into a three-neck, 250 ml flask equipped with magnetic stirrer, condenser, nitrogen inlet tube, dropping funnel and CaCl$_2$ drying tubes was added, 1.065 g (0.027 moles) of potassium dispersed as small particles in 20 ml of benzene. This mixture was heated to reflux with rapid stirring, causing the potassium to melt and disperse itself as fine particles with exposed fresh metal surface area. On cooling, this mixture was diluted with 75 ml of benzene. A solution of Ph$_3$SiOH (6.908g, 0.025 moles) dissolved in 75 ml of benzene was slowly added dropwise. This mixture was refluxed for five hours. An essentially clear solution was present after this time period. Any significant amount of excess potassium was removed by filtration prior to subsequent additions.

All solvents (C$_6$H$_6$ - THF) were freshly distilled after refluxing over molten potassium.

B. Synthesis of Tetrakis(triphenylsiloxy)molybdenum IV

Tetrakis(triphenylsiloxy)molybdenum IV was presumably synthesized according to the following reaction:

$$2 \text{ MoO}_2\text{Cl}_2 + 4 \text{ MOSiOPh}_3 + x \text{ H}_2\text{O} \xrightarrow{\text{TiCl}_4} \text{O}_2 + \text{"MoO}_2 \cdot x\text{H}_2\text{O"} + 4 \text{ MCl} + \text{Mo(OSiPh}_3)_4 \tag{4}$$
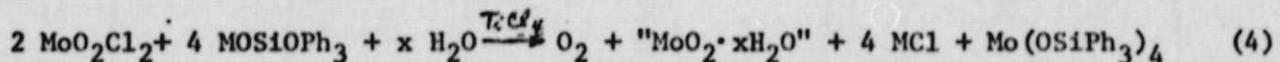
(where M is Na or K and Ph is C_6H_5)

1. Using Bench Techniques

Using a glove box containing a dry argon atmosphere, $\text{MoO}_2\text{Cl}_2 \cdot x\text{TiCl}_4$ (2.444g, 0.012 moles based upon MoO_2Cl_2) was placed into a 100 ml dropping funnel with 50.0 ml of THF. A yellow solution resulted on mixing[a]. The solution of $\text{MoO}_2\text{Cl}_2 \cdot x\text{TiCl}_4$ in THF was then slowly added to the refluxing solution of MOSiPh_3 (M is Na or K) in toluene and/or benzene. Preparation of the MOSiPh_3 solution as contained in the three-necked 250 ml flask is described in section 2a, page 29 of the experimental section.

The solution turned light yellow to light green to blue with the appearance of a fine white precipitate. The mixture was continually refluxed for six hours. At the end of this time, a large amount of white precipitate and blue solid was evident. The reaction mixture was then filtered (under vacuum using a Büchner filter) into a blue solid residue and blue filtrate solution. The blue solid residue was successively washed with 75 ml of THF and benzene[b]. A blue solid residue remained which was then washed with 200 ml of hot distilled water leaving a white solid residue, Compound A.

---

[a] Depending upon the small amount of TiCl_4 present, on mixing $\text{MoO}_2\text{Cl}_2 \cdot x\text{TiCl}_4$ with THF a mild to vigorous exothermic reaction of TiCl_4 with THF will result giving an initial red solution which shortly thereafter turns yellow.

[b] All solvents (i.c. both THF and benzene) were distilled from sodium immediately prior to use.

The distilled water filtrate consisted of a light blue solution. The water solvent was removed (under vacuum) using a steam bath. A blue solid, Compound B, remained. The original blue filtrate solution was stripped of solvent (THF and benzene) under vacuum and a blue solid residue remained, Compound C. All compounds were dried at 100° C for one hour.

Flow Diagram for the Synthesis of $Mo(OSiPh_3)_4$

REACTION MIXTURE

filtered using Büchner
funnel

BLUE SOLID RESIDUE   BLUE FILTRATE SOLUTION

washed with THF   solvent (THF and benzene)
stripped off under vacuum

BLUE SOLID RESIDUE

washed with benzene

BLUE SOLID RESIDUE   BLUE SOLID, Compound C

washed with hot water

WHITE SOLID RESIDUE, Compound A

blue filtrate solution
stripped of water solvent

COMPOUND B (blue solid)
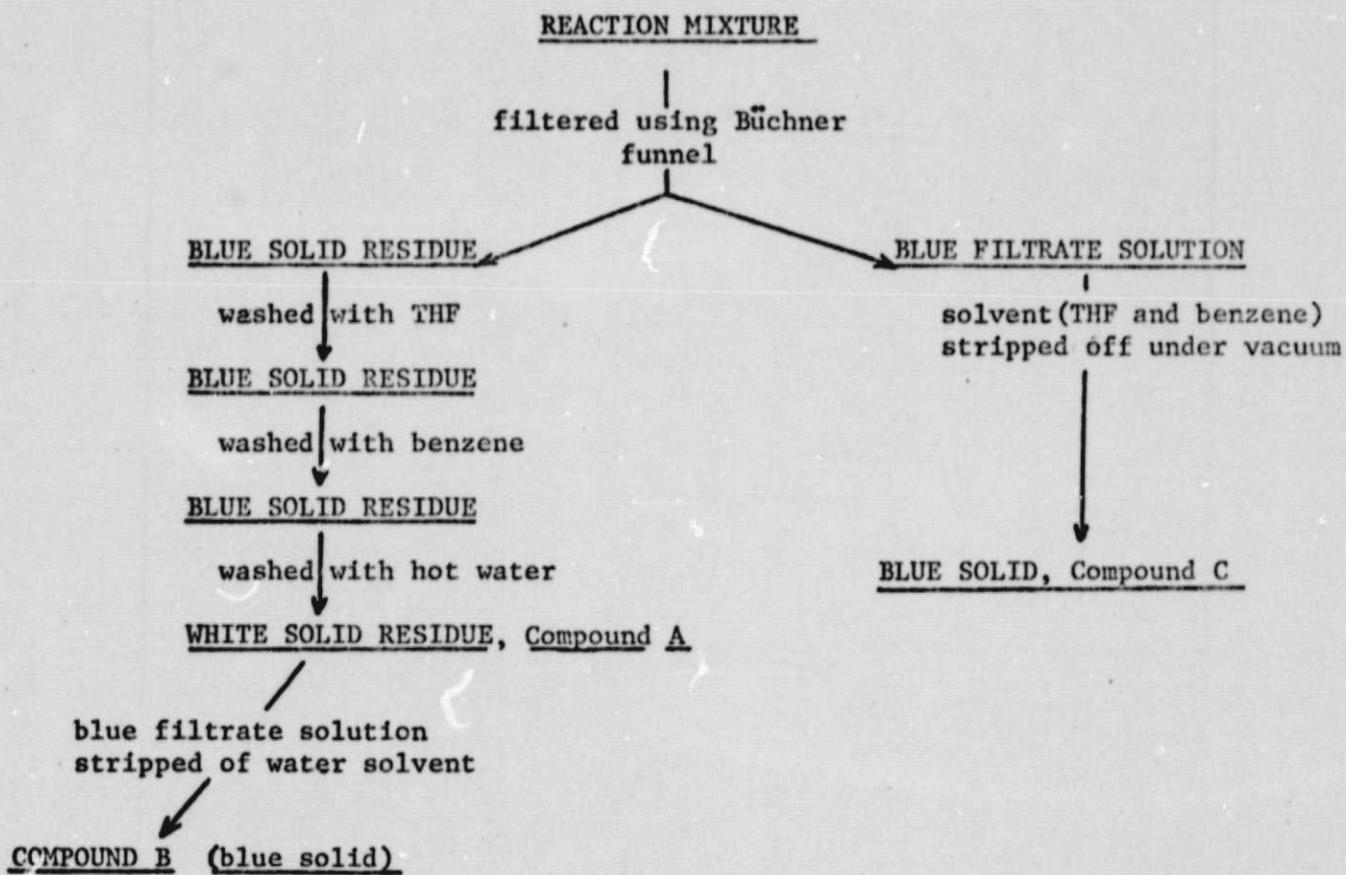
<u>COMPOUND A</u>   Identified as $Mo(OSiPh_3)_4$ by the following information:

(2.764g, 0.0023 moles) were recovered

yield = 38% [based upon reaction (4)].

Identified by infrared and H^1 n.m.r. analysis (discussion section, p. 1(

<u>Elemental Analysis</u>   (by Galbraith Laboratory)

% element	% calculated	% found[c]	% relative error
Mo	8.01	8.27	3.2
Si	9.38	9.63	2.7
C	72.21	73.51	1.8
H	5.05	5.23	3.6

Preliminary results indicate that $Mo(OSiPh_3)_4$ melts with

decomposition at 233°C and will sublime <u>in</u> <u>vacuo</u> at temperatures

above 200°C.

---

[c]
It should be noted that silicon grease (Dow Corning) used as a
lubricant on the joints of the reaction apparatus, has been identified as a
contaminate to the product, $Mo(OSiPh_3)_4$. It is very difficult to remove.
The grease probably enters the reaction mixture during the refluxing stage.
If analytically pure $Mo(OSiPh_3)_4$ is desired, either teflon tape, O-ring
joints or grease free joints should be used during the synthesis.

COMPOUND B   "$MoO_2 \cdot xH_2O$" with some NaCl (using $NaOSiPh_3$)

-blue solid residue from water filtrate.

 (1.345 gm) using $NaOSiPh_3$ reagent

-Infrared analysis gave the expected water absorption frequencies with
little else.

Determination of some chemical and physical properties of , Compound B.

	Compound B	"$Mo_2O_5 \cdot xH_2O$" [7]
Density	2.3 at 25°	3.6 at 18°
Solubility	H_2O soluble	H_2O soluble
	MeOH soluble	MeOH soluble
	HCl (2.4M) soluble	acids soluble
	acetaldehyde (slightly soluble)	insoluble
	benzene insoluble	insoluble
	$HCCl_3$ insoluble	insoluble

% Element	% Found
Mo	24.87

COMPOUND C   Probably a mixture of "$MoO_2 \, xH_2O$" with unreacted reagents
and intermediates.

   - blue precipitate from reaction mixture

  - (0.714g) using $NaOSiPh_3$ reagent

   - Infrared analysis showed characteristic water absorptions and
   a strong broad absorption centered at 1090 cm^{-1} which could be
   due to Si-O-Si stretching. [8]

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[7] Handbook of Chemistry and Physics (46th edition), Robert C.
Weast (ed.), The Chemical Rubber Co: Cleveland, Ohio. 1965-66. p. B-196.

[8] Colthrup, Norman B., L. H. Daly and S. E. Wiberley. Introduction

2. Using Extremely Dry Techniques

Using a glove box containing a dry argon atmosphere, 1.936 g (0.007m) of Ph$_3$SiOH was added to a 100 ml flat bottom flask with attached 18/9 O-ring joint and magnetic stirrer (see figure 2).


teflon stopcock for high vacuum

18/9 O-ring joint
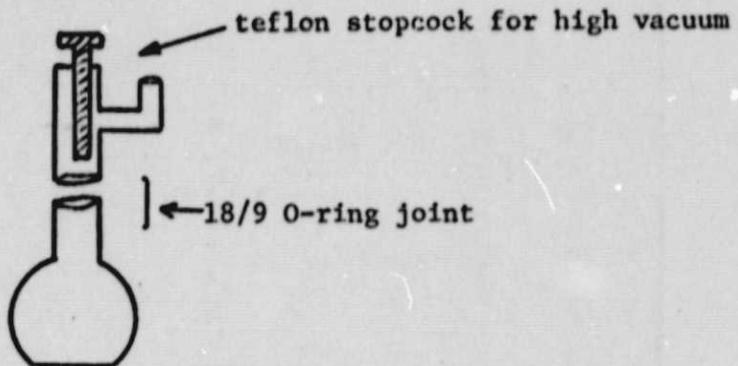
Figure 2

Potassium metal [(freshly shaved of K$_2$O) 0.274 gm (0.007m)] was then added to the flask. All transfers and weighings were carried out in the glove box. The apparatus was then connected to the vacuum system and all non-condensible gases (e.g. H$_2$ and Ar) were removed by degasing.

Approximatley 30 ml of C$_6$H$_6$[a] was then distilled into the reaction cell. The mixture was magnetically stirred and heated at 90° for six hours. At the end of this time, an essentially clear solution of KOSiPh$_3$ in C$_6$H$_6$ was realized according to reaction (5).

$$2K + 2Ph_3SiOH \longrightarrow 2Ph_3SiOK + H_2 \qquad (5)$$
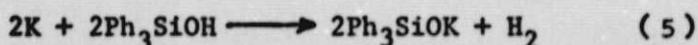
Evidence for completeness of reaction is the disappearance of potassium metal and the non-evolution of non-condensible, hydrogen gas.

_____

[a] All solvents (i.e. THF and C$_6$H$_6$) were freshly distilled from molten potassium to insure dryness.

Returning to the glove box containing an argon atmosphere (0.696g , 0.0035m) of $MoO_2Cl_2 \cdot xTiCl_4$ was added to side II of the apparatus described by figure 3

teflon stopcock for high vacuum →

18/9 O-ring joints

II

I
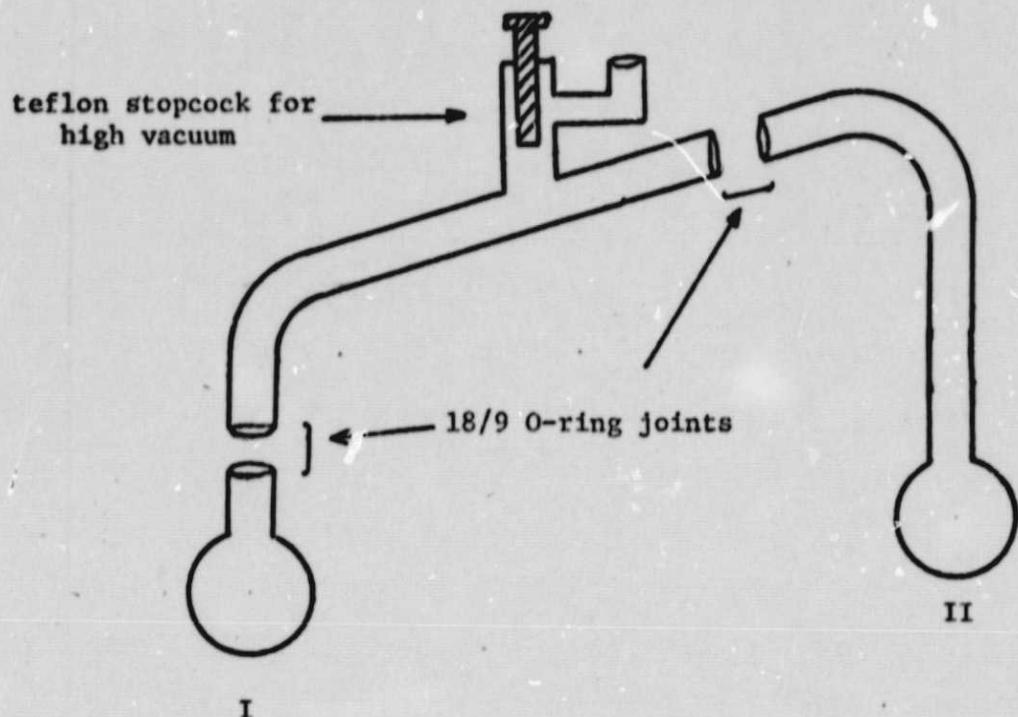
Figure 3

This apparatus was placed onto the vacuum system and side II was cooled to liquid nitrogen temperature.

All non-condensible gas (i.e. argon) was removed by pumping. The $TiCl_4$ attached to $MoO_2Cl_2 \cdot xTiCl_4$ was retained in side II by being held at liquid nitrogen temperature.

Approximately 30ml of THF[b] was then distilled into side II and on warming to room temperature with magnetic stirring, a clear yellow solution of MoO_2Cl_2 in THF was realized. The apparatus in figure 3 was then returned to the glove box. The C_6H_6 solution of $KOSiPh_3$ in the reaction cell described in figure 2 was then exchanged for side I of the apparatus in figure 3, resulting in the following apparatus :

yellow solution of MoO_2Cl_2 in THF

II

Clear solution of $KOSiPh_3$ in benzene

I
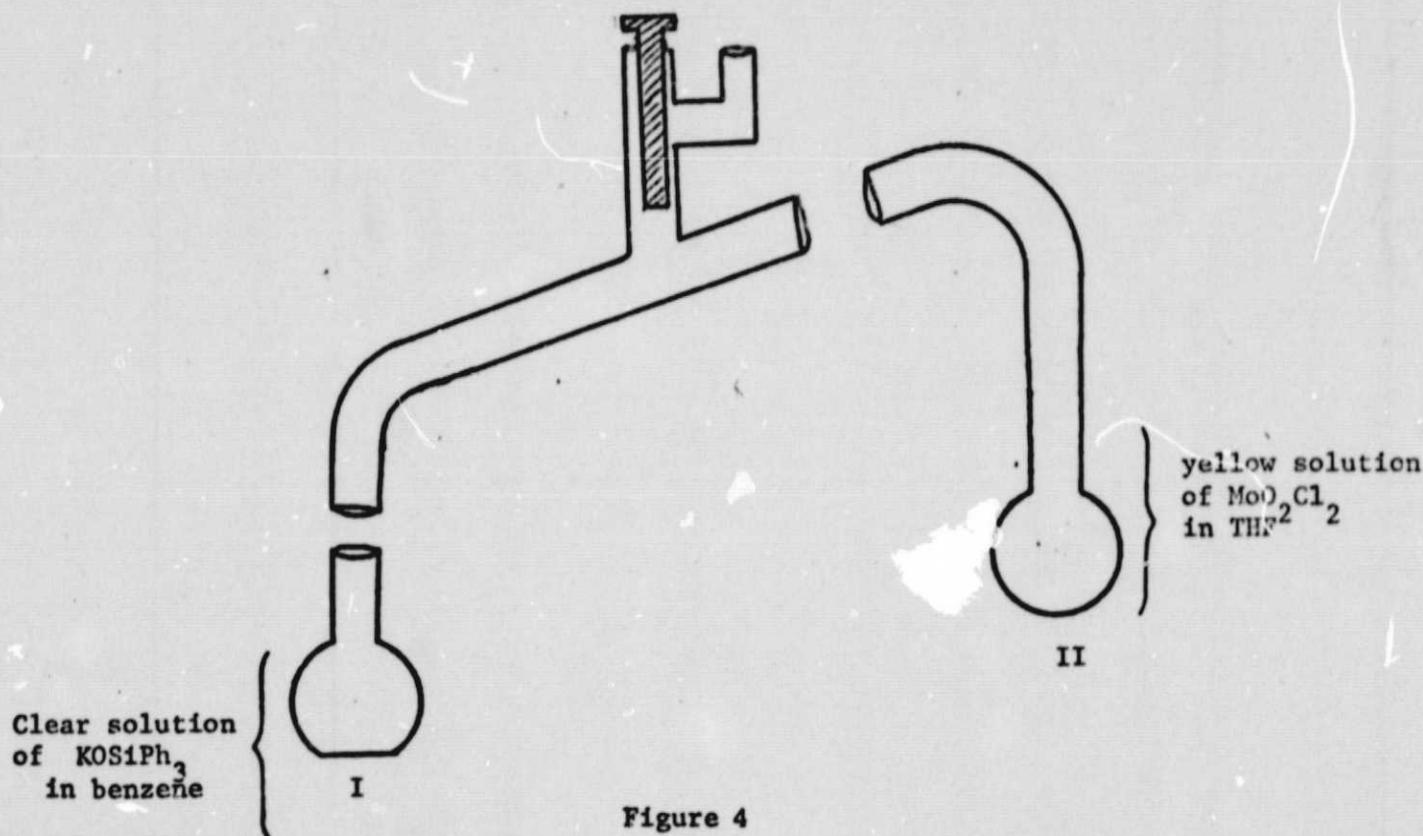
Figure 4

_____

[b] All solvents (i.e. THF and C_6H_6) were freshly distilled from molten potassium to insure dryness.

Both sides of the apparatus were cooled to liquid nitrogen temperature and any non-condensible gas (i.e. argon) removed by pumping. The procedure for degasing was carried out several times. On warming both sides to room temperature, side II was rotated 180° and the yellow solution of MoO_2Cl_2 in THF was slowly added to the clear solution of $KOSiPh_3$ in C_6H_6 with magnetic stirring. (see figure 5)
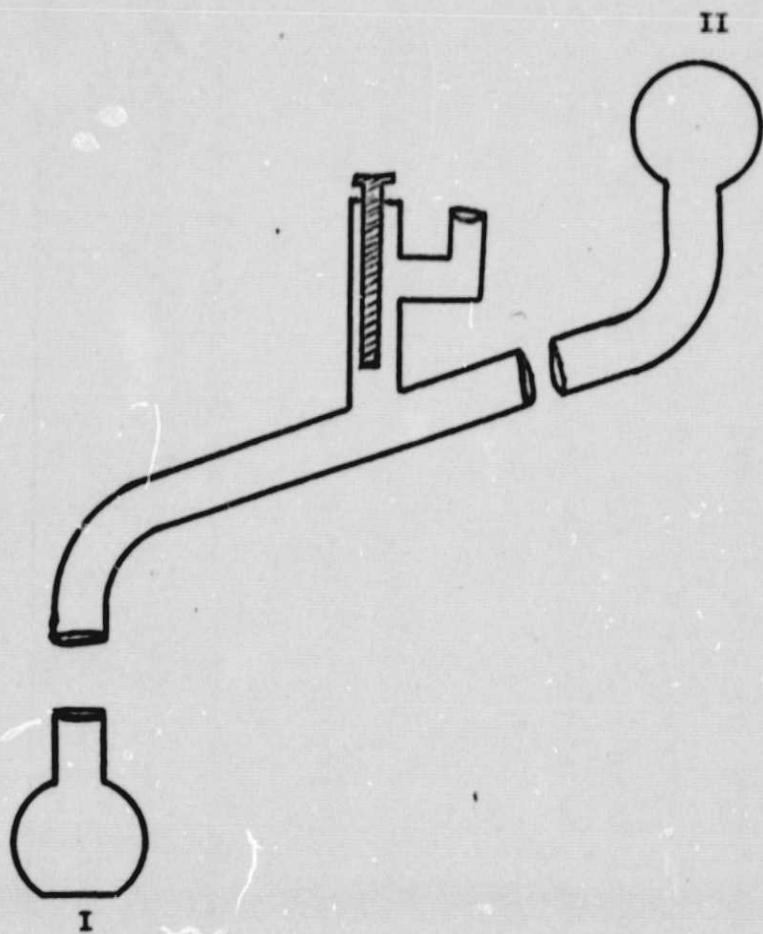
Figure 5

The resulting solution in side I was heated at 100° for six hours. At the end of this time period, a small amount of white solid had formed. There was little evidence for the formation of a blue solid. The apparatus was then attached to the vacuum system and side II was rotated 180° to its original position as shown in figure 4. Both sides I and II were cooled to liquid nitrogen temperature and the apparatus was simultaneously opened to the manometer and a Dumas molecular weight bulb of previously calibrated volume. The presence of a non-condensible gas was noted as a pressure difference in the manometer resulted. An ideal gas treatment (using the Dumas method) gave a molecular weight of 36.66 for this gas, presumed to be oxygen with a trace of solvent (i.e. C_6H_6 or THF) impurity.

The apparatus was returned to the glove box and the reaction mixture was filtered leaving an essentially white solid residue on the filter (either coarse sintered glass crucible or Büchner funnel with fine filter paper - Whatmann #43). This white solid was filtered in the glove box with 250ml of dry C_6H_6 and 50ml of dry THF. It was further washed and filtered outside of the glove box with 100ml of hot distilled water.

The white solid was identified as $Mo(OSiPh_3)_4$ by infrared analysis and melting point determination. Very low yields (on the order of less than 5%) were realized.

In conclusion, it is felt that this reaction demonstrates the following:

1. The presence of water is essential for the formation of the blue solid (presumably "$MoO_2 \cdot xH_2O$").

2. The formation of "$MoO_2 \cdot xH_2O$" is essential for good yields of $Mo(OSiPh_3)_4$.

C. A Study of the Chemical Properties of tetrakis(triphenylsiloxy)molybdenum IV

The chemical reactivity of $Mo(OSiPh_3)_4$ toward various common acids and bases was determined typically as follows:

Into a large pyrex test tube was placed 5.0 ml of the common acid or base. Approximately 100 mg of $Mo(OSiPh_3)_4$ was added. The mixture was shaken at room temperature for several minutes and any signs of reactivity were noted. If the $Mo(OSiPh_3)_4$ appeared not to react with the reagent at room temperature, the mixture was heated to its boiling point for several minutes and signs for reactivity noted. The mixture was then filtered using a pre-weighed sintered glass crucible. The residue in the crucible was washed free of excess reagent (typically with distilled water or in the case of NaOH with dilute HCl) and dried at 100° for one hour. The crucible was again weighed-the difference in weight being that of the white solid residue. The white solid residue was identified as unreacted $Mo(OSiPh_3)_4$ by its infrared absorption spectrum and its melting point characteristics. Whenever possible, the filtrate was stripped of reagent acid or base by heating under vacuum and the residue examined for the presence of unreacted $Mo(OSiPh_3)_4$ (or at least the presence of the Mo-O-Si bond whose distinctive absorption occurs at 10.92μ). This was done to distinguish true solubility from chemical reaction.

****

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ADDENDUM TO REPORT

Analytically pure $Mo(OSiPh_3)_4$ has been synthesized in good yields using the extremely dry techniques as outlined on page 35 and a four to one mole ratio of $KOSiPh_3$ to $MoO_2Cl_2 \cdot xTiCl_4$. No "molybdenum blue" was obtained. The "molybdenum blue" was found to be formed from the hydrolysis of MoO_2Cl_2 presumably by reaction (1).

$$MoO_2Cl_2 \quad + \quad 3H_2O \longrightarrow \text{"}MoO_2 2H\,O\text{"} \quad + \quad 1/2O_2 + 2HCl \quad (1$$
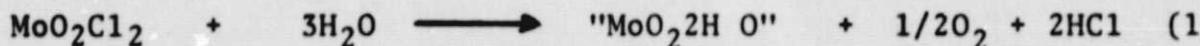
This side reaction which is observed when MoO_2Cl_2 is exposed to air is not conducive to the formation of $Mo(OSiPh_3)_4$. Reaction (1) may be eliminated using proper experimental techniques. The formation of $Mo(OSiPh_3)_4$ presumably may occur via reaction (2), the oxygen

$$MoO_2Cl_2 \quad + \quad 4KOSiPh_3 \xrightarrow{TiCl_4} Mo(OSiPh_3)_4 + \quad 2KCl \quad + \quad K_2O \quad + \quad 1/2O_2$$
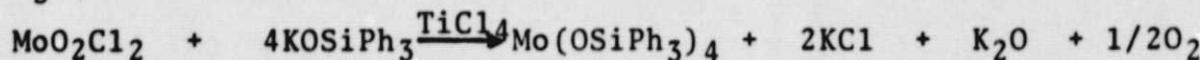
coming off as nascent oxygen and a majority reacting with the solvent.

The $TiCl_4$ serves as a drying agent to prevent the hydrolysis of MoO_2Cl_2 as well as a possible catalyst.

Analytically pure $Mo(OSiPh_3)_4$ decomposes above $330\,^{\circ}C$.

Most recent Elemental Analysis (by Galbraith) for $Mo(OSiPh_3)_4$

% element	% calculated	% found	% relative error
Mo	8.01	7.89	1.5
Si	9.38	9.47	1.0
C	72.21	72.81	0.8
H	5.05	5.01	0.8

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Reaction (3) has been found to be quantitative.

$$2K + 2Ph_3SiOH \longrightarrow 2Ph_3SiOK + H_2 \tag{3}$$
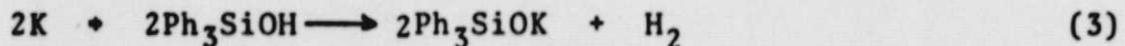
Page 23

Cohen's compound, originally reported as "$Mo_2(OSiPh_3)_6$" has been synthesized by distilling a relatively large amount of water (i.e. several hundred milligrams) into the reaction system. This compound must result from the extensive hydrolysis of $MoO_2Cl_2 \cdot xTiCl_4$ and its subsequent reaction with $KOSiPh_3$. It appears to contain no molybdenum (from elemental analysis and infrared absorptions).

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Some doubt has been cast upon the molecular weight data obtained for the non-condensible gas (presumed to be oxygen) by recent experimental data.