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NEW SUPERCONDUCTORS

James P. Collman, et al

Stanford University

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August 1, 1972 - January 31, 1973

NEW SUPERCONDUCTORS

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13. ABSTRACT

This report covers work on the study of possible high temperature superconductors. It describes theoretical work on filamentary organo-metallic materials - the conduction mechanism, band theory, and screening; progress towards the synthesis of metallic chain compounds and related organo-metallic complexes, and experimental studies of their solid state properties.

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I. INTRODUCTION

This report outlines the work on a program aimed at obtaining a better understanding of the problem of achieving superconductivity at higher temperatures. The program has concentrated on two main classes of compounds, the Krogmann compounds which are mixed valence transition metal stacked organometallic compounds and true covalently bonded metallic polymers. This report describes recent work we have done on the theoretical problems of computing the properties of these materials and recent work on the synthesis of such linear polymers.

II. THEORETICAL PROGRAM

During the past six months the principal effort of our theoretical work has been directed to the development of a program for calculating the superconducting transition temperature of linear chain compounds. The methods used are based on the work of Kirzhnits, Maksimov and Khomskii[10] and involve the full frequency dependent effective interaction.

During the same period work has continued on the calculation of the frequency dependent screening of the Coulomb field in linear chain compounds. This is an extension of earlier work on the contract by D. Davis (Phys. Rev. B 7, 129 (1973)) which involved a calculation of static screening of the Coulomb field.

These two developments are discussed in the two following sections by D. Davis and B. Bush, respectively.

Calculations of T_c for Linear Compounds - D. Davis

The calculation of superconducting transition temperatures presents several difficulties which are dealt with in different ways by the various equations for estimating T_c. The simplest approach is to combine all the factors involved in producing an attractive force between electrons at the Fermi surface into one effective potential well whose depth, V, and width ω_c then characterize the system. This is the approach first developed by BCS[1] and yields the simple formula

$$k_B T_c = 1.14\hbar\omega_c e^{-1/N(0)V} \qquad (1)$$

where N(0) is the density of states at the Fermi surface. While this method works quite well for the so called "weak-coupling" superconductors, it completely ignores the details of the interaction which leads to Cooper pair formation. An investigation of these details is necessary for the strong-coupling superconductors where the electron states involved in Cooper pair formation can no longer be treated as simple Landau quasiparticles since their decay rate becomes comparable with their energy.[2] In addition, phonon-induced superconductivity has the inherent difficulty of involving a retarded interaction. The large mass of the ions, whose fields interact with those produced by the electrons, results in induced fields which change on a time scale much slower than those of the light electrons. As a result overscreening and underscreening of frequency dependent charge densities are possible. Indeed, the overscreening of the Coulomb repulsion between electrons by the vibrating ions is the basic reason for the attractive interaction which results in Cooper pair formation.[3] The Hamiltonian scheme requires that two-body potentials be instantaneous, thus a retarded potential would have to be simulated by a velocity dependent potential. An alternative to this approach is the Green's function method.

As a first step the BCS approach was reformulated by Gorkov[4] in terms of the Green's function formation. Later Nambu[5] and Eliashberg[6,7] used the Green's function method but treated the details of the interaction mechanism that were not dealt with in the BCS treatment or by Gorkov. These were the first theories which allowed one in principle to take into account details of the structures of the material under investigation. Specifically, the phonon-spectral weight was required along with the electron-phonon coupling constant. The Coulomb contribution, however, was neglected. Eliashberg's result for the gap function is given by the integral equation:

$$\Delta(\varepsilon) = \frac{1}{4\pi^2 v_o} \frac{1}{1-f_o(\varepsilon)/\varepsilon} \int_{\Delta}^{\infty} \frac{d\varepsilon' \Delta(\varepsilon')}{\sqrt{\varepsilon'^2-\Delta^2}} \tanh\left(\frac{\varepsilon'}{2T}\right) \int dq \; q\alpha_q^2 \left(\frac{1}{\varepsilon'+\varepsilon+\omega_q} + \frac{1}{\varepsilon'-\varepsilon+\omega_q}\right) \quad (2)$$

In this equation, v_o is the Fermi velocity, $f_o(\varepsilon)$ is a renormalization factor arising from the small change in the normal self energy of the metal on entering the superconducting phase, α_q is the electron-phonon coupling constant and ω_q is the energy of a phonon of wavevector q. The Eliashberg treatment uses Dyson's equation for the interaction Green's function in terms of the irreducible self energy.

$$G^{-1} = G_o^{-1} - \Sigma$$

This is given diagramatically in Fig. 1a. Only the first order contribution to the self energy is used. See Fig. 1b. One can use these equations to calculate the energy dependent gap function with only a few assumptions as to the details of the phonon spectrum and the coupling constant. Whereas the

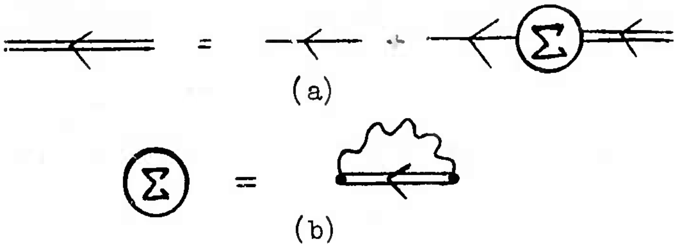

Fig. 1

(a) Dyson's Equation for the interacting Green's function
(b) First order contribution to the self energy

gap function is a constant in the BCS scheme, in the Eliashberg scheme there appears a resonance at the typical phonon frequency. Using an Einstein phonon spectrum one can easily see the resonant nature of the integrand in the gap equation.

It is interesting to note that an entirely different approach developed by Bogoliubov, the method of compensation of dangerous diagrams, leads to an integral equation for the gap function which, though similar to the Eliashberg equation, eliminates the resonant nature of the integrand. In this approach a canonical transformation is made on the interacting Hamiltonian which describes both electrons and phonons. The transformation is determined by the condition that to second order the creation of a pair of quasiparticles with opposite momenta be eliminated. This is shown diagramatically in Fig. 2a.

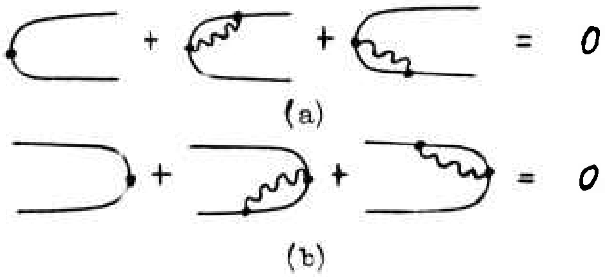

Fig. 2

Compensation of Dangerous Diagrams

Application of this transformation then leads to a gap in the excitation spectrum, again given by an integral equation

$$\Delta(k) = \frac{1}{2(2\pi)^3} \int g^2 \frac{\omega(k-k')}{\omega(k-k')+\varepsilon(k)+\varepsilon(k')} \frac{\Delta(k')\,dk'}{\sqrt{\Delta^2(k')+\xi^2(k')}}$$

where $\xi(k)$ is the quasiparticle energy, $\varepsilon(k) = \frac{\xi^2(k)}{\sqrt{\Delta^2(k)+\xi^2(k)}}$

and g is the electron-phonon coupling constant. It is interesting to note that the kernel of this equation does not show the resonance nature as in the Eliashberg equation. However, application of the same canonical transformation with the determining condition given in terms of the compensation of the destruction of pairs to second order gives an integral equation with a resonant kernal. See Fig. 2b.

Of these three methods for calculating transition temperatures, or equivalently, energy gap functions, only that of Eliashberg lends itself to detailed investigation of specific superconducting systems. The BCS equation averages together all the details and results in a constant energy gap function. Although the Bogoliubov method gives some structure to the energy gap function, the details are again averaged together into a constant electron-phonon coupling constant. In contrast to these, the Eliashberg method allows one to deal with individual substances by using particular phonon-spectral weight functions. In addition the Eliashberg method uses the powerful Dyson's equation to sum an infinite series of diagrams of a particular class. Much work has already been done using this method. Morel and Anderson[8] used this technique and included a contribution to the net interaction from the Coulomb repulsion. They were able to get good order-of-magnitude agreement with observed transition temperatures and they also estimated isotope effects. Scalapino, Schrieffer and

Wilkins[2] used the Eliashberg method to calculate single-particle tunneling density of states. McMillan[9] has also applied this method to investigate transition temperatures as a function of electron-phonon and electron-electron coupling constants. Thus the Eliashberg method is firmly established and might seem at first glance to be a reasonable choice for our investigation of superconductivity resulting from Cooper pairing due to excitonic interaction.

For the past several months we have been investigating a newly developed scheme for calculating the superconducting energy gap function and transition temperature. This method, developed by Kirzhnits, Maksimov and Khomskii,[10] offers several advantages over that of Eliashberg. Briefly, these advantages are: 1) a non-resonant kernal for the energy gap integral equation, and 2) a formalism which allows one to concentrate on the specific form of the interaction. Much computational difficulty is avoided by the non-resonant form of the kernal resulting in greater accuracy of the solution which must still be obtained by numerical methods. When dealing with the phonon interaction generally one would use experimental data to obtain the spectral weight function which would then be used in the calculation of the energy gap. This would allow one to account to a certain degree for electron screening of the phonon-interaction without including higher order graphs in the expression for the self energy. In our case, however, we are dealing with an excitonic interaction produced by an array of dyes. As yet we do not have sufficient data from low energy electron scattering from dyes to be able to construct an empirical spectral weight function. On the other hand, calculations have been made to determine the effective interaction between electrons in the vicinity of an array of dyes. The formalism of the Kirzhnits method requires the effective interaction in terms of the polarizability of the system, conducting spine and dyes. Thus we anticipate that this method will yield accurate transition temperatures and is particularly suited to the investigation of the excitonic mechanism.

In the Kirzhnits method one starts with an expression for the anomalous propagator for a Cooper pair at the transition temperature. The expression is given in diagram form in Fig. 3. Eqn. 3 gives the expression in terms of the anomalous propagator, $F(p, i\omega_n)$, normal quasiparticle propagator, $G(p, i\omega_n)$,

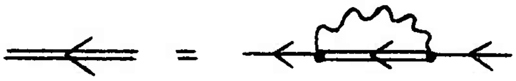

Fig. 3

Equation for the Anomalous Propagator

and the effective interaction $V(q, i\nu_n)$.

$$F(p, i\omega_n) = G(p, i\omega_n) G(-p, -i\omega_n) T_c \sum_m \int \frac{d^3k}{(2\pi)^3} V(p-k, i\omega_n - i\omega_m) F(k, i\omega_m) \qquad (4)$$

The anomalous propagator is written in the Lehmann representation:

$$F(p, i\omega_n) = \int_{-\infty}^{\infty} \frac{f(p,x)\,dx}{i\omega_n - x}$$

where $f(p,x) = -f(p,-x)$.

The effective interaction is written in terms of the bare electron-electron interaction, V_o, and the polarizability π.

$$V = V_o + V_o \pi V_o$$

The diagramatic form is given in Fig. 4.

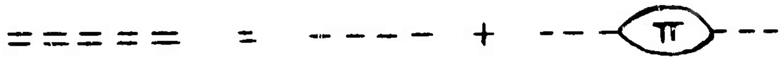

Fig. 4

Equation for the effective interaction

Writing πV_0 in the form of a spectral weight function, ρ, one has the Lehmann representation of the effective interaction

$$V(q,i\nu_n) = V_0(q)\left\{1 + \int_0^\infty dE\rho(q,E)\left(\frac{1}{E+i\nu_n} + \frac{1}{E-i\nu_n}\right)\right\} \tag{5}$$

Finally, one writes the non-interacting Green's function as

$$G_0^{-1}(k,i\omega_n) = i\omega_n - \xi_k.$$

Performing the indicated sum as a contour integral one obtains the following integral equation:

$$f(p,k) = -\int\frac{d^3k}{(2\pi)^3}\int_0^\infty dy\ \tanh\left(\frac{y}{2T_c}\right) K(p,k,x,y)\, f(k,y) \tag{6}$$

where

$$K(p,k,x,y) = V_0(p-k)\left\{\frac{\delta(x-|\xi p|)}{2|\xi p|}\left[1-\int_0^\infty dE\rho(p-k,E)\left(\frac{1}{E+y+x} + \frac{1}{E+y-x}\right)\right]+\frac{P}{x^2-\xi_p^2}\rho(p-k,x-y)\,\theta(x-y)\right\}$$

The derivation of this equation requires an identical simplifying step as does the Eliashberg equation. Further development of this approach by Kirzhnits, et al. lead them to introduce the function $\emptyset(p)$ which corresponds to the gap function in the Eliashberg scheme.

$$\emptyset(p) = 2|\xi p| \int_0^\infty f(p,x)\,dx \tag{7}$$

One then arrives at an intermediate equation for the gap function

$$\emptyset(p) = -\int \frac{d^3k}{(2\pi)^3} V_0(p-k) \int_0^\infty dy \tanh\left(\frac{y}{2T_c}\right) f(k,y) \left(1-2\int_0^\infty \frac{dE\rho(p-k,E)}{E+y+|\xi p|}\right), \qquad (8)$$

as shown by Kirzhnits, et al.

It is now necessary to take only the term singular at $T_c = 0$ by adding and substracting

$$\tanh\left(\frac{|\xi k|}{2T_c}\right)\left(1-2\int_0^\infty \frac{dE\rho(p-k,E)}{E+|\xi k|+|\xi p|}\right) \qquad (9)$$

yielding, finally, the integral equation for the gap function

$$\emptyset(p) = -\int \frac{d^3k}{(2\pi)^3} V_0(p-k) \frac{\tanh\left(\frac{\xi k}{2T_c}\right)}{2\xi k} \left(1-2\int_0^\infty \frac{dE\rho(p-k,E)}{E+|\xi k|+|\xi p|}\right) \emptyset(k) \qquad (10)$$

We have verified the derivation of this equation and are now preparing to write the necessary computer program to solve this equation. The previous calculations of the effective interaction in the presence of the dyes will be used to give $\rho(p-k,E)$ and the calculations of the energy bands will give the necessary electron energies ξ_k. With these we will then be able to solve for the eigenvalue, T_c.

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Dynamic Screening in Linear Compounds - B. Bush

We have developed a computational model[1] of collective electron response (frequency-dependent Coulomb screening) in one-dimensional metals such as Krogmann compounds and TCNQ salts. In such crystals, conduction electrons delocalize only along the filaments (stacks of transition-metal complexes or TCNQ radicals), occupying Bloch states in a one-dimensional phase space. Parallel filaments interact through a self-consistently screened Coulomb field; this three-dimensional coupling is especially important at long wavelengths and at frequencies near the bulk plasma frequency ω_p.

We treat this interaction between a given filament and its neighbors in the three-zone cylindrical geometry used by Davis,[2] in which the central filament is represented as a cylinder ($r<a$) and the other filaments are smeared into an infinite uniform zone ($b<r<\infty$). In the present calculation, lateral charge relaxation within a filament is not allowed. For any wavenumber q along the filaments, we calculate $V_q(\omega)$, the screened Coulomb matrix element between charges on the center filament; and $V_q(\omega,r)$, the interaction between the center filament and neighboring filaments (or dye molecules) located at a distance r from the central axis.

For illustration, we use a nearly-free electron model of the Krogamnn salt $K_2Pt(CN)_4Cl_{0.32}\cdot nH_2O$. The charge carriers (holes) along the Pt-Pt chains have a linear density 0.11/Å; their mass is taken as the bare electron mass. Interfilamentary separation is 10Å; we set $a = 1.3$Å and $b = 8.0$Å. Screening is treated within a modified random-phase approximation which allows for finite strand conductivity and reduces to the Lindhard, Thomas-Fermi, and Drude models in the appropriate limits.

Typical results are shown in Fig. 1, which plots $|V_q|$ against ω for a wavenumber, $q = 0.03\text{Å}^{-1}$, at which neighboring filaments interact strongly.

Results are given both with and without strong resistive damping.

In the static limit, V_q is only a fiftieth of its bare Coulomb value. Confining the charge carriers to one-dimensional phase space makes their density of states, and hence the Thomas-Fermi screening parameter, much greater than in the isotropic phase space assumed in other calculations.[2,3] In the absence of resistive damping, the screening becomes even stronger as $\omega \rightarrow qv_F$. A single filament in empty space has a resonance at $\hbar\omega^o_{fil}(q) = 0.28$eV. Below this frequency, but above qv_F, a positive source charge produces a negative ("overscreened") total potential; above ω^o_{fil}, the charge induced on the isolated filament is in phase with the source, and $V > V_{bare}$. When a single filament couples to its neighbors, its resonance is lowered slightly: $\hbar\omega_{fil} = 0.23$eV. Although many neighbors are involved in the resonance ($V_q(\omega,r)$ dies off spatially only as $r^{-1/2}$, whereas $V_q^{bare}(r)$ dies as e^{-qr}) the filaments oscillate with different phases and produce relatively little net field at the center.

As ω increases toward the bulk plasma frequency $\omega_p(q)$, more and more near neighbors oscillate in phase with the center filament, although each one singly becomes less responsive. At $\omega = \omega_p(q)$ the range of the disturbance is limited only by damping, and $V_q(\omega)$ goes through a collective resonance. Above this frequency the filaments remain in phase but respond less and less; the range of the disturbance shortens, and $V_q(\omega) \rightarrow V_q^{bare}$.

This example thus displays a single-filament resonance, absent in an isotropic metal, which remains strong in the presence of damping and which, unlike the spatially uniform resonance at $\omega_p(q)$, should couple well to laterally (radially) polarizable dyes.

By endowing the model system with ω-dependent dielectric constants, radial and longitudinal, one may use it to give a linear-response picture of the coupling between dye-exciton modes and the conduction electrons (or holes), or between phonons and electrons. The model can also incorporate the screening functions appropriate to other one-dimensional band structures, or to finite temperatures.

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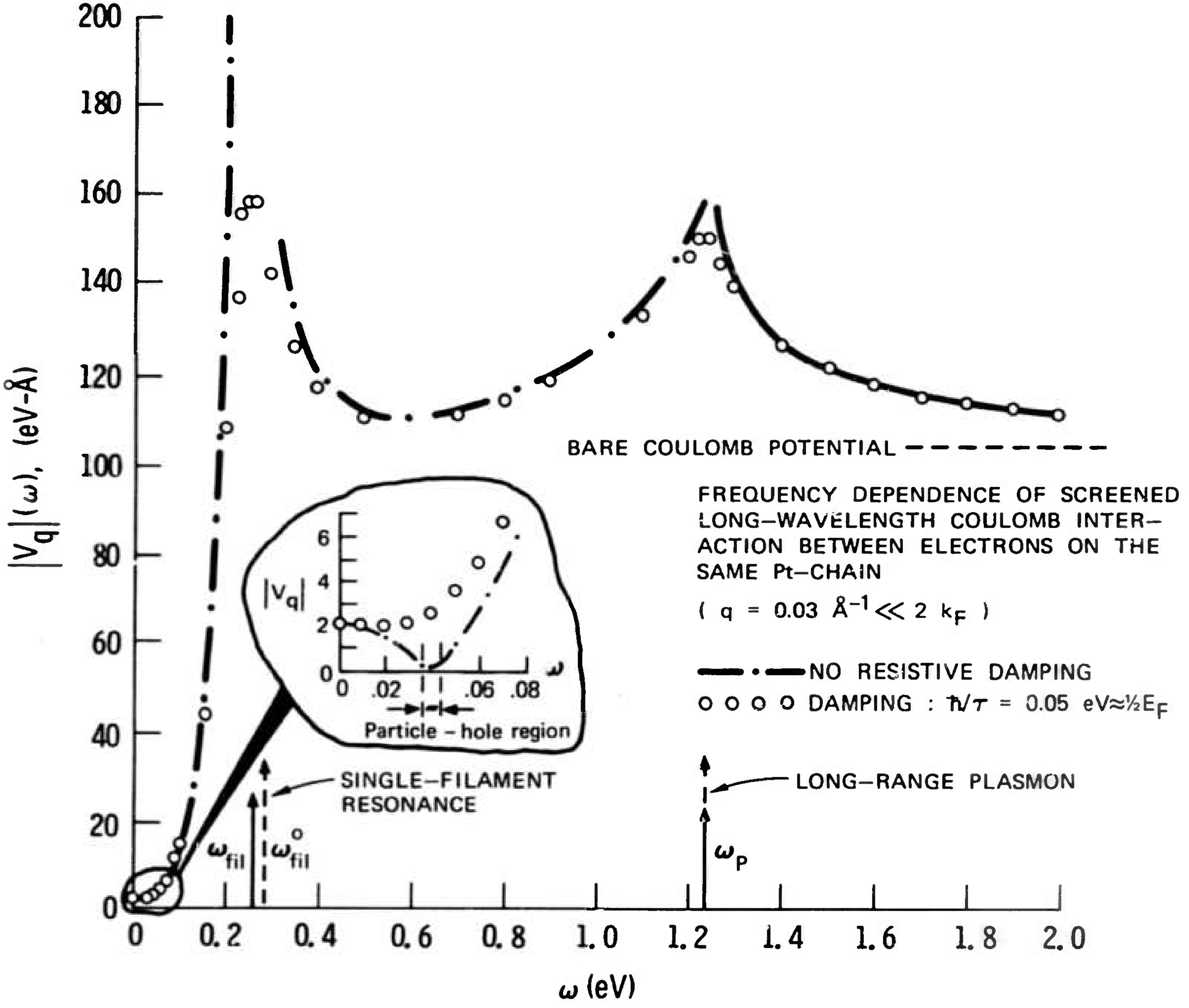

$|V_q|(\omega)$, (eV-Å)
200
180
160
140
120
100
80
60
40
20
0
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
ω (eV)
BARE COULOMB POTENTIAL
FREQUENCY DEPENDENCE OF SCREENED LONG-WAVELENGTH COULOMB INTERACTION BETWEEN ELECTRONS ON THE SAME Pt-CHAIN
($q = 0.03$ Å$^{-1} \ll 2\ k_F$)
NO RESISTIVE DAMPING
O O O O DAMPING : $\hbar/\tau = 0.05$ eV$\approx\frac{1}{2}E_F$
$|V_q|$
6
4
2
0
0
.02
.06
.08
ω
Particle - hole region
SINGLE-FILAMENT RESONANCE
ω_{fil}
$\overset{\circ}{\omega}_{fil}$
LONG-RANGE PLASMON
ω_p

Figure 1

III. SYNTHETIC PROGRAM

The past six month's synthetic studies directed towards the preparation of linear chains of covalently bonded metals is summarized in the following four manuscripts.

The first deals with the linear tin-osmium-tin system described in earlier reports and is in submission to "Inorganic Chemistry". The second describes both the synthesis and X-ray crystallographic characterization of the rhodium DOH system. This manuscript will not be published as such but will be combined with structural and synthetic studies in progress in a full paper--probably next summer. The third, describes the oxidative addition reactions of the rhodium DOH system and is in press as a Communication to the Editor in the "Journal of the American Chemical Society". The fourth manuscript describes the synthesis of intermetallic oligomers employing the transition metal substituted tin and germanium hydrides which have been developed in this project and have been briefly described in earlier reports. This manuscript is in submission as a Communication to the Editor of the "Journal of the American Chemical Society".

Current research efforts are focused on attempts to derive covalent intermetallic polymers (including some with chalconides ligands) from the rhodium DOH system. Some of these efforts will make use of the newly developed transition metal substituted germanium hydride reactions. As a part of this work, we have found it necessary to prepare additional DOH analogues which are more soluble and amenable to analysis by nuclear magnetic resonance techniques. This work is already far along and will form the basis for a full paper concerning the rhodium DOH chemistry.

To summarize: our progress to date has been principally along two lines of endeavor--(a) the synthesis of rigid transoid intermetallic oligomers and (b) the development of non ionic metal-metal coupling reactions using transition metal substituted germanium hydrides.

Synthesis of Linear Metallic Oligomers. Organotin Complexes of Tetracarbonylosmium.

by James P. Collman*, Donald W. Murphy,
Everly B. Fleischer and David Swift

Contribution from the Departments of Chemistry, Stanford University, Stanford, California 94305, and the University of California at Irvine 92664.

Organotin complexes of tetracarbonyl osmium were prepared by nucleophilic displacement reactions with $Na_2Os(CO)_4$ on organotin halides and by elimination reactions of $H_2Os(CO)_4$ with organotin oxides, alkoxides and amides. Stable, trans complexes $(R_3Sn)_2Os(CO)_4$ were prepared for R = Ph and n-Bu. The structure of the $(Ph_3Sn)_2$-$Os(CO)_4$ was ascertained by a complete X-ray diffraction study. The linear Sn-Os-Sn cluster has a Os-Sn bond distance of 2.712 Å indicating little or no double band character in the system. Difunctional organotins gave di-μ-tin complexes of formula $[(CO)_4Os\text{-}SnBu_2]_2$. Phenyl groups on tin coordinated to osmium were selectively cleaved by electrophilic reagents affording a number of halogen functionalized Sn-Os-Sn complexes. Treatment of t$(ClBu_2Sn)_2Os(CO)_4$ with $Re(CO)_5^-$ afforded the pentametallic $((CO)_5Re\text{-}SnBu_2)_2Os(CO)_4$. Attempts to prepare linear polymers from the colinear t$(ClBu_2Sn)_2Os(CO)_4$ gave only the di-μ-tin complex $[(CO)_4Os\text{-}SnBu_2]_2$.

Introduction

In view of the interesting unidimensional electron transport properties[1] associated with intermetallic chains in certain crystal lattices, several years ago we set as our long range goal[1a] the synthesis of linear molecular polymers with backbones comprised entirely of covalently bonded metal atoms. We hope that such metallic polymers, whose electron transport properties would be largely independent of the crystal lattice, will serve as the conducting spine for Little's hypothetical excitonic superconductor.[2,3] Noting the marked tendency for organo transition metal complexes to form cycles and clusters of metal-metal bonds, our strategy has been to prepare colinear trimetallic monomers of octahedral transition metal complexes which might then be elaborated into oligomers or polymers. Oligomers formed from linear trimetallic segments would have to become quite large to cycle back on themselves and thus would have a higher probability of growing linearly. The use of tin for a portion of the backbone is attractive in view of its versatility in forming metal-metal bonds.[4] The synthesis and properties of colinear Sn-Os-Sn complexes are described herein.

Bis tin complexes of iron[5,6] and ruthenium[7] tetracarbonyls have been reported. In all cases the iron complexes were <u>cis</u> whereas the ruthenium compounds were reported to be mixtures of <u>cis</u> and <u>trans</u> isomers. The stability of the ruthenium complexes was substantially greater than their iron analogs. We decided to investigate the osmium analogs in hopes of finding increased stability and greater tendency toward <u>trans</u>

stereochemistry. One such complex of osmium, the bis trimethyltin complex, was reported during the course of this work.[8]

Experimental

General Information. Microanalyses were performed by the Stanford Microanalytical Laboratories. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer and standardized against atmospheric carbon dioxide and polystyrene.

Tetrahydrofuran (THF) was distilled under nitrogen from LAH. All solvents were purged by bubbling nitrogen through them for 20 minutes prior to use.

Organotin compounds were purchased from Metal & Thermite Chemical/ Company and were recrystallized or distilled prior to use. Other organotin compounds and triosmium dodecacarbonyl were prepared according to literature methods.

Disodium tetracarbonylosmium(-II),[9] **1.** The reaction was run in a 100 ml three neck round bottom flask fitted with a gas inlet tube from an ammonia cylinder, a gas inlet tube on a tee joint to an argon bubbler, and a tipping tube containing osmium carbonyl. The mixture was stirred magnetically with a glass covered stirring bar. The flask was thoroughly flushed with argon and a weighed amount of sodium (130 mg, 5.65 mmol) added. Ammonia (30 ml) was condensed into the flask using a dry ice bath. Triosmium dodecacarbonyl (715 mg, 2.37 mmol) was then tipped into the reaction mixture a few crystals at a time over about one half hour until the characteristic blue color of the sodium vanished. The sides of the reaction vessel were rinsed by touching a cold (-78 °C) plug of glass wool attached to a stirring rod to the outside of the flask, condensed ammonia then dripped down the sides. The ammonia was then allowed to evaporate, leaving the cream colored, air sensitive product **1**, which was then immediately used in subsequent reactions.

***Trans*-bis(triphenyltin)tetracarbonylosmium, 2a.** Tetrahydrofuran (25 ml) was added to the dianion **1** (2.37 mmol) under argon to give a suspension. Triphenyltin chloride (1.92 g, 5.0 mmol) in THF (10 ml) was then added and the mixture stirred ten minutes. The resulting solution was evaporated under reduced pressure. The solid was extracted with benzene and passed through a short silica gel column (25 g). The benzene solution was evaporated and the resulting white solid recrystallized from dichloromethane-hexane to give colorless crystals of the product **2a** (2.06 g, 91% based on osmium carbonyl).

***Trans*-bis(tributyltin)tetracarbonylosmium 2b.** A suspension of the dianion **1** (0.66 mmol) in THF (10 ml) under argon was treated with tributyltin chloride (440 mg, 1.36 mmol). The mixture was stirred ten minutes. The resulting solution was concentrated and passed through a short silica gel column (25 g) with pentane. The pentane was removed under vacuum to give the product **2b** as a colorless oil (525 mg, 85%).

Dihydridotetracarbonylosmium[10] 3. Solid dianion **1** (5.92 mmol) was dried at 0.1 mm pressure for one hour to remove the last traces of ammonia. The flask was cooled in a dry ice-isopropanol bath and syrupy phosphoric acid (35 ml dexoygenated by bubbling nitrogen through it for two hours) was added. The cold flask was attached to a high vacuum line and allowed to warm to room temperature. The volatile hydride (and water) was pumped out of the reaction vessel over 12 hours and collected in a liquid nitrogen cooled trap. The hydride and water were then transferred onto phosphorous pentoxide (25 g) to remove water. Care must be taken to allow slow thawing to avoid excess heat which may decompose the hydride. The hydride was then transferred to a storage vessel and weighed (1.60 g, 89%): ir (Hexane); ν_{CO} = 2065(s), 2055(s), 2050(s), 2016(c) cm^{-1}, ν_{Os-H} = 1940(w) – identical with literature values.[10]

Reaction of dihydridotetracarbonylosmium 3 with triphenyltin chloride. Using high vacuum techniques, the dihydride **3** (50 mg, 0.164 mmol) was transferred into a reaction vessel containing triphenyltin chloride (150 mg, 0.39 mmol), benzene (2 ml) and diethylamine (1 ml). The reaction vessel was warmed to room temperature and the mixture was stirred five minutes, giving a white precipitate. The vessel was removed from the vacuum line and dichloromethane was added to dissolve the precipitate. The mixture was passed through a short silica gel column (25 g). Crystallization from dichloromethane with hexane gave the bis triphenyltin adduct identical with **2a** by ir and tlc (110 mg, 67%).

Bis(di-μ-dibutyltintetracarbonylosmium), 4a. The reaction was performed using high vacuum techniques. Benzene (3 ml) was transferred onto dibutyltin dichloride (277 mg, 0.92 mmol) followed by the dihydride **3** (277 mg, 0.92 mmol) and diethylamine (1 ml). The mixture was warmed to room temperature and stirred two hours. Tlc showed two spots close together at $r_f = 0.6$ in hexane. Addition of carbon tetrachloride destroyed the lower spot (presumably a hydride). The mixture was filtered through a short silica gel column (25 g), then concentrated to give a colorless solid which was recrystallized from ether - ethanol to give the product **4a** as large colorless crystals (115 mg, 23%).

***Bis*(di-μ-diphenyltintetracarbonylosmium), 4b.** The dihydride **3** (130 mg, 0.43 mmol) was transferred onto a THF (3 ml) suspension of diphenyltin oxide (0.5 g, 1.73 mmol). The mixture was stirred one hour, then filtered through a short silica gel column with dichloromethane, and concentrated to give a white solid. Recrystallization from dichloromethane-hexane gave the product as colorless crystals (100 mg, 40%).

Reaction of dihydridotetracarbonylosmium 3 with tributyltin, (N-phenyl)-formamide. The dihydride **3** (64.2 mg, 0.211 mmol) was transferred into an acetonitrile (5 ml) solution of the tin formamide (160 mg, 0.386 mmol). The mixture was allowed to warm to room temperature and stirred for one hour. Treatment with carbon tetrachloride and filtration through silica gel (25 g) gave, after removal of solvent, pure bis tributyltin complex (135 mg, 71%) identical to **2b** by tlc and ir.

Reaction of dihydridotetracarbonylosmium 3 with triphenyltin oxide. A small amount of the dihydride **3** (unweighed) was transferred onto an acetonitrile suspension of the tin oxide. After warming to room temperature and stirring for one hour, the mixture was filtered through silica gel with dichloromethane. Concentration and addition of hexane gave a product identical with the bis triphenyltin compound **2a** by ir and tlc.

Reaction of dihydridotetracarbonylosmium 3 with dibutyldimethoxytin. The dihydride **3** (87.8 mg, 0.289 mmol) was transferred into an acetonitrile solution (3 ml) of the methoxy tin compound (87 mg, 0.291 mmol). After warming the product precipitated rapidly from solution. The product was filtered and recrystallized from ether methanol to give the di-μ-tin complex identical with **4a** by ir and tlc.

***Cis*-hydridotriphenyltintetracarbonylosmium 6.** Acetic acid (1.58 mmol) was added to a THF (15 ml) slurry of the dianion **1** (1.58 mmols). The mixture was stirred ten minutes to give a clear solution. Triphenyltin chloride (610 mg, 1.58 mmols) in THF (5 ml) was added and stirring continued for ten minutes. Tlc showed two spots close together at $r_f = 0.4$ in hexane-dichloromethane (85:15). The mixture was separated on two 20 x 20 cm silica gel plates. The lower band was identical to the bis triphenyltin derivative **2a**. The upper band, after recrystallization from methanol gave colorless crystals of the product (110 mg, 10%).

***Trans*-bis(dichlorophenyltin)tetracarbonylosmium 7a.** Dry hydrogen chloride gas was bubbled through a solution of the bis triphenyltin complex **2a** (227 mg, 0.255 mmol) in carbon tetrachloride (20 ml) held at -15°C in an ice-salt bath for ten minutes. A white slurry formed which was filtered and recrystallized from dichloromethane to give colorless crystals of the product **7a** (70 mg, 64%).

***Trans*-bis(tribromotin)tetracarbonylosmium 7b.** Dry gaseous hydrogen bromide was bubbled for ten minutes through a solution of the bis triphenyltin complex **2a** (200 mg, 0.20 mmol) in carbon tetrachloride (25 ml).

Nitrogen was bubbled through the solution for ten minutes to remove hydrogen bromide. The solution was concentrated to give colorless crystals which were filtered and washed with ether. Recrystallization from dichloromethane-hexane afforded the product **7b** (150 mg, 73%).

***Trans*-dichlorotetracarbonylosmium**[11] **8.** Chlorine gas was bubbled through a carbon tetrachloride (20 ml) solution of the bis triphenyltin complex **2a** (121 mg, 0.12 mmol) for 25 minutes at room temperature. A white slurry formed which was filtered and recrystallized from dichloromethane to give the product **8** as colorless crystals (38 mg, 85%).

***Trans*-bis(phenyldibutyltin)tetracarbonylosmium 2c.** Dianion **1** prepared from osmium carbonyl (311 mg, 1.03 mmols) was treated with phenyldibutyltin bromide[12] (1.0 g, 2.57 mmols) in THF (10 ml). The mixture was stirred 30 minutes. Solid sodium bromide was filtered off with the aid of celite. The filtrate was concentrated to give a thick oil which was purified by preparative tlc ($r_f = 0.3$) on silica gel (20 x 20 cm plate) using hexane to develop. The main contaminant wasdiphenyldibutyltin ($r_f = 0.4$). The product was removed from silica gel with pentane and the solvent removed under vacuum to give the product as a slightly impure colorless oil (650 mg, 68%): nmr (60 MHz, CCl_4); δ 0.6 to 1.6 (m, 18H), δ 7.2-7.4 (m, 10H).

***Trans*-bis(chlorodibutyltin)tetracarbonylosmium 7c.** Dry gaseous hydrogen chloride was bubbled through a carbon tetrachloride (25 ml) solution of the phenyldibutyl derivative **2c** (1.50 g, 1.61 mmols) held at -15°C in an ice-salt bath for 15 minutes. Nitrogen was then bubbled through the solution for ten minutes to remove hydrogen chloride. Solvent was evaporated and the product was crystallized from methanol. Recrystallization from methanol afforded the product **7c** as large colorless crystals (0.83 g, 66%): nmr (60 MHz, CCl_4); δ 0.6 to 1.6 (m), no phenyl protons.

***Bis*(pentacarbonylrheniumdibutyltin)tetracarbonylosmium 10**. The reaction utilized high vacuum techniques. Benzene (5 ml) was transferred onto the solid difunctional **7c** (90.5 mg, 0.107 mmol), followed by hydridopentacarbonylrhenium (70.47 mg, 0.215 mmol) and diethylamine (1 ml). The mixture was allowed to warm to room temperature and stirred for 15 minutes. Solvent was removed under vacuum and the reaction mixture was filtered through a short silica gel column (15 g) with pentane. Removal of the pentane under vacuum gave the product **10** as a slightly yellow viscous oil, pure by tlc (r_f = 0.5 in hexane) (94 mg, 55%).

Reaction of *trans*-bis(chlorodibutyltin)tetracarbonylosmium 7c with dihydridotetracarbonylosmium 3. On a high vacuum line benzene (2 ml), the dihydride **3** (43.93 mg, 0.145 mmol), and triethylamine (0.5 ml) were successively transferred into a reaction vessel containing the difunctional **7c** (121.55 mg, 0.134 mmol). After warming to room temperature the reaction mixture was stirred for one half hour. Filtration of the mixture through a short silica gel column (15 g) and crystallization from ether-ethanol yielded the di-μ-tin compound **4a** (19 mg, 12%). This sample was identical by ir and tlc to that previously prepared.

Results and Discussion

The method of choice for preparation of ruthenium tin complexes was treatment of dodecacarbonyl triruthenium with the appropriate tin hydride in a hydrocarbon solvent at elevated temperature.[7] The osmium cluster proved more robust. The prolonged time and temperature necessary for these reactions (125°, 24 hours) led to extensive decomposition of the tin hydrides to the corresponding tin tin coupled product although Stone[8] reported preparation of the bis trimethyltin osmium complex by this method. These organotin dimers have nearly the same r_f's on tlc and boiling or melting points as the desired bis-tin osmium compounds making purification difficult. We have found a more satisfactory route employing disodium tetracarbonylosmium 1 prepared by reducing dodecacarbonyl triosmium with sodium in liquid ammonia. Treatment of the dianion 1 with the appropriate tin halides yielded the colorless, stable, bis tin complexes 2a-c (eq. 1).

$$Os_3(CO)_{12} \xrightarrow[NH_{3(l)}]{Na} \underset{1}{Na_2Os(CO)_4} \xrightarrow{R_3SnX} \underline{t}(R_3Sn)_2Os(CO)_4 \qquad (1)$$

2a, R = Ph
2b, R = n-Bu
2c, R_3 = $Ph(n\text{-}Bu)_2$

The yields were near 90% whereas with ruthenium[7] the analogous reaction was reported to be poor, affording yields of less than 10%. The bis tin complexes 2a-c were all of <u>trans</u> stereochemistry as determined from their ir and Raman vibrational spectra. One strong carbonyl frequency in the ir and two strong Raman peaks were observed as predicted on the basis of C_{4v} symmetry (Table I). Analytical data given in Table II are consistent with the suggested stoichiometries.

The structural assignment of 2a has been confirmed by a complete X-ray crystallographic study. The compound $(Ph_3Sn)_2Os(CO)_4$ was crystallized by slow evaporation from hexane to yield clear prisms suitable for X-ray diffraction analysis. The space group was determined to be C2/c (No. 15 International Tables) with cell constants that were determined by a least-squares fit of 13 accurately measured 2 θ values to be a=47.552(.03), b=9.31(.007), c=31.968(.019), Å, β=148.87(.02)°. The measured density of 1.8 g/cm^3 leads to 8 molecules per unit cell; d_{cal} = 1.819 gm/cm^3.

A set of diffraction data was collected with a Picker automatic diffractometer employing MoKα radiation. There were 3444 peaks surveyed resulting in 2785 intensities with counts greater than 3σ that were used in the subsequent analysis. The raw intensities were corrected for some crystal decay and also for absorption. The structure was solved by the Patterson method and refined by full-matrix least-squares; the temperature factors of osmium and tin atoms were treated anisotropically while all the carbon atoms had isotropic temperature factors. The final R-factor for all the observed data is 6.3%. The atomic coordinates for the structure are in Table III. The molecules lie on special positions in the cell (b and d) which are centers of symmetry instead of being in a general position. A picture of the molecule is given in Figure 1. The other molecule in the cell has a similar molecular conformation. The main structural features of interest are the linear Sn-Os-Sn cluster with the two independent Sn-Os bonds with distances of 2.712 (.001) and 2.711 (.001) Å. All other distances on the molecule are as expected; ie the 36 C-C distances in the benzene ring average 1.399 Å with a standard deviation of 0.03 Å in each individual bond distance.

The observed Sn-Os distance of 2.71 Å in 2a is very close to that calculated for a single bond, 2.75 Å, using as values for covalent radii: 1.35 Å for Os (from the metal) and 1.40 Å for Sn (from α-Sn)[13]. Thus it is unnecessary to propose $d\pi$-$d\pi$ multiple bonding (which would lead to a decreased Sn-Os distance) nor a σ bonding trans effect of one Sn upon the other (which would lead to a lengthened Sn-Os distance).

The dianion 1 had been previously prepared by L'Eplattenier[9] from reduction of osmium carbonyl with sodium in THF using 2,2'-bipyridyl as electron carrier. We obtained only low yields of products using dianion 1 generated by this method. The preparation of solvent free dianion 1 afforded an improved synthesis of dihydridotetracarbonylosmium 3.[10] Addition of phosphoric acid followed by vacuum transfer gave the hydride 3 in 90% yield (eq. 2).

$$\underset{1}{Na_2Os(CO)_4} \xrightarrow{H_3PO_4} \underset{3}{H_2Os(CO)_4} \qquad (2)$$

We feel this is more convenient than the literature synthesis utilizing high pressures of H_2 and CO on OsO_4.

The dihydride 3 proved to be a convenient starting material for many osmium tin complexes. The dihydride 3 (pKa ~ 5-6) was used to generate an osmium anion by treatment with an amine (diethylamine and pyridine were used). In the presence of an amine the dihydride 3 gave the bis tin complex 2a on treatment with triphenyltin chloride (eq. 3).

$$\underset{3}{H_2Os(CO)_4} \xrightarrow{:B} [(B{:}H)^+(HOs(CO)_4)^-] \xrightarrow{Ph_3SnCl} \underset{2a}{\underline{t}(Ph_3Sn)_2Os(CO)_4} \qquad (3)$$

No reaction occurred in the absence of added base. This type of anion generation from hydrides has been reported by Graham[14] and promises to be of utility in many reactions. Anions made from sodium or sodium mercury amalgam are generally not pure and their titer is difficult to assay, especially for small scale reactions. The hydride, by contrast, may be purified and weighed so that stoichiometry may be easier to control. Caution should be used with this type of anion generation to avoid systems likely to form carbamoyl complexes.[15]

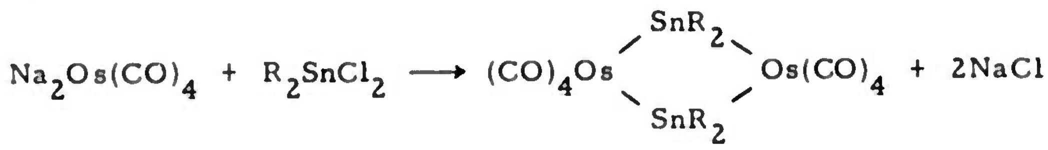
In other reactions of the dihydride **3**, the base may be bonded directly to the organotin moiety. Tin oxides, alkoxides, and amides gave tin osmium complexes with elimination of the corresponding water, alcohol, or amine (e q. 4).

$$\underset{\mathbf{3}}{H_2Os(CO)_4} + 2R_3Sn\text{-}B \;\text{——}\; \underset{\mathbf{2a\text{-}b}}{\underline{t}(R_3Sn)_2Os(CO)_4} + 2BH \qquad (4)$$

$$B = 1/2\ O,\ OR,\ NR_2$$

All the bis tin complexes **2** were not made by each of these methods, but enough cases were done to indicate generality. In each case the products formed from the different reactions were identical.

With difunctional organotin moieties, each of these types of reaction gave the four membered di-μ-tin cycles **4**, illustrated for the dianion **1** (eq. 5).



$$\underset{\mathbf{1}}{Na_2Os(CO)_4} + R_2SnCl_2 \longrightarrow (CO)_4Os(\mu\text{-}SnR_2)_2Os(CO)_4 + 2NaCl \qquad (5)$$

4a R=n-Bu
4b R=Ph

Analogous compounds of iron[16] and ruthenium[17] were known. This reaction conceivably could have given a polymer with alternating osmium and tin atoms in its backgone. This points to the necessity of achieving a rigid *trans* arrangement of tins before attempting polymerization.

Attempts to prepare compounds with two different organotin moieties on the same osmium by sequential addition of organotin chlorides to the dianion **1** failed. The two symmetrically substituted products were formed, probably because of the insolubility of the dianion **1** in THF. Addition of one equivalent of acetic acid rendered the dianion soluble, presumably as the hydrido anion **5**. Addition of triphenyltin chloride to this solution gave a mixture of the disubstituted **2a** and the *cis* hydrido triphenyltin compound **6**. The mixture was separated by thin layer chromatography (eq. 6).

$$\underset{\mathbf{1}}{Na_2Os(CO)_4} \xrightarrow{HOAc} \underset{\mathbf{5}}{[NaHOs(CO)_4]} \xrightarrow{Ph_3SnCl} \underset{\mathbf{2a}}{t(Ph_3Sn)_2Os(CO)_4} + \underset{\mathbf{6}}{\underline{c}(Ph_3Sn)HOs(CO)_4} \qquad (6)$$

The osmium hydride stretch was not observed in the ir, but gave a strong peak in the Raman at 1946 cm^{-1}.

Obtaining functionalized bis tin derivatives held in *trans* positions on osmium was our next goal. Treatment of the dianion **1** with an excess of a diorganotin dichloride gave a mixture of products inseparable in our hands. These osmium tin bonds are quite stable to electrophilic reagents and functionalization was accomplished by cleavage of phenyl groups from coordinated tins. A summary of the electrophilic reactions of the bis triphenyltin derivative **2a** is shown below (eq. 7-9).

$$\underset{\mathbf{2a}}{t(Ph_3Sn)_2Os(CO)_4} \xrightarrow[-15°]{HCl} \underset{\mathbf{7a}}{\underline{t}(Cl_2PhSn)_2Os(CO)_4} \qquad (7)$$

$$\mathbf{2a} \xrightarrow{HBr} \underset{\mathbf{7b}}{\underline{t}(Br_3Sn)_2Os(CO)_4} \qquad (8)$$

$$\mathbf{2a} \xrightarrow{Cl_2} \underset{\mathbf{8}}{\underline{t}Cl_2Os(CO)_4} \qquad (9)$$

All of these reactions were clean, and gave high yields. Stoichiometric amounts of bromine and mercuric chloride gave complex mixtures of products. The reaction with chlorine is noteworthy in that the *cis* isomer of dichlorotetracarbonylosmium is thermodynamically more stable than the *trans* isomer obtained from this reaction.[18] Cleavage of $\underline{t}(Me_3Si)_2Os(CO)_4$ with hydrogen chloride has also been reported to give the *trans* **8**.[11] Efforts to obtain monofunctionalized derivatives by disproportionation reactions of the dichlorophenyl **7a** and tribromo **7b** compounds with the triphenyl **2a** failed.

Substitution of a single halogen on each tin was accomplished by treatment of the bis phenyldibutyl derivative 2c with hydrogen chloride, cleaving the phenyl groups (eq. 10).

$$\underset{\textbf{2c}}{\underline{t}(\mathrm{PhBu_2Sn})_2\mathrm{Os(CO)_4}} \xrightarrow{\mathrm{HCl}} \underset{\textbf{7c}}{\underline{t}(\mathrm{ClBu_2Sn})_2\mathrm{Os(CO)_4}} \qquad (10)$$

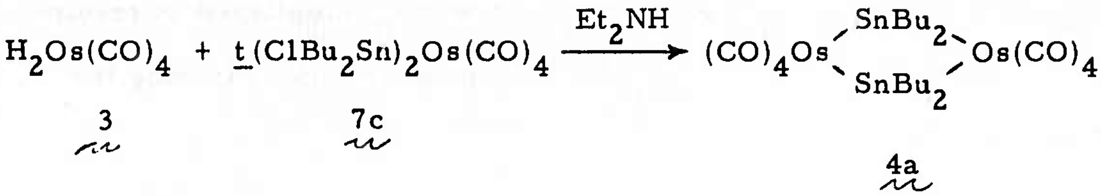
The desired trans stereochemistry was maintained during all cleavage reactions as determined by vibrational spectra.

We then attempted to elaborate the preformed, colinear 7c into higher metallic oligomers. Treatment with the $Re(CO)_5^-$ anion generated from the hydride with diethylamine gave a good yield of the pentametallic chain 10 (eq. 11).

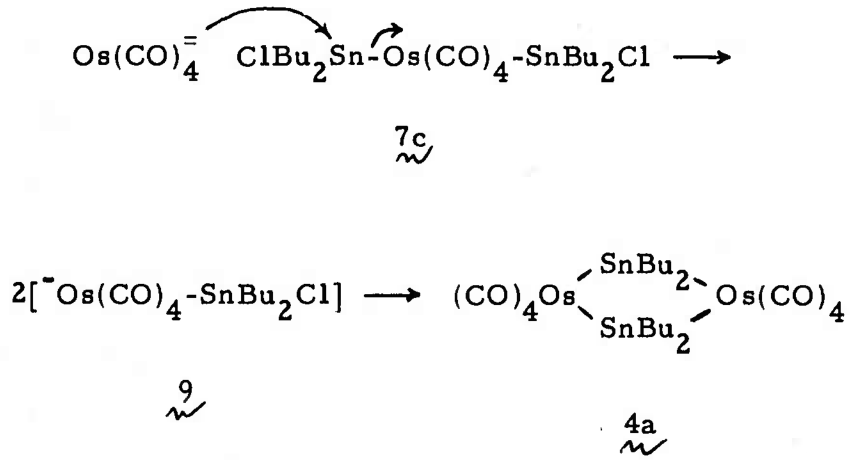
$$\mathrm{HRe(CO)_5} + \underset{\textbf{7c}}{\underline{t}(\mathrm{ClBu_2Sn})_2\mathrm{Os(CO)_4}} \xrightarrow{\mathrm{Et_2NH}} \underset{\textbf{10}}{((\mathrm{CO})_5\mathrm{Re\text{-}SnBu_2})_2\mathrm{Os(CO)_4}} \qquad (11)$$

The oligomer 10 is a viscous liquid at room temperature and characterization includes a molecular weight. Only one other pentametallic chain involving transition metals has been reported,[14] that being $Cl_2Sn[Cl_3SiMn(CO)_2C_5H_4CH_3]_2$. The vibrational spectrum of the chain 10 is complex and a definite stereochemistry about osmium could not be confirmed. Surprisingly, treatment with the dihydride 3 in the presence of diethylamine gave the di-μ-tin cycle 4a (Eq. 12).

(12)



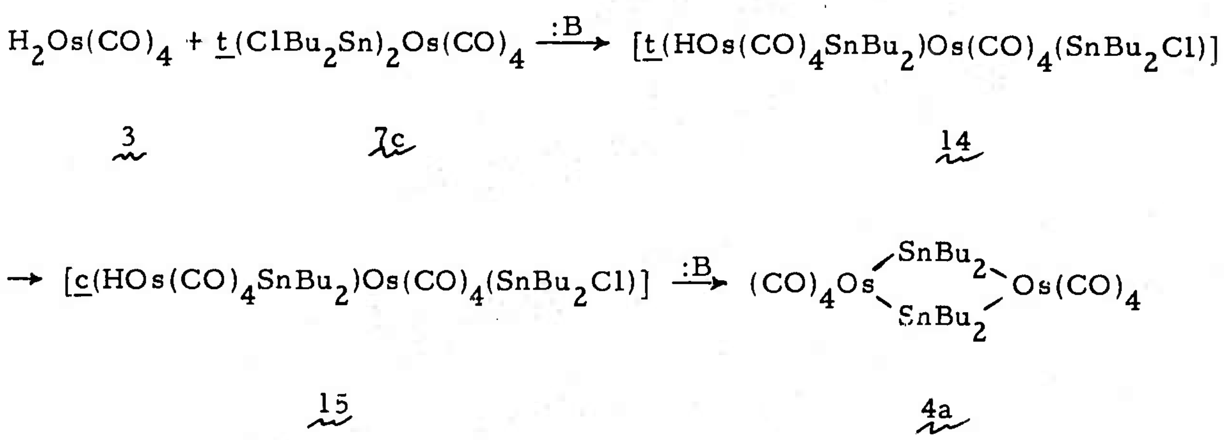
This result was unexpected since it involves an isomerization of tins from *trans* positions to *cis*. One possibile pathway to this result is displacement of an osmium tin anion 9 which would be set up to react with another identical anion 9 to give the observed product (Scheme 1).



Scheme 1

Other anions (e.g. $Re(CO)_5^-$) might be expected to initiate such a mechanism, but $Re(CO)_5^-$ (eq. 11) gave no indication of such tin osmium fragmentation. Treatment of the functionalized 7c with the anion generated from *c*$(Ph_3Sn)HOs(CO)_4$ gave a small amount of the cycle 4a (detected on tlc), but none of the expected seven membered Sn-Os-Sn-Os-Sn-Os-Sn chain was isolated.

When we began work on this system we assumed that organotin moieties bonded in *trans* positions would retain that geometry during subsequent reactions at tin because of the high energy barrier to isomerization of octahedral complexes[19]. Graham[20] has recently found, however, that $(Me_3Sn)_2Os(CO)_4$ and similar molecules are a dynamic mixture of *cis* and *trans* isomers. The mechanism of this interconversion has not been established, but such an isomerization provides an alternative explanation for the formation of the four membered cycle 4a in eq. 12. An initially formed *trans* intermediate 14 might isomerize to the *cis* 15 which would be well suited for ring closure to give the cycle 4a (Scheme 2).



$$H_2Os(CO)_4 + \underline{t}(ClBu_2Sn)_2Os(CO)_4 \xrightarrow{:B} [\underline{t}(HOs(CO)_4SnBu_2)Os(CO)_4(SnBu_2Cl)]$$

$$\rightarrow [\underline{c}(HOs(CO)_4SnBu_2)Os(CO)_4(SnBu_2Cl)] \xrightarrow{:B} (CO)_4Os(SnBu_2)_2Os(CO)_4$$

Scheme 2

Such non rigidity of metal metal bonded carbonyl complexes may not be limited to group IVA derivatives. The reaction of $Os_3(CO)_{12}$ with chlorine[11] affording the centrosymmetric $Cl(Os(CO)_4)_3Cl$ must involve an isomerization of the central osmium from a cis to trans arrangement of the Os-Os bonds. We suggest that this type of isomerization may occur via a transient bridged carbonyl or a metallo acyl ($M'-\overset{O}{\overset{\|}{C}}-M(CO)_3-M'$) species. Such intermediates have been postulated to account for non dissociative ligand exchange in $Re_2(CO)_{10}$[21] and equivalence of all carbonyls (by ^{13}C nmr) in dodecacarbonyl tetrarhodium.[22] Regardless of the mechanism of this isomerization, non rigidity seems to preculde formation of linear polymers in such systems since a pathway is apparently available to give the thermodynamically more stable products, which appear to be small ring closed metal clusters. Consequently we have focused our attention on more rigid intermetallic trimers[23] which do not have the possibility of using a migratory insertion mechanism for rearrangement.

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TABLE I. PHYSICAL PROPERTIES

Compound	m.p. °C	i.r. $^{\nu}$CO cm^{-1}	R^{a} νCO cm^{-1}	R^{a} ν(MX) cm^{-1}
$\underline{t}(\mathrm{Ph\ {}_3Sn})_2\mathrm{Os(CO)_4}$ **2a**	222-223	2017(s), 2110(wk)^{b}	2055, 2111	112 ($^{\nu}$Os-Sn)
$\underline{t}(\text{n-Bu}\ {}_3\mathrm{Sn})_2\mathrm{Os(CO)_4}$ **2b**	oil	1955(s), 2080(wk)^{c}	2030, 2089	105 ($^{\nu}$Os-Sn)
$\underline{t}(\text{Ph n-Bu}\ {}_2\mathrm{Sn})_2\mathrm{Os(CO)_4}$ **2c**	oil	1995(s), 2038(wk), 2078(wk)^{c}	2036, 2094	
$((\mathrm{CO})_4\text{Os-Sn n-Bu}\ {}_2)_2$ **4a**	103-103.5	1999, 2008, 2087^{c}	1978(wk), 1999, 2008, 2087	76, 102, 117, 139
$((\mathrm{CO})_4\text{Os-Sn Ph}\ {}_2)_2$ **4b**	dec. 200	2010, 2025, 2080^{c}	2013, 2031, 2106	77(bd), 145
$\underline{\mathrm{cis}}(\mathrm{Ph\ {}_3Sn})\mathrm{Os(CO)_4H}$ **6**	224-225	2030, 2055, 2120^{b}	2038, 2057, 2123	1946 ($^{\nu}$Os-H)
$\underline{t}(\mathrm{Ph\ Cl_2Sn})_2\mathrm{Os(CO)_4}$ **7a**	158-160	2065(s), 2100(wk), 2140(wk)^{c}	2107, 2163	113 ($^{\nu}$Os-Sn)
$\underline{t}(\text{n-Bu}\ {}_2\mathrm{ClSn})_2\mathrm{Os(CO)_4}$ **7c**	94.5-96	2025(s), 2050(wk), 2100(wk)^{c}	2067, 2118	

TABLE I. continued

Compound	m.p. °C	i.r. νCO cm^{-1}	R^a νCO cm^{-1}	R^a ν(MX) cm^{-1}
$\underline{t}(Br_3Sn)_2Os(CO)_4$ **7b**	180 (sub)	2085^b	2125, 2164	138 (νOs-Sn)
$\underline{t}Cl_2Os(CO)_4$ **8**	300	2075^b	2127, 2187	327 (νOs-Cl)
$((CO)_5Re\text{-}Sn\ n\text{-}Bu_2)_2Os(CO)_4$ **10**	oil	1960(wk), 1980(sh), 1990, 2000, 2070(wk) 2090(m), 2095(m), $2105(m)^c$	2014(wk), 2022 2031, 2041 2055(wk), 2112	90, 112, 180

[a] Raman spectra on neat compounds sealed in capillary tubes.

[b] Dichloromethane solution.

[c] Hexane solution.

TABLE II. Analytical Data for Osmium Tin Complexes

Compound	% Found				% Calcd			
	C	H	X	MW	C	H	X	MW
$\underline{t}(Ph_3Sn)_2Os(CO)_4$ **2a**	47.22	3.10			47.93	3.02		
$\underline{t}(Bu_3Sn)_2Os(CO)_4$ **2b**	38.39	6.32			38.12	6.17		
$[Bu_2SnOs(CO)_4]_2$ **4a**	26.90	3.41		1032[a]	26.93	3.39		1070
$[Ph_2SnOs(CO)_4]_2$ **4b**	33.24	1.79			33.24	1.88		
$\underline{c}(Ph_3Sn)HOs(CO)_4$ **6**	40.45	2.61			40.44	2.49		
$\underline{t}(Cl_2PhSn)_2Os(CO)_4$ **7a**	22.95	1.23	16.88		23.00	1.21	16.97	
$\underline{t}(Br_3Sn)_2Os(CO)_4$ **7b**	4.68	0.0	46.97		4.71	0.0	47.05	
$\underline{t}(ClBu_2Sn)_2Os(CO)_4$ **7c**	28.66	4.31	8.17		28.61	4.33	8.45	

TABLE II. continued

Compound	% Found				% Calc			
	C	H	X	MW	C	H	X	MW
$\underline{t}Cl_2Os(CO)_4$ **8**	12.83	0.00	18.78		12.81	0.00	18.91	
$((CO)_5ReSnBu_2)_2Os(CO)_4$ **10**	25.79	2.50		1362[a]	25.36	2.55		1420

[a] Vapor pressure osmometry in chloroform.

TABLE III

Atomic Parameters and Temperature Factors[a] for $(Ph_3Sn)_2Os(CO)_4$

Atom	X	Y	Z	B
Os(1)[c]	.5000	.2500	.7500	b
Os(2)[c]	.5000	.0000	.5000	b
Sn(11)	.33299(5)	.78975(16)	.05102(8)	b
Sn(21)	.08878(5)	.66694(15)	.12608(7)	b
C(11)	.2988(1)	.7317(25)	.1048(14)	6.3(5)
O(11)	.3327(8)	.7173(19)	.1743(11)	8.0(4)
C(12)	.2488(10)	.5482(31)	-.0110(14)	7.3(b)
O(12)	.2488(10)	.4262(24)	-.0149(11)	9.3(5)
C(13)	.3117(7)	.9199(21)	-.0288(10)	4.2(4)
C(14)	.3412(9)	.9084(25)	-.0269(13)	6.4(5)
C(15)	.3266(10)	.9890(28)	-.0814(15)	7.7(6)
C(16)	.2817(11)	1.0843(30)	-.1377(15)	7.5(6)
C(17)	.2514(10)	1.0926(30)	-.1402(14)	7.3(6)
C(18)	.2670(9)	1.0158(26)	-.0842(13)	6.3(6)
C(19)	.3661(9)	.5947(23)	.0659(12)	5.2(5)
C(110)	.3321(10)	.4871(28)	.0106(14)	7.3(6)
C(111)	.3577(12)	.3586(33)	.0238(17)	8.8(7)
C(112)	.4130(11)	.3504(31)	.0932(16)	8.1(6)
C(113)	.4444(11)	.4613(32)	.1427(16)	8.1(7)
C(114)	.4220(10)	.5852(28)	.1340(14)	7.1(6)
C(115)	.4023(8)	.8860(23)	.1684(12)	4.8(4)
C(116)	.4338(11)	.8140(28)	.2359(16)	7.2(6)
C(117)	.4811(12)	.8762(34)	.3126(17)	8.8(7)
C(118)	.4949(12)	1.0165(34)	.3189(18)	8.9(7)
C(119)	.4644(14)	1.0912(38)	.2529(21)	10.1(.9)
C(120)	.4149(12)	1.0213(32)	.1723(16)	8.6(7)
C(21)	.0318(8)	.3443(24)	.0718(12)	5.0(5)
O(21)	.0509(7)	.2507(19)	.1150(10)	7.7(4)
C(22)	-.0318(9)	.5661(25)	.0098(13)	5.9(5)
O(22)	-.0513(7)	.6054(18)	.0151(9)	7.2(4)
C(23)	.0922(8)	.7615(21)	.1915(11)	4.2(4)
C(24)	.1346(9)	.7231(25)	.2740(14)	6.3(5)

TABLE III. continued

Atom	X	Y	Z	B
C(25)	.1370(12)	.7941(33)	.3159(17)	8.8(7)
C(26)	.0986(12)	.8950(32)	.2783(17)	8.5(7)
C(27)	.0573(10)	.9355(29)	.1977(15)	7.6(6)
C(28)	.0533(9)	.8669(26)	.1527(13)	6.2(5)
C(29)	.1625(7)	.5500(20)	.2093(10)	3.9(4)
C(210)	.1995(9)	.5962(25)	.2265(13)	6.0(5)
C(211)	.2488(10)	.5167(27	.2826(14)	6.7(5)
C (212)	.2581(10)	.3937(28)	.3149(13)	6.6(5)
C (213)	.2222(11)	.3389(29)	.2979(14)	7.4(6)
C(214)	.1730(10)	.4247(27)	.2444(13)	6.7(5)
C(215)	.0938(8)	.8406(21)	.0893(11)	4.5(4)
C(216)	.0850(8)	.8181 (23)	.0347(12)	5.2(5)
C(217)	.0909(8)	.9345(25)	.0124(12)	5.8(5)
C(218)	.1055(9)	1.0659(26)	.0461(13)	6.1(5)
C(219)	.1154(9)	1.0908(26)	.1003(13)	6.3(5)
C(220)	.1108(9)	.9776(26)	.1239(14)	6.4(5)

a) Fractional coordinates; numbers in parenthesis are standard deviation.

b) See Anisotropic temperature factors

c) Fixed by symmetry

TABLE IV

Anisotropic Temperature Factors (X 10^4) for $(Ph_3Sn)_2Os(CO)_4$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Os(1)	14	134	37	-7	19	-10
Os(2)	11	126	32	5	15	11
Sn(11)	15	140	39	-5	20	-5
Sn(21)	14	141	37	2	18	7

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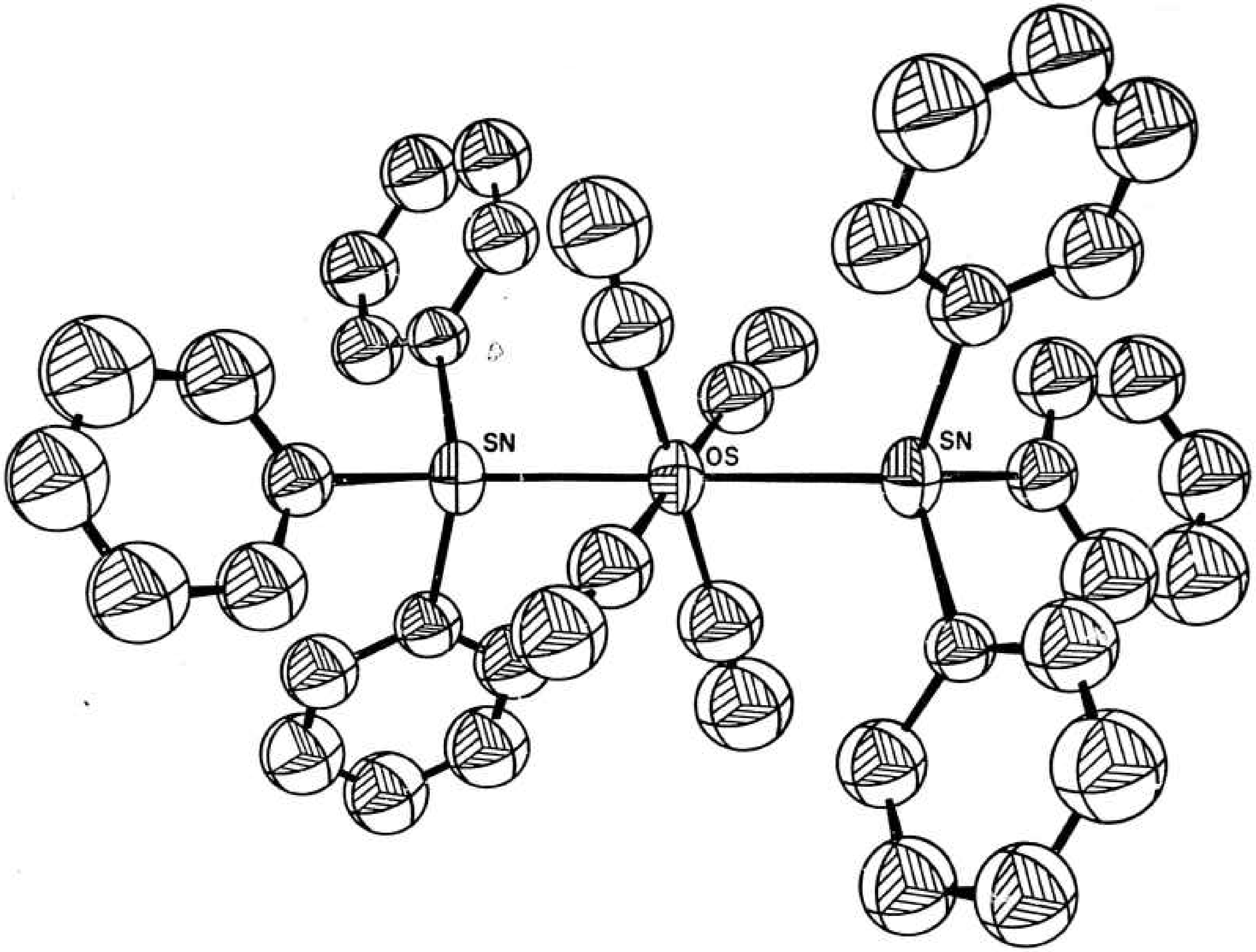

Figure I. The molecular structure of t$(Ph_3Sn)_2Os(CO)_4$

Synthesis and Structure of a Novel Rhodium(I) Schiff Base Complex

We report here the synthesis and solid state structure of a reactive new planar d^8 complex of Rh(I) with the uninegative Schiff base ligand [[3,3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)], $(DO)(DOH)_{pn}$[1]. This complex and its phosphine adducts represent neutral, molecular analogs of the anionic "supernucleophiles" of Co(I) and Rh(I) with dinegative Schiff bases.[2] The lustrous, green-gold dichroic crystals of the Rh(I) complex exhibit semiconductivity ($\sigma(25°) = 10^{-5}$ to $10^{-9}\,\Omega^{-1}\,cm^{-1}$)[3] in the range reported for stacked planar d^8 complexes suggesting intracrystalline metal-metal interaction.[4]

Treatment of $RhCl_3 \cdot 3H_2O$ with the ligand in boiling ethanol in the presence of added LiCl and a stream of CO afforded, after extraction with CH_2Cl_2, and recrystallization from CH_2Cl_2-EtOH, a 60% yield of *t* $Cl_2Rh(DO)(DOH)_{pn}$ **1** as yellow needles: pmr ($CDCl_3$); δ 2.35 and 2.45 (s on m, 14H total) and δ 4.05 (m, 4H). The oxime bridge proton was not observed in the pmr, possibly due to an equilibrium with an open bridge structure. The ir ($\nu_{OH} = 3400\ cm^{-1}$) indicated a closed oxime bridge in the solid state.

The dichloride **1** was reduced to the planar Rh(I) complex **2** with basic aqueous ethanol forming tiny green-gold, analytically pure flakes (80%) which were collected by filtration and washed with water, ethanol, and ether. The coordinatively unsaturated 2 is quite air sensitive even in the solid state and all transfers were carried out under inert atmosphere.

The planar 2 is only sparingly soluble in good ligating solvents (acetonitrile, tetrahydrofuran, acetone, and pyridine) to give red violet solutions. Single crystals suitable for electron transport and X-ray analysis were grown by slow cooling of a hot acetonitrile solution of the complex. The crystals belonged to space group $P2_1/c$ of the monoclinic system with four molecules per unit cell of dimensions $\underline{a}$ = 6.962(11), $\underline{b}$ = 15.87 (3), $\underline{c}$ = 13.41 (2) Å, β = 117.17 (5)°. Usual heavy atom techniques and anisotropic least squares refinement gave a conventional R-factor of 0.0355 for 1526 reflections having $F^2 > 3\sigma\ (F^2)$.

The planar coordination geometry was found as expected. Bond distances and angles are given on the figure. The structure of $[Me(H_2O)Co(DO)(DOH)_{pn}]ClO_4$ has been reported.[5] The tetradentate macrocycle in each is planar within 0.05 Å except for C_{10} which is 0.78 Å out of the plane for the Co complex and 0.70 Å out for the Rh compound. The ligand is capable of expanding to accommodate the Rh; the Rh-N distances average 0.11 Å longer than the corresponding Co-N bond lengths in accord with the differences in covalent radii (Co(III)=1.22, Rh(I) = 1.40)[6]. The oxime oxygens for the Rh 2 are 2.56 Å apart, consistent with a closed hydrogen bonded bridge.

The intermolecular structure did not show the expected stacked columnar arrangement of rhodium atoms. Instead, the C_2-C_3 bond of one molecule lies 3.5 Å above the C_2-C_3 bond of another molecule to form parallel planes of the complex with the closest Rh-Rh distance 6.7 Å. The electron transport properties of the crystal are apparently due to electron transfer through the ligand system. Such a mechanism for electron transport has generally been ignored in interpreting conductivity of stacked d^8 complexes, even though some purely organic π systems form stacked semiconductors.[7] Conductivity values varied over a wide range for individual crystals possibly because of surface oxidation.

The unsaturated 2 readily added tertiary phosphines to give deep blue 1:1 adducts 3 reminescent of the anionic Co(I) and Rh(I) Schiff base complexes. Costa[8] prepared the analogous $Co(DO)(DOH)_{pn}(Ph_3P)$, but with cobalt the four coordinate complex could not be isolated. Some distortion from planarity of the (DOH) ligand is apparent from three ligand methyl resonances in the pmr of 3 (PEt_3) at δ 1.55, 1.80 and 2.30 in the ratio 1:1:2. Carbon monoxide failed to coordinate with 2, presumably because the potential backbonding orbitals d_{xz} and d_{yz} are used in backbonding to the (DOH) ligand. We know of no other case of an unsaturated d^8 complex which adds phosphines but not CO.

Whereas the unsaturated complex 2 is very reactive forming oxidative adducts with a wide range of alkyl halides,[9] the saturated phosphine adduct 4 adds only reactive substrates such as methyl iodide affording the cationic complex 5 (eq. 1).

$$\mathrm{Rh(DO)(DOH)_{pn}(PPh_3)} + \mathrm{MeI} \longrightarrow \mathrm{[Me(Ph_3P)\,Rh(DO)(DOH)_{pn}]I} \qquad (1)$$

4 **5**

A similar reactivity was reported for the cobalt analog.[8] We were surprised to find **3** so much less reactive (no change after prolonged heating with cyclohexyl bromide) than **2**. The difference may be due to steric hindrance caused by distortion from square pyramidal geometry in **3**.

Further aspects of the solid state properties and reactions of this unusual complex will be reported later.

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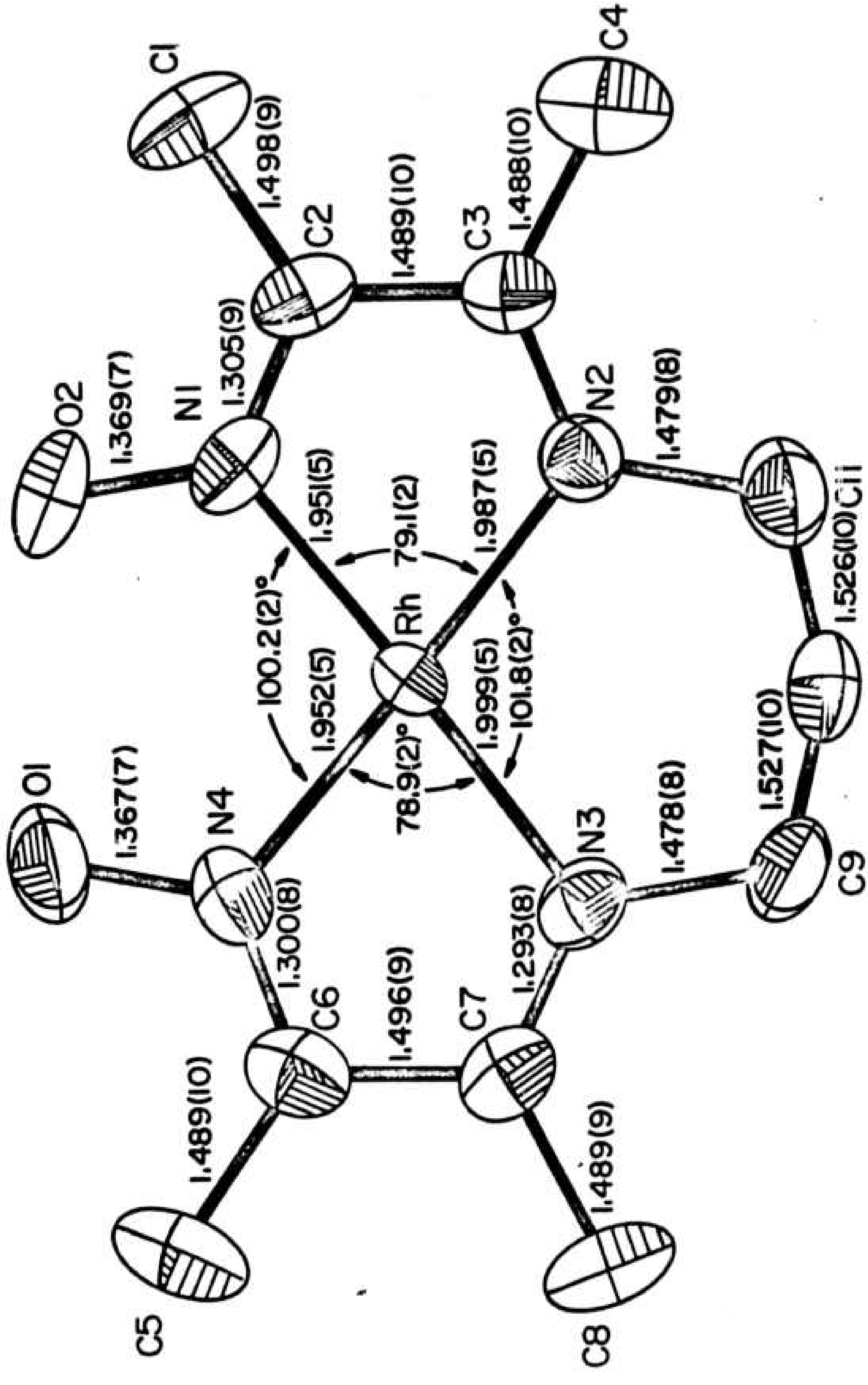
C1
1.498(9)
C4
1.488(10)
1.489(10)
C2
C3
O2
1.369(7)
N1
1.305(9)
N2
1.479(8)
1.951(5)
1.987(5)
79.1(2)
C11
100.2(2)°
101.8(2)°
Rh
1.526(10)
C10
1.952(5)
1.999(5)
O1
1.367(7)
N4
78.9(2)°
1.527(10)
N3
1.478(8)
C9
1.300(8)
1.293(8)
C6
1.496(9)
C7
1.489(10)
1.489(9)
C5
C8

A Reactive New d^8 Metal Center for Oxidative Addition Reactions

Herein we report oxidative addition[1] reactions of $Rh(DO)(DOH)_{pn}$[2] 1a and its BF_2 derivative 1b. The structure and reactivity patterns of 1a,b are strikingly similar to those of anionic "supernucleophilic" cobalt(I) and rhodium(I) complexes with dinegative tetradentate ligands.[3] The novel features of 1a,b are: The highest reactivity yet reported for an isolated, neutral d^8 complex, the steric constraints afforded by the DOH ligand, and competing chemistry of the oxime bridge.

Treating THF suspensions of 1a with addenda X-Y affords high yields of the trans rhodium(III) adducts 2a (eq. 1). Adducts have been obtained and characterized using the well known addenda: iodine, bromine, acetyl chloride, benzoyl chloride, methyl iodide, ethyl iodide, benzyl chloride, cyclohexyl bromide, triphenyltin chloride and 6-bromohexene, as well as neopentyl bromide, chloroform, and dichloromethane which seldom form oxidative-adducts. The cobalt analogs of some of these complexes have been prepared by other routes by Costa[4] and coworkers. The relative rates of alkyl halide additions--simple primary halides reacting very rapidly but cyclohexyl and neopentyl bromides requiring several hours at reflux--are suggestive of two electron changes (nucleophilic attack at carbon). Further support for this hypothesis is provided by the absence of byproducts or rearrangement in the addition of 6-bromohexene since the 6-hexenyl radical closes irreversibly and rapidly ($k_1 = 10^5$ sec^{-1})[5] to a 5-membered ring. A final decision on this point must await the results of kinetic and stereochemical studies in progress. It may be that either a one or two electron path will dominate depending on the nature of the alkylating agent or reaction conditions as observed for $(Me_3P)_2Ir(CO)Cl$.[6,7] A one electron path (radical) is likely for the reactions of 1a with CCl_4 and trimethyltin chloride, both of which yield 2a (X=Y=Cl).

All of the adducts 2 described above exhibit the trans stereochemistry anticipated in view of the tendency for the tetradentate ligand to remain coplanar. This assignment is based on pmr spectra showing two distinct ligand methyl singlets (6H each) near δ 2.25 on or near a multiplet (2H) due to the central bridge CH_2, as well as an NCH_2 multiplet near δ 4.0 (4H) and an O-H---O resonance near δ 11.0 to δ 13.0. The α CH groups are shifted upfield (CH_3 = 0.20, CH_2Cl = 3.38, $CHCl_2$ = 5.85, and $(CH_3)_3CH_2$ = 1.00) and split by ^{103}Rh (J_{Rh-H} = 1.2 Hz). The structure assigned to the 6-hexenyl adduct is based on pmr data showing a terminal olefin (δ 4.70 (m, 1-H), δ 4.90 (m, 1-H), and δ 5.5 (m 1-H)).

Certain molecules have a marked tendency to form cis-adducts with d^8 centers.[1] At first it seemed that the steric constraint of the DOH ligand might preclude cis addition. For example H_2, simple olefins and acetylenes gave no indication of adduct formation although H_2 under forcing conditions (100°, 100 psi) decomposed 1a to form a Rh mirror. However, activated olefins and acetylenes (TCNE, dimethyl furmarate, and dimethyl acetylenedicarboxylate) do form stable 1:1 adducts. The tetradentate ligand is distorted from planarity as indicated by four DOH methyl signals (δ1.60, 1.70, 1.90, and 2.15) and two ester methyl signals (δ 3.35, and 3.45) in the pmr spectrum of the dimethyl acetylene adduct.

The oxime O-H---O bridge in 1a reacts with protonic and Lewis acids complicating their oxidative addition reactions. One eq. HCl afforded a simple adduct 2a (X=H, Y=Cl, $^{\nu}$Rh-H=2065 cm^{-1}) with a closed oxime bridge (νOH=3400 cm^{-1}) whereas excess HCl yielded a hydride (ν Rh-H=2030 cm^{-1}) with a ruptured oxime bridge[8] (ν OH 2400 cm^{-1} bond). Both adducts spontaneously decompose over a few hours in the solid state. The latter complex afforded the dichloride 2a(X=Y=Cl), and the simple adduct (X=H, Y=Cl) gave an uncharacterized species with an open oxime bridge. Stannic chloride gave an adduct analyzing for Rh(DO)(DOH)$_{pn}$Sn$_2$Cl$_7$ thought to have structure 2c (X=SnCl$_3$, Y=Cl).

In order to rule out the participation of the oxime bridge in reactions of 1a, the corresponding BF$_2$ adduct was prepared by stirring 2a (X=Y=Cl) with BF$_3$ · O(C$_2$H$_5$)$_2$[9] and reducing to the rhodium(I) complex 1b, which underwent rapid oxidative-additon reactions as before. The BF$_2$ adducts were less soluble and more soluble alkyls were needed to obtain satisfactory pmr spectra. For example, the amyl iodide adduct 2b (X=n-C$_5$H$_{11}$, Y=I) was prepared and characterized by pmr and elemental analyses. Apparently the BF$_2$ bridge does not introduce enough additional rigidity into the ligand to prevent cis additions. A 2:1 adduct was formed from CH$_3$O$_2$CC≡CCO$_2$CH$_3$ and 2b whose spectral properties are consistent with a metallocyclopentadiene[10] structure. Again the presence of four DOH methyl signals (δ 1.75, 1.85, 2.00, and 2.25) are indicative of deviation from coplanarity. The change in stoichiometry of the acetylene adducts of 1a and 1b is puzzling. Strong Lewis acids add to 1b without interference by the bridge. Thus $SnCl_4$ gave 2b (X=$SnCl_3$, Y=Cl). A more interesting example is the addition of π-$C_5H_5Fe(CO)_2SnCl_3$ to 1b forming an adduct thought to have the structure 2b (X = π-$C_5H_5Fe(CO)_2SnCl_2$, Y=Cl) although the alternative structure (X=$SnCl_3$, Y = $\pi C_5H_5Fe(CO)_2$) cannot be ruled out by available spectral data. Treatment of this adduct with Cl_2 gave 2b (X = $SnCl_3$, Y=Cl) consistent with either structure. A novel aspect of this adduct is the presence of ten different elements of which seven were analyzed.

The similarity in structure and patterns of reactivity of the neutral $Rh(DO)(DOH)_{pn}$ and the anionic "supernucleophiles" of Co(I) and Rh(I) make one wonder if the mechanistic pathways are not similar, and if so do those pathways extend to other metal centers.

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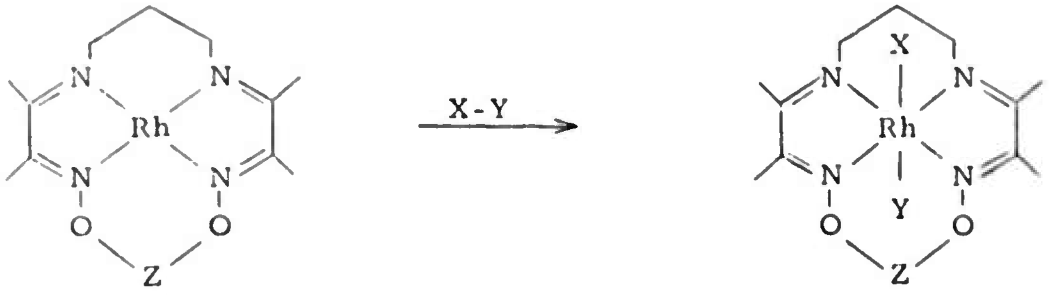

(1)

1a Z=H, **1b** Z=BF_2

2a Z=H, **2b** Z=BF_2, **2c** Z=$SnCl_3$

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Syntheses of Intermetallic Oligomers Employing Transition Metal Substituted Tin and Germanium Hydrides

The eventual synthesis of linear polymers having backbones comprised entirely of covalently bonded metal atoms is a long range goal of our laboratory[1]. Our interest in such materials stems from the expectation that a coaxially oriented solid derived from such substances would exhibit anisotropic electron transport properties which would be principally dependent upon the structure of the individual polymer molecules.

Consequently, we are interested in preparing metal-metal bonds by methods which avoid strongly basic conditions that might sever metal chains. Most of the known metal-metal bond forming reactions involve a nucleophilic metal anion reacting with another metal halide[2]. The paucity of alternative methods for preparing metal-metal bonds is not surprising when one considers that the great majority of carbon-carbon bond forming reactions employ p-π orbitals which are energetically disfavored for elements beyond the first short period.

Group IVA (Si, Ge, Sn) hydrides are attractive intermediates for intermetallic syntheses in view of three reactions[3]: (a) the widely reported, base catalyzed, self-coupling of Sn-H groups (eq. 1), (b) condensations between Sn-H and Sn-X groups (eq. 2)[3], and (c) the additions of group IVA hydrides to polynuclear metal carbonyls[4] (cf. --eq. 3).

$$2R_3SnH \xrightarrow{\text{base}} R_3Sn\text{-}SnR_3 + H_2 \qquad (1)$$

$$R_3SnH + R'_3SnX \longrightarrow R_3Sn\text{-}SnR'_3 + HX \qquad (2)$$

$$X = NR''_2,\ NArCHO$$

$$2\,Ph_2SiH_2 + Co_2(CO)_8 \longrightarrow 2\,HPh_2SiCo(CO)_4 \qquad (3)$$

Reaction (c) is the method of choice for preparing silicon to transition metal bonds[4a] and a few cases have been reported for simple germanium[4b] and tin hydrides[4c]; however the latter afford low yields and complex mixtures[4c].

We decided to study transition metal substituted germanium and tin hydrides as models for metal-metal bond forming reactions which might be employed in polymerizations of metallic monomers. At the outset of this work a few examples of transition metal substituted germanium hydrides were known[5] but the tin analogues were not. Reduction of the requisite tin and germanium chlorides[6] with $(i\text{-}Bu)_2AlH$ afforded transition metal substituted tin and germanium hydrides in good to excellent yields (eg. --eq. 4).

$$[(OC)_5Mn]_2SnCl_2 + 2(i\text{-}Bu)_2AlH \xrightarrow{\text{hexane}} H_2Sn[Mn(CO)_5]_2 \qquad (4)$$

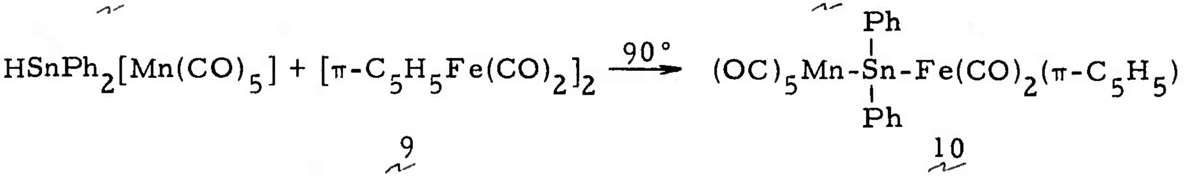
Using this method the following hydrides were prepared and characterized[8]: 1, $(OC)_5MnSnPh_2H$ (oil); 2, $(OC)_5ReSnPh_2H$ (oil); 3, $[(OC)_5Mn]_2SnH_2$ (yellow, m.p. 89-92°); 4, $[(OC)_5Re]_2SnH_2$ (yellow, m.p. 94-97°); 5, $[(OC)_5Mn]_3SnH$ (orange, m.p. 127-130°); 6, $(OC)_5MnGePh_2H$ (oil); and 7, $(OC)_5ReGePh_2H$ (white, m.p. 47-49°). The Ge derivatives 6 and 7 are more stable towards heat and O_2 than the Sn compounds 1-5. The stability of such tin hydrides appears to be sensitive to the nature of the attached transition metal and our attempts to prepare tin hydrides containing Co, Mo, W, or Fe substituents were unsuccessful.

Coupling reactions of transition metal substituted silicon, germanium, and tin hydrides have not been previously reported[9]. Having these transition metal-tin hydrides in hand we first examined tin-tin coupling reactions modeled after those in eq. 1 and 2. Both procedures afforded complex, often intractable mixtures. Careful analysis of these reactions (cf. eq. 5) indicated varying degrees of disproportionation about tin.

$$(OC)_5MnSnPh_2H + Et_2NSnPh_3 \longrightarrow Et_2NH + Ph_3Sn\text{-}SnPh_3 + Ph_3SnMn(CO)_5 \\ + \text{unidentified products} \qquad (5)$$

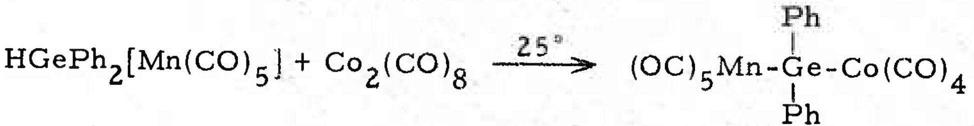
However reactions of these tin hydrides with binuclear metal carbonyls were more successful and in some cases selectively afforded metal oligomers. For example the dihydride 3 reacts with $Co_2(CO)_8$ under ambient conditions forming the pentametallic derivative 8 (eq. 6). Similarly at 90° the monohydride 1 reacts with the dimeric iron complex 9 to form the trimer 10 (eq. 7).

$$\underset{3}{H_2Sn[Mn(CO)_5]_2} + Co_2(CO)_8 \xrightarrow{25°} \underset{8}{[(OC)_4Co]_2Sn[Mn(CO)_5]_2} \qquad (6)$$



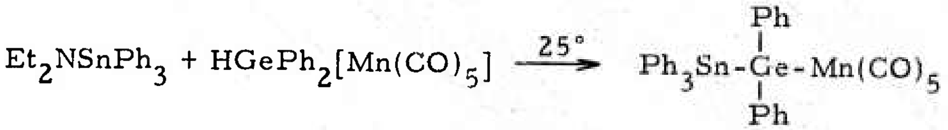
$$HSnPh_2[Mn(CO)_5] + \underset{9}{[\pi\text{-}C_5H_5Fe(CO)_2]_2} \xrightarrow{90°} \underset{10}{(OC)_5Mn\text{-}\overset{Ph}{\underset{Ph}{Sn}}\text{-}Fe(CO)_2(\pi\text{-}C_5H_5)} \qquad (7)$$

The moderate thermal instability of these tin hydrides limits the scope of this sort of reaction. For example $Mn_2(CO)_{10}$ fails to react with the dihydride 3 up to 120° at which point 3 undergoes self-coupling forming cyclic oligomers of the type $[Sn[Mn(CO)_5]_2]_n$. Because of this thermal instability we turned our attention to the more robust metal substituted germanium hydrides. $Co_2(CO)_8$ reacts with 6 affording the trimer 11 in high yield (eq. 8). These germanium hydrides can also be coupled with tin amido derivatives as illustrated in the formation of 12 (eq. 9).



$$HGePh_2[Mn(CO)_5] + Co_2(CO)_8 \xrightarrow{25^\circ} (OC)_5Mn\text{-}\overset{Ph}{\underset{Ph}{Ge}}\text{-}Co(CO)_4 \qquad (8)$$

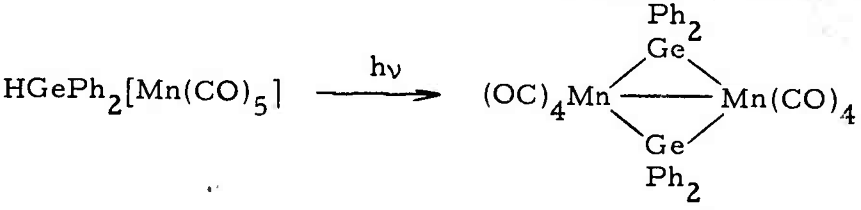
6 11



$$Et_2NSnPh_3 + HGePh_2[Mn(CO)_5] \xrightarrow{25^\circ} Ph_3Sn\text{-}\overset{Ph}{\underset{Ph}{Ge}}\text{-}Mn(CO)_5 \qquad (9)$$

12

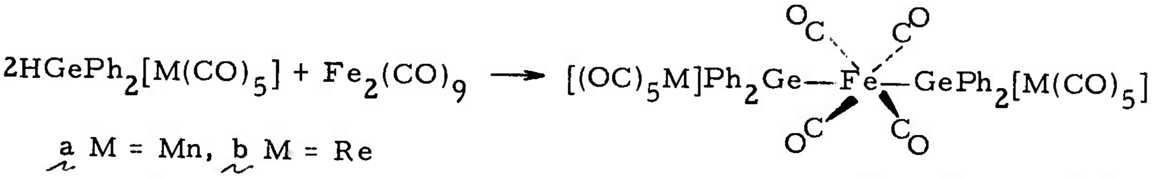
When irradiated the manganese substituted germanium hydride 6 undergoes related self coupling affording the dimer 13[10] (eq. 10) which is thought to have the indicated bicyclic structure because of the similarity of its infrared spectrum with that of the structurally characterized silicon analogue[11].



(10)

13

The most interesting reaction is that of $Fe_2(CO)_9$ with 6 and 7 affording the metallic pentamers 14a, b under mild conditions (eq. 11). These new



(11)

a M = Mn, b M = Re

14 a M = Mn, b M = Re

metallic oligomers 8-14 have been characterized by elemental analyses, vibrational spectroscopy, and molecular weight measurements. A *trans* configuration about iron is most consistent with the $^{\nu}$CO region in the ir spectra of 14a, b. If this steric assignment (which is currently being examined by X-ray diffraction) is correct, this reaction (eq. 11) takes on great importance because difunctional germanium hydrides may react with $Fe_2(CO)_9$ forming linear intermetallic polymers. The apparent transoid nature of the germanium-iron bond forming reaction augers well for directing linear polymerization, avoiding the formation of cycles. We plan to test this hypothesis.

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(6) Prepared by the metathetical reaction of the appropriate transition metal carbonyl anion with the corresponding tin or germanium chloride. Physical and spectroscopic properties were consistent with the formulations and agreed with those previously reported[7].

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(8) Characterization of the complexes by elemental analyses, molecular weight measurements, infrared spectra in the νCO region, and pmr spectra was in agreement with our formulations. For example, the complexes $H_2Sn[Mn(CO)_5]_2$ and $HPh_2GeRe(CO)_5$ show sharp singlets in the pmr spectra for the hydride protons at τ 6.10 and 4.55 respectively.

(9) The following reaction has been observed:

$$2HCl_2SiMn(CO)_5 + Mn_2(CO)_{10} \longrightarrow Cl_2Si[Mn(CO)_5]_2$$

J. K. Hoyano and W. A. G. Graham, unpublished results.

(10) Previously prepared by heating Ph_2GeH_2 with $Mn_2(CO)_{10}$ at ca. 160°. Note that in reactions of this type transition metal substituted germanium hydrides cannot be isolated (see references 4(b)).

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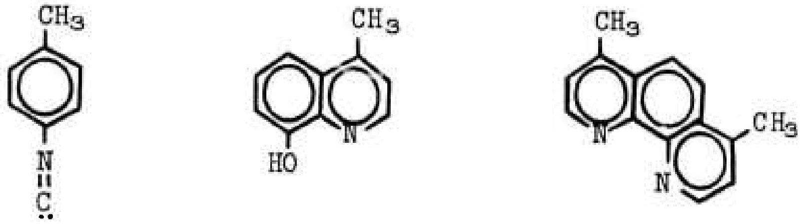
Synthesis of Planar Dye-Ligand System

Dr. Craig McAllister

Introduction

Three distinct but similar ligand systems have been chosen for further evaluation in our continuing study of high-temperature superconductivity. We expect that ligand-metal systems should be planar, compact, and have a high dye-to-metal-atom ratio. Compounds of types **I-III** have been chosen because of their basic synthetic simplicity, their relatively planar and dense aromatic structure, and because known analogs chelate transition metal ions very well. Each has a particular feature of note: the isocyanide species **I** is a neutral ligand which could "spear" the metal ion analogous to metal-carbonyl complexes; the 8-hydroxy-quinoline species **II** can be ionized to an anionic ligand which could replace any counter ions in the complex, such as Cl^-; and the 1,10-phenanthroline species **III** spatially occupies a large disk-like volume element, which presumably would strongly effect crystal growth asymmetry.



I II III

Figure 1 Three precursors for ligand-dyestuffs. Each CH_3 group can be derivatized to form a suitable dye chromophoric system.

I. Isonitrile Dyestuffs

The various isonitrile complexes of transition metals which have been reported[1] have provoked our interest in the synthesis of a species suitable for superconductivity studies. Based on an earlier procedure by Ugi and Meyr,[2] the construction of species Ia-c was begun.

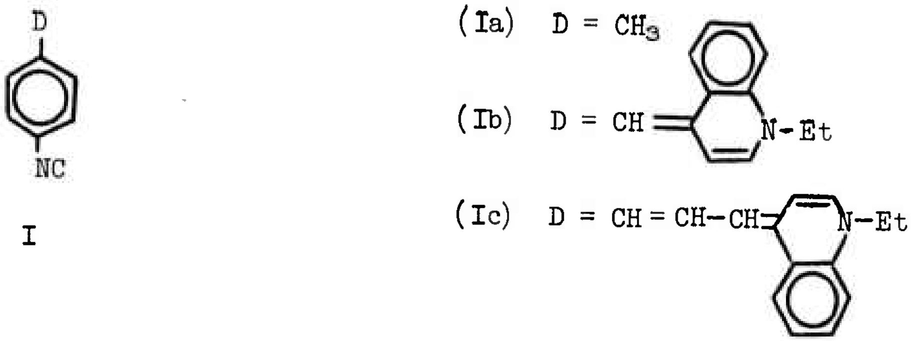
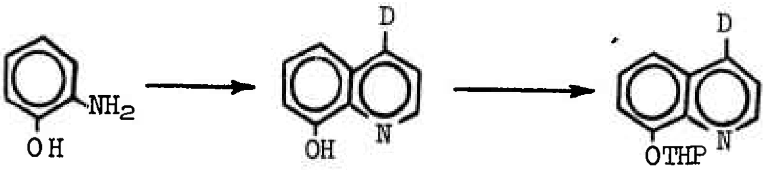


Figure 2

A vile-smelling substance (Ia) was obtained conveniently as a colorless oil, and was stored with only slow decomposition at 0°. Further modification of Ia to form Ib or Ic was postponed, to await developments with other alternatives (see below).

II. Dyestuffs Based on 8-Hydroxy-quinoline

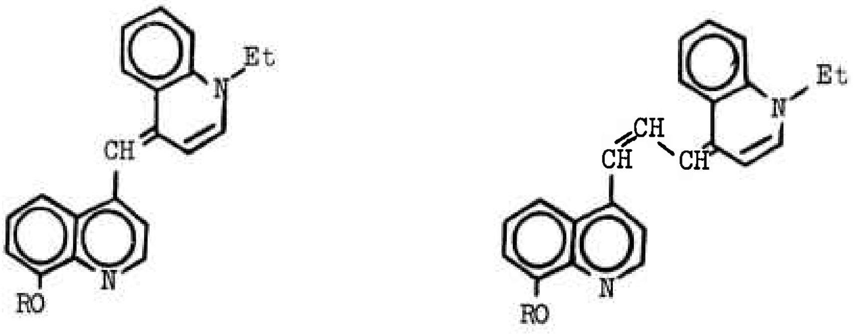
After some initial difficulties, a satisfactory synthesis of 4-methyl-8-hydroxy-quinoline IIa was established,[3] as outlined in Figure 3. (A stable derivative of IIa, the tetrahydropyranyl "THP" ether, IIa', was prepared to



IIa IIa'

Figure 3

prevent crosslinking between quinoline moieties through the hydroxyl function. Removal of the ether group is accomplished in mild, acidic conditions,[4] not unlike those in metal chelate formation reactions.) Direct condensation of IIa with chosen quinoline ethiodide salts, to produce cyanine dyes of type IIb and IIc proved inconclusive. Although visual spectroscopic evidence was obtained to suggest the formation of the desired products, subsequent isolation and characterization steps apparently allowed decomposition. No satisfactory dyestuffs were obtained in this manner. Condensation with the protected species IIa' however afforded several interesting, stable, dyestuffs which are under investigation.



IIb

IIc

Figure 4

III. Cyanine Dyes Based on 1,10-Phenanthroline

A third avenue of approach is the construction of neutral ligands of the form IIIa-c.

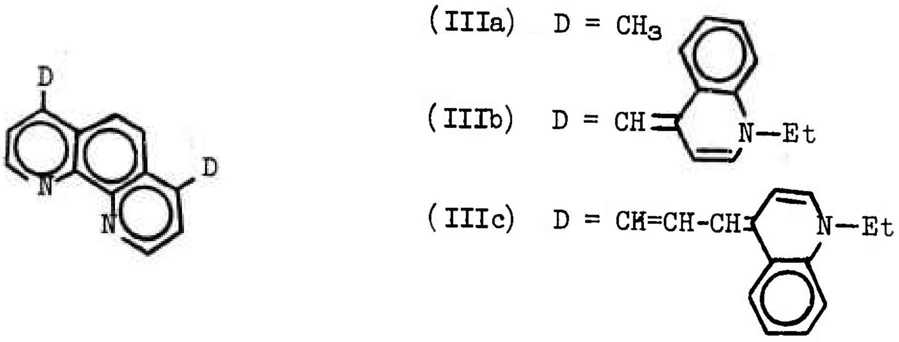


Figure 5

It has been in this area that some of our most promising results have occurred. Dyestuffs IIIb and IIIc have been synthesized, although not fully characterized. On a preliminary level however, IIIc has been mixed with several metal systems to test chelate-crystal formation. A summary of preliminary results is tabulated below. Results suggest additional experiments using various soluble metal salts, such as $(C_6H_5CN)_2PtCl_2$,[5] or $[(C_6H_5)_3P]_3RhCl$,[6] and the dye-ligands IIIb and IIIc in more controlled conditions of complex formation. Preparations have been made for these tests, and initial results have been favorable. No stoichiometric complex has been fully isolated and characterized however.

Table 1. Preliminary Results from Metal-Dyestuff Chelation Study

#	Metal Salt (color)	Filtered Product
1.	$[(c\text{-}C_8H_{12})_2IrCl]_2$ (yellow)	non-stoichiometric blue solid
2.	$[(c\text{-}C_8H_{12})_2IrCl]_2$ (orange)	non-stoichiometric dark blue solid
3.	(p-toluidine)$Ir(CO)_2Cl$ (purple)	non-stoichiometric blue-green solid
4.	$(DMSO)_2CuBr_2$ (yellow)	non-stoichiometric dark brown solid (reaction appears to decompose dyestuff)
5.	K_2PtCl_4 (orange)	non-stoichiometric dark blue solid

Reaction conditions: 0.1mmole dye/1ml CH_3CN + 0.1mmole metal salt/1ml DMF;
mix and let stand 14 hours, triturate with Et_2O.

IV. Experimental Section

p-Toluidine Isocyanide (Ia): To a suspension of 54g (0.48mole) potassium t-butoxide in 300ml t-butanol was added 32.3g (0.24mole) p-tolyl-formamide. The mixture was cooled to 10-20° and rapidly stirred while 18.4g (0.12mole) phosphorous oxychloride was added dropwise over 30 minutes. The reaction mixture became thick and sluggish, but was warmed to 30-35° and stirred an additional 60 minutes. The crude product mixture was poured over a mixture of 12.5g $NaHCO_3$ in 1ℓ H_2O. The oil which formed was decanted, and the aqueous layer was further extracted with 4 x 125ml portions of 40-60 petroleum ether. The organic portions were combined and dried over solid KOH. The solvents were removed at reduced pressure, and the remaining product was fractionated *in vacuo*. Yield: 22.2g (86%) colorless oil BP 42°/0.2mm.

This material has a vile odor, and becomes yellow after standing at room temperature. Storage at 0° retards decomposition. (Synthesis of the formamide was accomplished in 95% yield from freshly distilled p-toluidine and 98% formic acid by standard methods, BP 115°/0.25mm, MP 51-52°.)

4-Methyl-8-hydroxy-quinoline (IIa): A solution of 27.3g (0.25mole) o-amino-phenol in 100 ml con. HCl was heated to 100° with stirring. Over a 45 minute period 35.0g (0.50mole) methyl vinyl ketone was added dropwise. The reaction mixture was kept at 100-120° for an additional 5 hours of stirring, and then allowed to stand at room temperature for 10 hours. Volatile side products and excess starting materials were removed by steam distillation of ~100ml condensate. The crude reaction mixture was then made alkaline to litmus with solid KOH, and steam distilled. Crude product was filtered from the first 10ℓ of condensate, washed with cold H_2O, and recrystallized from benzene. Yield: 8.49g (21%) pale white plates, MP 138-139°. Anal. Calc. C 75.59, H 5.66, N 8.80;

Found C 75.24, H 5.88 N 8.73.

4-Methyl-8-hydroxy-quinoline tetrahydropyranyl ether (IIa'): A quantitative conversion to the THP ether was obtained by standard methods.[4]

Typical syntheses of 8-hydroxy-quinoline dyestuffs

Cyanine Dyes Type IIb: An ethanolic solution of the 4-methyl-8-hydroxy-quinoline (or THP ether), quinoline ethiodide, and m-dinitro-benzene in the ratios 1:3:1.5 is heated at reflux. A solution of KOH in ethanol is added dropwise to the hot mixture over ~30 minutes, and the entire reaction mixture is heated an additional 4 hours. The solution changes from yellow-orange to dark red-purple. Dark purple solid materials can be obtained upon trituration with ether. Typical spectral characteristics include $\lambda_{max}^{EtoH} \approx 570$nm, $\log \varepsilon \geq 4.5$. Upon further isolation and/or mild chromatography, however, these characteristics are replaced by $\lambda_{max}^{EtoH} \approx 450$nm. Work is in progress to prevent decomposition of the product dyestuffs.

Cyanine Dyes Type IIc: An ethanolic solution of 4-methyl-8-hydroxy-quinoline and 4-[β-anilino-vinyl]-quinoline ethiodide is heated at reflux while an ethanolic solution of KOH is added dropwise. Additional heating results in a solution color change from violet to dark red-purple. Trituration with ether, and sublimation yields very dark blue crystals which are hygroscopic and apparently air sensitive. Spectral characteristics include $\lambda_{max}^{EtoH} = 708$nm $\log \varepsilon \geq 4.5$. Further purification of this material induced decomposition. Work is in progress to prevent decomposition of the product dyestuffs.

Cyanine Dye IIIc: A mixture of 0.214g (1.0mmole) 4,7-dimethyl-1,10-phenanthroline and 4.871g (12.0mmole) 4-(β-anilino-vinyl)-quinoline ethiodide in 50ml absolute ethanol was heated at reflux. A solution of 0.81g KOH in 25ml EtOH was added dropwise over a period of 30 minutes to the rapidly stirred solution. The reaction mixture was heated at reflux an additional 10 hours. The solution changed from purple to very dark green to blue-green. Trituration with benzene or ether produced dark blue plates with a golden luster. Hygroscopic. MP 192-193°d $\lambda_{max}^{EtOH} = 705nm$ $\log \varepsilon \geq 5.0$ This material is soluble in polar, organic solvents and water, and decomposes in aqueous acid. Work is in progress to obtain an analytical sample suitable for crystal-growth studies.

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2. "Concept of Generalized Chladni Forces: Application to an Electron-Optical Light Pipe," W. A. Little, J. Appl. Phys. 43, 2901 (1972).
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9. "Synthesis of Linear Metallic Oligomers. Organotin Complexes of Tetracarbonylosmium," J. P. Collman, D. W. Murphy, E. B. Fleischer and D. Swift, Inorg. Chem., to be published.
10. "A Reactive New d^8 Metal Center for Oxidative Addition Reactions," J. P. Collman, D. W. Murphy and G. Dolcetti, J. Amer. Chem. Soc., to be published.
11. "Synthese of Intermetallic Oligomers Employing Transition Metal Substituted Tin and Germanium Hydrides," J. P. Collman, J. K. Hoyano, and D. W. Murphy, to be published.

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