Synthesis of Linear Metallic Oligomers. Organotin Complexes of Tetracarbonylosmium

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Organotin complexes of tetracarbonylosmium 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 $(Ph_3Sn)_2Os(CO)_4$ was ascertained by a complete X-ray diffraction study. The linear Sn–Os–Sn cluster has an Os–Sn bond distance of 2.712 Å indicating little or no double-bond character in the system. Difunctional organotins gave di-μ-tin complexes of formula $[(CO)_4OsSnBu_2]_2$. 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 trans-$(ClBu_2Sn)_2Os(CO)_4$ with $Re(CO)_5^-$ afforded the pentametallic $((CO)_5ReSnBu_2)_2Os(CO)_4$. Attempts to prepare linear polymers from the collinear trans-$(ClBu_2Sn)_2Os(CO)_4$ gave only the di-μ-tin complex $[(CO)_4OsSnBu_2]_2$.

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 collinear 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 collinear 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 cis whereas the ruthenium compounds were reported to be mixtures of cis and trans 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 trans stereochemistry. One such complex of osmium, the bis(trimethyltin) complex, was reported during the course of this work.[8]

Experimental Section

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 min prior to use.

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

Disodium Tetracarbonylosmate(–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 g-atoms) was 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 0.5 hr until the characteristic blue color of the sodium vanished. The sides of the reaction vessel

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were rinsed by touching a cold (−78°) 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 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 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 was stirred 10 min. 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 1 (0.66 mmol) in THF (10 ml) under argon was treated with tri-butyltin chloride (440 mg, 1.36 mmol). The mixture was stirred 10 min. 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 1 (5.92 mmol) was dried at 0.1 mm pressure for 1 hr to remove the last traces of ammonia. The flask was cooled in a Dry Ice-2-propanol bath and syrupy phosphoric acid (35 ml dexoygenated by bubbling nitrogen through it for 2 hr) was added. The cold flask was attached to a high-vaccum line and allowed to warm to room temperature. The volatile hydride (and water) was pumped out of the reaction vessel over 12 hr and collected in a liquid nitrogen cooled trap. The hydride and water were then transferred onto phosphorus pentoxide (25 g) to remove water. Care was taken to allow slow thawing to avoid excess heat which may have decomposed 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 tri-phenyltin 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 5 min, 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 spectroscopy and tlc (110 mg, 67%).

Bis(μ-dibutyltin-tetracarbonylosmium), 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 2 hr. 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) and 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(μ-diphenyltin-tetracarbonylosmium), 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 1 hr, 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 *N*-(Tributyl-stannio)-*N*-phenylformamide. The dihydride 3 (64.2 mg, 0.211 mmol) was transferred into an acetonitrile (5 ml) solution of the stannioformamide (160 mg, 0.386 mmol). The mixture was allowed to warm to room temperature and stirred for 1 hr. Treatment with carbon tetrachloride and filtration through silica gel (25 g) gave, after removal of solvent, pure bis(tributyltin) complex (135 mg, 71%) identical with 2b by tlc and ir spectroscopy.

Reaction of Dihydridotetracarbonylosmium (3) with Triphenyl-tin 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 being stirred for 1 hr, 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 spectroscopy and tlc.

Reaction of Dihydridotetracarbonylosmium (3) with Dibutyldi-methoxytin. The dihydride 3 (87.8 mg, 0.289 mmol) was transferred into an acetonitrile solution (3 ml) of the methoxytin 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 spectroscopy and tlc.

cis-Hydrido(triphenyltin)tetracarbonylosmium, 6. Acetic acid (1.58 mmol) was added to a THF (15 ml) slurry of 1 (1.58 mmol). The mixture was stirred 10 min to give a clear solution. Triphenyltin chloride (610 mg, 1.58 mmol) in THF (5 ml) was added and stirring was continued for 10 min. Tlc showed two spots close together at R_f 0.4 in hexane–dichloromethane (85:15). The mixture was separated on two 20 × 20 cm silica gel plates. The lower band was identical with the bis(triphenyltin) derivative 2a. The upper band, after recrystallization from methanol, gave colorless crystals of the product 6 (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° in an ice-salt bath for 10 min. 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 10 min 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 10 min 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(tri-phenyltin) complex 2a (121 mg, 0.12 mmol) for 25 min 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. Compound 1 prepared from osmium carbonyl (311 mg, 1.03 mmol) was treated with phenyldibutyltin bromide[12] (1.0 g, 2.57 mmol) in THF (10 ml). The mixture was stirred 30 min. 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 × 20 cm plate) using hexane to develop. The main contaminant was diphenyldibutyltin (R_f 0.4). The product was removed from silica gel with pentane and the was solvent removed under vacuum to give the product as a slightly impure colorless oil (650 mg, 68%). Nmr (60 MHz, CCl$_4$): δ 0.6–1.6 (m, 18 H), δ 7.2–7.4 (m, 10 H).

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 mmol) held at −15° in an ice-salt bath for 15 min. Nitrogen was then bubbled through the solution for 10 min 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 0.6–1.6 (m), no phenyl protons.

Bis((pentacarbonylrhenium)dibutyltin)tetracarbonylosmium, 10. High-vacuum techniques were employed for this reaction. 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 min. 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

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Table I. Physical Properties

Compd	Mp, °C	Ir ν_{CO}, cm⁻¹	R^a ν_{CO}, cm⁻¹	R^a ν_{MX}, cm⁻¹
trans-(Ph₃Sn)₂Os(CO)₄, **2a**	222–223	2017 s, 2110 w^b	2055, 2111	112 (ν_{OsSn})
trans-(*n*-Bu₃Sn)₂Os(CO)₄, **2b**	Oil	1955 s, 2080 w^c	2030, 2089	105 (ν_{OsSn})
trans-(Ph-*n*-Bu₂Sn)₂Os(CO)₄, **2c**	Oil	1995 s, 2038 w, 2078 wk^c	2036, 2094	
((CO)₄OsSn-*n*-Bu₂)₂, **4a**	103–103.5	1999, 2008, 2087^c	1978 w, 1999, 2008, 2087	76, 102, 117, 139
((CO)₄OsSnPh₂)₂, **4b**	200 dec	2010, 2025, 2080^c	2013, 2031, 2106	77, 145
cis-(Ph₃Sn)Os(CO)₄H, **6**	224–225	2030, 2055, 2120^b	2038, 2057, 2123	1946 (ν_{OsH})
trans-(PhCl₂Sn)₂Os(CO)₄, **7a**	158–160	2065 s, 2100 w, 2140 w^c	2107, 2163	113 (ν_{OsSn})
trans-(*n*-Bu₂ClSn)₂Os(CO)₄, **7c**	94.5–96	2025 s, 2050 w, 2100 w^c	2067, 2118	
trans-(Br₃Sn)₂Os(CO)₄, **7b**	180 subl	2085^b	2125, 2164	138 (ν_{OsSn})
trans-Cl₂Os(CO)₄, **8**	300	2075^b	2127, 2187	327 (ν_{OsCl})
((CO)₅ReSn-*n*-Bu₂)₂Os(CO)₄, **10**	Oil	1960 w, 1980 sh, 1990, 2000, 2070 w, 2090 m, 2095 m, 2105 m^c	2014 w, 2022, 2031, 2041, 2055 w, 2112	90, 112, 180

^{a} Raman spectra on neat compounds sealed in capillary tubes. ^{b} Dichloromethane solution. ^{c} Hexane solution.

0.5 hr. 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 with that previously prepared.

Results and Discussion

The method of choice for preparation of ruthenium–tin complexes was treatment of dodecacarbonyltriruthenium 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 hr) 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 exhibited nearly the same R_f values upon thin-layer chromatography (tlc). Boiling or melting points were close to the desired bis(tin)osmium compounds making purification difficult. We have found a more satisfactory route employing disodium tetracarbonylosmium, **1**, prepared by reducing dodecacarbonyltriosmium with sodium in liquid ammonia. Treatment of **1** with the appropriate tin halides yielded the colorless, stable bis(tin) complexes **2a–c** (eq 1). The yields

$$\text{Os}_3(\text{CO})_{12} \xrightarrow[\text{NH}_3(l)]{\text{Na}} \underset{\mathbf{1}}{\text{Na}_2\text{Os}(\text{CO})_4} \xrightarrow{\text{R}_3\text{SnX}} \textit{trans-}(\text{R}_3\text{Sn})_2\text{Os}(\text{CO})_4 \quad (1)$$

2a, R = Ph
b, R = *n*-Bu
c, R₃ = Ph(*n*-Bu)₂
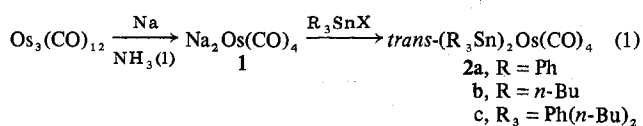
were near 90% whereas with ruthenium[7] the analogous reaction was reported to be poor, affording yields of less than 10%. The bis(tin) complexes **2a–c** were all of trans stereochemistry as determined from their ir and Raman vibrational spectra. One strong carbonyl frequency in the ir spectra and two 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 (Ph₃Sn)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 in the "International Tables for X-Ray Crystallography") with cell constants that were determined by a least-squares fit of 13 accurately measured 2θ values to be $a = 47.55$ (0.03), $b = 9.313$ (0.007), $c = 31.97$ (0.02) Å, and $\beta = 148.87$ (0.02)°. The measured density of 1.8 g/cm³ leads to 8 molecules per unit cell; $d_{calcd} = 1.819$ g/cm³.

A set of diffraction data was collected with a Picker auto-

matic diffractometer employing Mo Kα radiation. There were 3444 peaks surveyed resulting in 2785 intensities with counts greater than 3σ that were used in the subsequent analysis. The observed data are listed in Table V.[13] 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;[14] the temperture factors of osmium and tin atoms were treated anisotropically while all the carbon atoms had isotropic temperature factors. A virial weighting scheme $\sigma_{F_o} = A + B|F_o| + C|F_o|^2$ was used with $A = 1.47, B = 0.02,$ and $C = 0.0002$.

The last cycle of least-squares refinement converged to $R_1 = 0.063$ and $R_2 = 0.081$ {$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_o|)^2/\Sigma w|F_o|^2]^{1/2}$}. The final difference map showed no unusual features.

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 drawing 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 cluster with the two independent Sn–Os bonds with distances of 2.712 (0.001) and 2.711 (0.001) Å. All other distances on the molecule are as expected; *i.e.*, 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).[15] Thus it is unnecessary to propose dπ–dπ multiple bonding (which would lead to a decreased Sn–Os distance) nor a σ-bonding trans influence of one Sn upon the other (which would lead to a lengthened Sn–Os distance).

Compound **1** had been previously prepared by L'Eplattenier[9] from reduction of osmium carbonyl with sodium in

(13) See paragraph at end of paper regarding supplementary material.
(14) This refinement made use of J. A. Iber's diffractometer setting program PICK. Other computer programs used in this work include local versions (for use on a PDP-10 computer) of PICKOUT (R. J. Doedens, J. A. Ibers) for data processing, GONO (W. C. Hamilton) for absorption correction, FORDAP (A. Zalkin) for Fourier summation, UCIGLS (derived from Busing, Martin, and Levy's ORFLS) for structure factor calculations and least-squares refinement, ORFFE (Busing, Martin, Levy) for function and error calculations, PLANET (D. L. Smith) for least-squares plane calculations, DANFIG (R. J. Dellaca, W. T. Robinson) and ORTEP (C. K. Johnson) for preparation of the figures, RSCAN (R. J. Doedens) for evaluation of weighting scheme, and various local programs.
(15) K. M. Mackay and R. W. Watt, *Organometal. Chem. Rev. A,* 4, 137 (1969).

Table II. Analytical Data for Osmium–Tin Complexes

	% calcd			% found		
Compd	C	H	X	C	H	X
trans-(Ph₃Sn)₂Os(CO)₄, **2a**	47.93	3.02		47.22	3.10	
trans-(Bu₃Sn)₂Os(CO)₄, **2b**	38.12	6.17		38.39	6.32	
[Bu₂SnOs(CO)₄]₂,ᵃ **4a**	26.93	3.39		26.90	3.41	
[Ph₂SnOs(CO)₄]₂, **4b**	33.24	1.88		33.24	1.79	
cis-(Ph₃Sn)HOs(CO)₄, **6**	40.44	2.49		40.45	2.61	
trans-(Cl₂PhSn)₂Os(CO)₄, **7a**	23.00	1.21	16.97	22.95	1.23	16.88
trans-(Br₃Sn)₂Os(CO)₄, **7b**	4.71	0.0	47.05	4.68	0.0	46.97
trans-(ClBu₂Sn)₂Os(CO)₄, **7c**	28.61	4.33	8.45	28.66	4.31	8.17
trans-Cl₂Os(CO)₄, **8**	12.81	0.00	18.91	12.83	0.00	18.78
((CO)₅ReSnBu₂)₂Os(CO)₄,ᵇ **10**	25.36	2.55		25.79	2.50	

ᵃ Molecular weight: calcd, 1070; found (vapor pressure osmometry), 1032.   ᵇ Molecular weight: calcd, 1420; found, 1362.

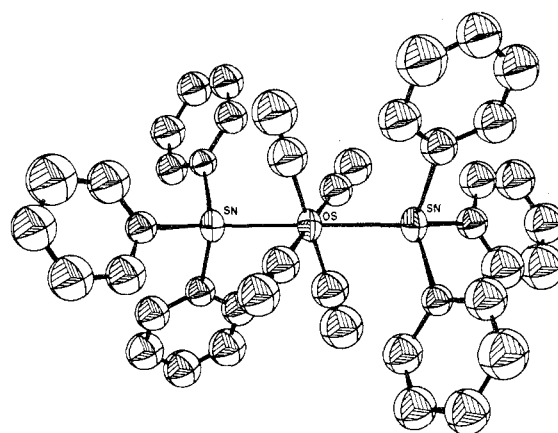**Table III.** Atomic Parameters and Temperature Factorsᵃ for (Ph₃Sn)₂Os(CO)₄

Atom	x	y	z	B, Å²
Os(1)ᶜ	0.5000	0.2500	0.7500	b
Os(2)ᶜ	0.5000	0.0000	0.5000	b
Sn(11)	0.33299 (5)	0.78975 (16)	0.05102 (8)	b
Sn(21)	0.08878 (5)	0.66694 (15)	0.12608 (7)	b
C(11)	0.2988 (1)	0.7317 (25)	0.1048 (14)	6.3 (5)
O(11)	0.3327 (8)	0.7173 (19)	0.1743 (11)	8.0 (4)
C(12)	0.2488 (10)	0.5482 (31)	−0.0110 (14)	7.3 (b)
O(12)	0.2488 (10)	0.4262 (24)	−0.0149 (11)	9.3 (5)
C(13)	0.3117 (7)	0.9199 (21)	−0.0288 (10)	4.2 (4)
C(14)	0.3412 (9)	0.9084 (25)	−0.0269 (13)	6.4 (5)
C(15)	0.3266 (10)	0.9890 (28)	−0.0814 (15)	7.7 (6)
C(16)	0.2817 (11)	1.0843 (30)	−0.1377 (15)	7.5 (6)
C(17)	0.2514 (10)	1.0926 (30)	−0.1402 (14)	7.3 (6)
C(18)	0.2670 (9)	1.0158 (26)	−0.0842 (13)	6.3 (6)
C(19)	0.3661 (9)	0.5947 (23)	0.0659 (12)	5.2 (5)
C(110)	0.3321 (10)	0.4871 (28)	0.0106 (14)	7.3 (6)
C(111)	0.3577 (12)	0.3586 (33)	0.0238 (17)	8.8 (7)
C(112)	0.4130 (11)	0.3504 (31)	0.0932 (16)	8.1 (6)
C(113)	0.4444 (11)	0.4613 (32)	0.1427 (16)	8.1 (7)
C(114)	0.4220 (10)	0.5852 (28)	0.1340 (14)	7.1 (6)
C(115)	0.4023 (8)	0.8860 (23)	0.1684 (12)	4.8 (4)
C(116)	0.4338 (11)	0.8140 (28)	0.2359 (16)	7.2 (6)
C(117)	0.4811 (12)	0.8762 (34)	0.3126 (17)	8.8 (7)
C(118)	0.4949 (12)	1.0165 (34)	0.3189 (18)	8.9 (7)
C(119)	0.4644 (14)	1.0912 (38)	0.2529 (21)	10.1 (0.9)
C(120)	0.4149 (12)	1.0213 (32)	0.1723 (16)	8.6 (7)
C(21)	0.0318 (8)	0.3443 (24)	0.0718 (12)	5.0 (5)
O(21)	0.0509 (7)	0.2507 (19)	0.1150 (10)	7.7 (4)
C(22)	−0.0318 (9)	0.5661 (25)	0.0098 (13)	5.9 (5)
O(22)	−0.0513 (7)	0.6054 (18)	0.0151 (9)	7.2 (4)
C(23)	0.0922 (8)	0.7615 (21)	0.1915 (11)	4.2 (4)
C(24)	0.1346 (9)	0.7231 (25)	0.2740 (14)	6.3 (5)
C(25)	0.1370 (12)	0.7941 (33)	0.3159 (17)	8.8 (7)
C(26)	0.0986 (12)	0.8950 (32)	0.2783 (17)	8.5 (7)
C(27)	0.0573 (10)	0.9355 (29)	0.1977 (15)	7.6 (6)
C(28)	0.0533 (9)	0.8669 (26)	0.1527 (13)	6.2 (5)
C(29)	0.1625 (7)	0.5500 (20)	0.2093 (10)	3.9 (4)
C(210)	0.1995 (9)	0.5962 (25)	0.2265 (13)	6.0 (5)
C(211)	0.2488 (10)	0.5167 (27)	0.2826 (14)	6.7 (5)
C(212)	0.2581 (10)	0.3937 (28)	0.3149 (15)	6.6 (5)
C(213)	0.2222 (11)	0.3389 (29)	0.2979 (14)	7.4 (6)
C(214)	0.1730 (10)	0.4247 (27)	0.2444 (13)	6.7 (5)
C(215)	0.0938 (8)	0.8406 (21)	0.0893 (11)	4.5 (4)
C(216)	0.0850 (8)	0.8181 (23)	0.0347 (12)	5.2 (5)
C(217)	0.0909 (8)	0.9345 (25)	0.0124 (12)	5.8 (5)
C(218)	0.1055 (9)	1.0659 (26)	0.0461 (13)	6.1 (5)
C(219)	0.1154 (9)	1.0908 (26)	0.1003 (13)	6.3 (5)
C(220)	0.1108 (9)	0.9776 (26)	0.1239 (14)	6.4 (5)

ᵃ Fractional coordinates; numbers in parentheses are standard deviations.   ᵇ See anisotropic temperature factors in Table IV.   ᶜ Fixed by symmetry.

Table IV. Anisotropic Temperature Factors (×10⁴) for (Ph₃Sn)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

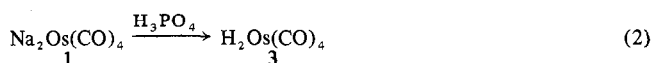**Figure 1.** The molecular structure of *trans*-(Ph₃Sn)₂Os(CO)₄.

THF using 2,2′-bipyridyl as an electron carrier. We obtained only low yields of products using **1** generated by this method. The preparation of solvent-free **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). We feel this is more

$$\text{Na}_2\text{Os(CO)}_4 \xrightarrow{\text{H}_3\text{PO}_4} \text{H}_2\text{Os(CO)}_4 \qquad (2)$$
$$\phantom{\text{Na}_2\text{Os(CO)}_4}\,\mathbf{1} \phantom{\xrightarrow{\text{H}_3\text{PO}_4}} \mathbf{3}$$

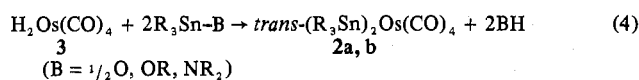convenient than the literature synthesis utilizing high pressures of H₂ and CO on OsO₄.

The dihydride **3** proved to be a convenient starting material for many osmium–tin complexes. The dihydride **3** (p$K_a \approx$ 5–6) was used to generate an osmium anion by treatment with an amine (diethylamine and pyridine were used). The dihydride **3** gave the bis(tin) complex **2a** on treatment with triphenyltin chloride in the presence of an amine (eq 3). No

$$\text{H}_2\text{Os(CO)}_4 \xrightarrow{\text{:B}} [(\text{BH})^+(\text{HOs(CO)}_4)^-] \xrightarrow{\text{Ph}_3\text{SnCl}} \qquad (3)$$
$$\mathbf{3}$$
$$\text{\textit{trans}-(Ph}_3\text{Sn)}_2\text{Os(CO)}_4$$
$$\mathbf{2a}$$
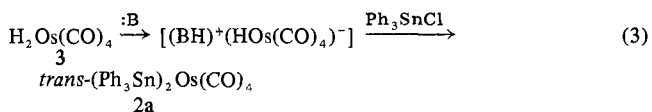
reaction occurred in the absence of added base. This type of anion generation from hydrides has been reported by Graham[16] and promises to be of utility in many reactions. Anions made from sodium or sodium mercury amalgam are generally not pure and their titer is difficult to assay, especially for small-scale reactions. The hydride, by contrast, may be purified and weighed so that stoichiometry may be easier to control, especially in small-scale reactions.
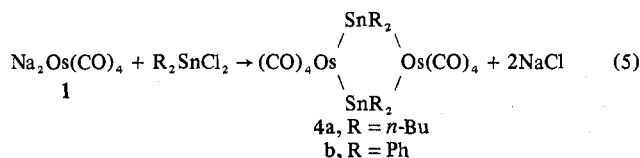
In other reactions of the dihydride **3**, the base may be bond-

(16) W. Jetz and W. A. G. Graham, *Inorg. Chem.*, **10**, 1647 (1971).

ed directly to the organotin moiety. Tin oxides, alkoxides, and amides gave tin–osmium complexes with elimination of the corresponding water, alcohol, or amine (eq 4). All the
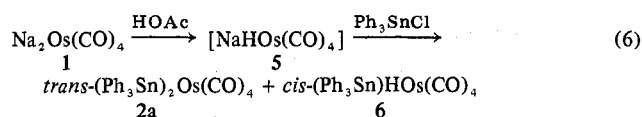
$$H_2Os(CO)_4 + 2R_3Sn-B \rightarrow trans\text{-}(R_3Sn)_2Os(CO)_4 + 2BH \quad (4)$$
$$\underset{\mathbf{3}}{} \qquad \underset{\mathbf{2a, b}}{\phantom{trans\text{-}(R_3Sn)_2Os(CO)_4}}$$
$$(B = \frac{1}{2}O, OR, NR_2)$$

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 **1** (eq 5). Analogous compounds of iron[17] and ruthe-

$$Na_2Os(CO)_4 + R_2SnCl_2 \rightarrow (CO)_4Os\begin{array}{c}SnR_2\\ \diagup \quad \diagdown\\ \quad \\ \diagdown \quad \diagup\\ SnR_2\end{array}Os(CO)_4 + 2NaCl \quad (5)$$
$$\underset{\mathbf{1}}{}$$
$$\mathbf{4a}, R = n\text{-Bu}$$
$$\mathbf{b}, R = Ph$$

nium[18] were known. This reaction conceivably could have given a polymer with alternating osmium and tin atoms in its backbone. This points to the necessity of achieving a rigid trans arrangement of tins before attempting polymerization.
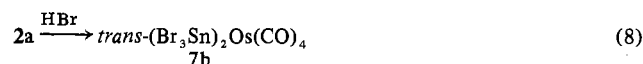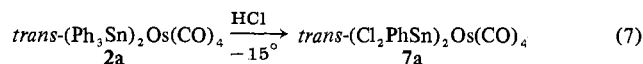
Attempts to prepare compounds with two different organotin moieties on the same osmium by sequential addition of organotin chlorides to **1** failed. The two symmetrically substituted products were formed, probably because of the insolubility of **1** in THF. Addition of 1 equiv of acetic acid rendered **1** soluble, presumably as the hydrido complex **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). The Os–H vibration was not detect-

$$Na_2Os(CO)_4 \xrightarrow{HOAc} [NaHOs(CO)_4] \xrightarrow{Ph_3SnCl} \quad (6)$$
$$\underset{\mathbf{1}}{} \qquad \underset{\mathbf{5}}{}$$
$$\underset{\mathbf{2a}}{trans\text{-}(Ph_3Sn)_2Os(CO)_4} + \underset{\mathbf{6}}{cis\text{-}(Ph_3Sn)HOs(CO)_4}$$

ed in the ir spectrum, but a strong peak assigned to this mode was observed in the Raman spectrum at 1946 cm^{-1}.

Obtaining functionalized bis(tin) derivatives held in trans positions on osmium was our next goal. Treatment of **1** with an excess of a diorganotin dichloride gave a mixture of products inseparable in our hands. These osmium–tin bonds proved to be quite stable toward 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 in eq 7–9. All of these reactions were clean and gave high
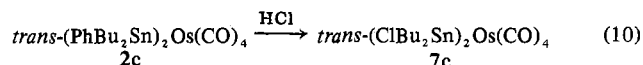
$$\underset{\mathbf{2a}}{trans\text{-}(Ph_3Sn)_2Os(CO)_4} \xrightarrow[-15°]{HCl} \underset{\mathbf{7a}}{trans\text{-}(Cl_2PhSn)_2Os(CO)_4} \quad (7)$$

$$\mathbf{2a} \xrightarrow{HBr} \underset{\mathbf{7b}}{trans\text{-}(Br_3Sn)_2Os(CO)_4} \quad (8)$$

$$\mathbf{2a} \xrightarrow{Cl_2} \underset{\mathbf{8}}{trans\text{-}Cl_2Os(CO)_4} \quad (9)$$

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.[19] Cleavage of *trans*-(Me$_3$Si)$_2$Os(CO)$_4$ with hydrogen chloride has also been reported to give 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). The

$$\underset{\mathbf{2c}}{trans\text{-}(PhBu_2Sn)_2Os(CO)_4} \xrightarrow{HCl} \underset{\mathbf{7c}}{trans\text{-}(ClBu_2Sn)_2Os(CO)_4} \quad (10)$$

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

We then attempted to elaborate the preformed, collinear **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). The

$$HRe(CO)_5 + \underset{\mathbf{7c}}{trans\text{-}(ClBu_2Sn)_2Os(CO)_4} \xrightarrow{Et_2NH} \quad (11)$$
$$\underset{\mathbf{10}}{((CO)_5Re-SnBu_2)_2Os(CO)_4}$$

oligomer **10** is a viscous liquid at room temperature and was characterized by elemental analyses and a molecular weight measurement. Only a few pentametallic chains involving transition metals have been reported.[16,20] 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). This result

$$H_2Os(CO)_4 + \underset{\mathbf{7c}}{trans\text{-}(ClBu_2Sn)_2Os(CO)_4} \xrightarrow{Et_2NH} \quad (12)$$
$$\underset{\mathbf{3}}{}$$

$$(CO)_4Os\begin{array}{c}SnBu_2\\ \diagup \quad \diagdown\\ \quad \\ \diagdown \quad \diagup\\ SnBu_2\end{array}Os(CO)_4$$
$$\mathbf{4a}$$

was unexpected since it involves an isomerization of the tin atoms from trans to cis positions. One possible pathway to this result is displacement of the osmium–tin complex **9** which might be expected to react with another identical complex **9** to give the observed product (Scheme I). Other an-

Scheme I

$$HOs(CO)_4^- \overset{\frown}{} ClBu_2Sn \overset{\frown}{} Os(CO)_4-SnBu_2Cl \rightarrow$$
$$\underset{\mathbf{7c}}{}$$

$$2[HOs(CO)_4SnBu_2Cl] \xrightarrow{Et_2NH} (CO)_4Os\begin{array}{c}SnBu_2\\ \diagup \quad \diagdown\\ \quad \\ \diagdown \quad \diagup\\ SnBu_2\end{array}Os(CO)_4 + Et_2NH_2Cl$$
$$\underset{\mathbf{9}}{} \qquad \underset{\mathbf{4a}}{}$$

ions (*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 *cis*-(Ph$_3$Sn)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.

(17) J. D. Cotton, S. A. R. Knox, I. Paul, and F. G. A. Stone, *J. Chem. Soc. A*, 264 (1967).

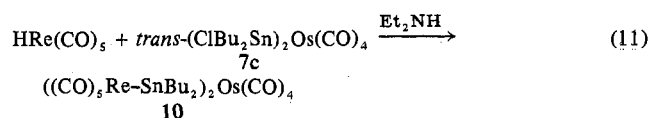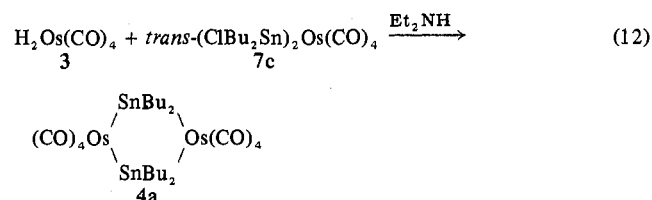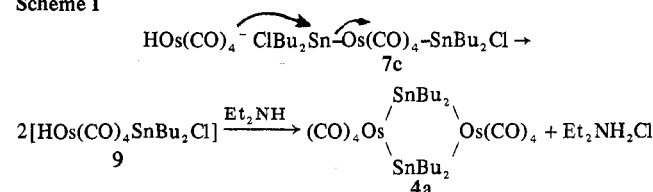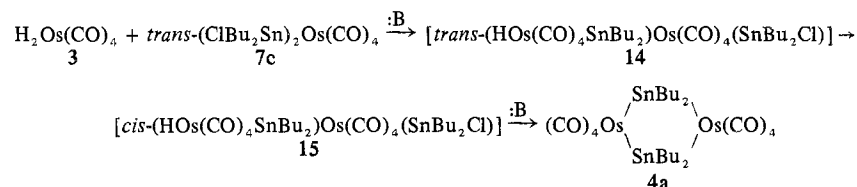(18) S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 2559 (1969).

(19) W. Hieber and H. Stallman, *Chem. Ber.*, 75, 1472 (1942).

(20) J. P. Collman, J. K. Hoyano, and D. W. Murphy, *J. Amer. Chem. Soc.*, 95, 3424 (1973).

Scheme II

$$H_2Os(CO)_4 + \textit{trans-}(ClBu_2Sn)_2Os(CO)_4 \xrightarrow{:B} [\textit{trans-}(HOs(CO)_4SnBu_2)Os(CO)_4(SnBu_2Cl)] \rightarrow$$

$$\underset{\textbf{3}}{} \qquad \underset{\textbf{7c}}{} \qquad \underset{\textbf{14}}{}$$

$$[\textit{cis-}(HOs(CO)_4SnBu_2)Os(CO)_4(SnBu_2Cl)] \xrightarrow{:B} (CO)_4Os \overset{SnBu_2}{\underset{SnBu_2}{\diagup \diagdown}} Os(CO)_4$$

$$\underset{\textbf{15}}{} \qquad \underset{\textbf{4a}}{}$$

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.[21] Graham[22] has recently found, however, that $(Me_3Sn)_2$-$Os(CO)_4$ 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 II). Such nonrigidity of metal–metal bonded carbonyl complexes may not be limited to group IVa derivatives. The reaction of $Os_3(CO)_{12}$ with chlorine[23] 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 metalloacyl $(M'C(=O)M$-$(CO)_3M')$ species. Such intermediates have been postulated to account for nondissociative ligand exchange in Re_2-$(CO)_{10}$[24] and equivalence of all carbonyls (by ^{13}C nmr) in dodecacarbonyl tetrarhodium.[25] Regardless of the mechanism of this isomerization, the lack of stereochemical integrity in these systems seems to rule out the synthesis of linear polymers using these tin–osmium complexes since there is apparently a kinetically accessible pathway to small cyclic

metal clusters which appear to be the thermodynamically favored products. Because of our suppositions that this stereochemical rearrangement involves migratory insertion we have focused our attention on more rigid intermetallic trimers[26] which do not seem to have a possible migratory insertion mechanism.

Registry No. Na, 7440-23-5; $Os_3(CO)_{12}$, 15696-40-9; Na_2Os-$(CO)_4$, 27857-55-2; Ph_3SnCl, 639-58-7; *trans-*$(Ph_3Sn)_2Os(CO)_4$, 41553-07-5; Bu_3SnCl, 1461-22-9; *trans-*$(Bu_3Sn)_2Os(CO)_4$, 42230-33-1; H_3PO_4, 7664-38-2; $H_2Os(CO)_4$, 22372-70-9; Bu_2SnCl_2, 683-18-1; $[(CO)_4OsSnBu_2]_2$, 42230-35-3; Ph_2SnO, 2273-51-0; $[(CO)_4OsSn$-$Ph_2]_2$, 42230-36-4; $Ph_3SnN(Ph)C(O)H$, 42246-20-8; $Ph_3SnOSnPh_3$, 1262-21-1; $Bu_2Sn(OMe)_2$, 1067-55-6; *cis-*$(Ph_3Sn)Os(CO)_4H$, 42230-48-8; HCl, 7647-01-0; *trans-*$(PhCl_2Sn)_2Os(CO)_4$, 42230-37-5; HBr, 10035-10-6; *trans-*$(Br_3Sn)_2Os(CO)_4$, 42230-38-6; Cl_2, 7782-50-5; *trans-*$Cl_2Os(CO)_4$, 42230-39-7; $PhBu_2SnBr$, 2322-57-8; *trans-*$(Ph$-$Bu_2Sn)_2Os(CO)_4$, 42230-40-0; *trans-*$(Bu_2ClSn)_2Os(CO)_4$, 42230-41-1; $HRe(CO)_5$, 16457-30-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1.

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(23) B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc. A*, 2859 (1968).

(24) L. J. B. Haines and A. J. Poe, *J. Chem. Soc. A*, 2826 (1969).

(25) F. A. Cotton, L. Krucynski, B. L. Shapiro, and L. F. Johnson, *J. Amer. Chem. Soc.*, **94**, 6191 (1972).

(26) (a) J. P. Collman, D. W. Murphy, and G. Dolcetti, *J. Amer. Chem. Soc.*, **95**, 2687 (1973). (b) During the submission of this manuscript a paper has appeared describing some of the same tin–osmium-tin systems: R. G. George, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 972 (1973).