Reduction of bis(triorganotin) oxides by metals: an easy route to hexaorganoditins

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2.115 and 2.144 Å. The two sets of trans Os–C bonds are of approximately equal angles (144.2° and 144.8°). The N–Os distance in 1, 1.631 Å is longer than that of the tetrachloro complex, 1.604 Å, and even longer than that of $[Os(N)Cl_5]K_2$, 1.614 Å.[15] This is consistent with changes in the IR spectrum. The nitrogen–osmium stretching vibration is at lower energy in the alkyl complex than in $[Os(N)Cl_4]^-$, decreasing to 1100 from 1123 cm^{-1}.

In $Os(NMe)(CH_2SiMe_3)_4$, the osmium–nitrogen distance is 1.686 Å. In general, an alkylimido metal–nitrogen bond is 0.05 Å longer than that in the corresponding nitride complex.[6] As seen in Figure 2, the Os–N–C bond is bent to 164°. It is also interesting to note the large variation in the Os–C distances. The two longer Os–C distances are trans to each other at an angle of 151.2°, while the two shorter Os–C bonds are at an angle of 128°.

The alkyl complexes $[Os(N)R_4][N\text{-}n\text{-}Bu_4]$, where R = Me or $CH_2C_6H_5$, react cleanly with $[Me_3O][BF_4]$ to form methylimido complexes $[Os(NMe)R_4]$. $[Os(N)(CH_2SiMe_3)_4]^-$ reacts with $[Et_3O][BF_4]$ or $EtOSO_2CF_3$ to form $[Os(NEt)(CH_2SiMe_3)_4]$, and with $Me_3SiOSO_2CF_3$ to form $[Os(NSiMe_3)(CH_2SiMe_3)_4]$.[16]

We have found that the osmium(VI) anions, $[Os(N)R_4]^-$ react with a variety of electrophiles.[17] There are three possible sites for electrophilic attack in these complexes: at the open coordination site on the d^2 osmium center, at the nitride, or at an Os–C bond. Although the the reaction of 1 with $[Me_3O][BF_4]$ ultimately gives a product which has been alkylated at the nitride preliminary low-temperature studies indicate the presence of an intermediate. We are currently investigating the mechanism of the methylation reaction and the identity of this intermediate.

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Registry No. 1, 92544-03-1; 2, 101810-25-7; $[Os(N)Me_4][N\text{-}n\text{-}Bu_4]$, 92544-09-7; $[Os(N)(CH_2C_6H_5)_4][N\text{-}n\text{-}Bu_4]$, 92544-05-3; $Os(NMe)Me_4$, 101810-26-8; $Os(NMe)(CH_2C_6H_5)_4$, 101810-27-9; $Os(NEt)(CH_2SiMe_3)_4$, 101810-28-0; $Os(NSiMe_3)(CH_2SiMe_3)_4$, 101810-29-1; $[Os(N)(CH_2SiMe_3)_4]^-$, 92544-02-0; $EtOSO_2CF_3$, 425-75-2; $Me_3SiOSO_2CF_3$, 27607-77-8.

Supplementary Material Available: Tables of analytical data for new compounds and crystal data, fraction coordinates, anisotropic thermal parameters, bond distances and angles, listings of F_o and F_c for 1 and 2 (54 pages). Ordering information is given an any current masthead page.

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(16) $Os(NMe)Me_4$: ^1H NMR (200 MHz, 298 K, C_6D_6) δ 2.95 (s, 4 H, OsMe), 0.27 (s, 1 H, NMe); IR (KBr pellet) 1261 cm^{-1} (MeNOs). Anal. $(OsNC_5H_{15})$ C, H, N. $Os(NMe)(CH_2Ph)_4$: ^1H NMR (200 MHz, 298 K, C_6D_6) δ 7.2 (m, 20 H, Ph), 5.19 (s, 8 H, $OsCH_2$), 0.93 (s, 3 H, NMe); ^{13}C NMR (50 MHz, 298 K, C_6H_6) δ 130.13 (CH), 128.0 (CH), 124.9 (CH), 54.9 (CH_3), 49.9 (CH_2), the DEPT NMR pulse sequence was used to assign methyl, methylene, and methyne carbons and to suppress resonances from solvent; IR (KBr pellet) 1211 cm^{-1} (MeNOs). Anal. $(OsNC_{29}H_{31})$ C, H, N. $Os(NSiMe_3)(CH_2SiMe_3)_4$: ^1H NMR (200 MHz, 295 K, C_6D_6) δ 3.32 (s, CH_2), 0.27 (s, CH_2SiMe_3), 0.10 (s, $NSiMe_3$); IR (KBr pellet) 1248 cm^{-1} (Me_3SiNOs). Anal. $(OsNSi_5C_{19}H_{53})$ C, H. N. $Os(NEt)(CH_2SiMe_3)_4$: ^1H NMR (200 MHz, C_6D_6, 298 K) δ 0.204 (s, 36 H, Me_3Si), 0.827 (t, 3 H, CH_3CH_2), 2.152 (q, 2 H, CH_3CH_2), 3.47 (s, 8 H, CH_2Si). Anal. $(OsNSi_4C_{18}H_{49})$ C, H, N.

(17) (Belmonte) Shapley, P. A.; Own, Z.-Y.; Huffman, J. C.; manuscript in preparation.

(18) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Reduction of Bis(triorganotin) Oxides by Metals: An Easy Route to Hexaorganoditins

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Summary: Bis(triorganotin) oxides have been reduced in high yield to hexaorganoditins by titanium, magnesium, potassium, and sodium.

Hexaorganoditins are finding increasing applications in reduction reactions,[1] as organic radical sources[2] or as precursors of tin–metal derivatives.[3] They also show interesting bactericidal and fungicidal activity.[4] They are usually prepared by reactions between organotin halides with metals, tin hydrides with tin oxides, alkoxides or amines,[5] and tin oxides with formic acid[6] or electrolytically.[7] But, with the exception of the method we developed with formic acid, there is no synthetic route for producing hexaorganoditins directly from tin oxides.

Low-valent titanium species have been extensively used as reducing agents in organic chemistry.[8] Although dialkyl ethers are usually not cleaved by these reagents, low-valent titanium species are not unreactive with compounds containing a carbon–oxygen single bond: for instance, epoxides[9] and *vic*-diols[10] are easily reduced to give alkenes. Therefore, we postulated that hexaorganotin oxides, which are more labile than ethers,[5] could be reduced to form ditins.

We report here a new way of preparing hexaorganoditin from bis(triorganotin) oxides, $(R_3Sn)_2O$, and metals. When bis(tri-*n*-butyltin) oxide is allowed to react with a freshly prepared titanium slurry,[11] hexa-*n*-butylditin is obtained in satisfactory yield after a smooth reduction of the oxide (eq 1) (Table I).

$$Bu_6Sn_2O \xrightarrow{\text{Ti(0), THF, room temp}} Bu_6Sn_2 \qquad (1)$$

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Table I. Reduction of Organotin Oxides into Ditins

reducing agent	solv	ditin	yield,[a,b] %
$TiCl_3$, K	THF	n-Bu_6Sn_2	70
K	THF	n-Bu_6Sn_2	62
K	toluene	n-Bu_6Sn_2	71
K	none	n-Bu_6Sn_2	60
Na	none	n-Bu_6Sn_2	71
Na	none	i-Bu_6Sn_2	62
Na	none	n-Pen_6Sn_2	77
Na	none	n-Oct_6Sn_2	68
Mg	THF	n-Bu_6Sn_2	81
Mg	none	n-Bu_6Sn_2	58
Mg	THF	i-Bu_6Sn_2	82
Mg	THF	n-Oct_6Sn_2	82

[a] Pure isolated products. [b] Reaction mixtures and ditins were analyzed by reversed-phase HPLC and ^{119}Sn NMR spectroscopy.[6]

Since titanium powder was prepared from titanium trichloride and potassium in THF, we checked if potentially unreacted potassium could have any influence on the course of the reaction. If the reduction is performed directly with a stoichiometric amount of potassium (2 mol for 1 mol of bis(tri-n-butyltin) oxide), it works nearly as well (see Table I), although the cleavage of ditins with metals to give tin–metal derivatives is known.[3] This unobserved cleavage is probably the result of the higher reactivity of the oxide toward potassium. The results with sodium were equally good (see Table I). Finally, we found that the reaction could be carried out in the absence of solvent (eq 2) (see Table I).

$$R_6Sn_2O + 2Na \xrightarrow{120\ °C,\ 48\ h} R_6Sn_2 + Na_2O \qquad (2)$$

Byproducts, mainly tetraalkyltin (1–5%) and unconverted $(R_3Sn)_2O$ (5–15%), are present in small amounts and can be removed easily: $(R_3Sn)_2O$ by filtration of the mixture (10 g diluted in 200 mL of pentane) through a short SiO_2 column (100 g, 230–400 mesh) and R_4Sn by distillation. With bis(triphenyltin) oxide, ^{119}Sn NMR analysis of the crude mixture showed that tetraphenyltin is the main product of the reaction, hexaphenylditin being formed in 20% yield.

The reduction with magnesium has also been studied: bis(trialkyltin) oxides react cleanly with magnesium powder which has been activated by 1,2-dibromoethane or iodine, in the presence of a small amount of THF (eq 3). In this case no tetraalkyltin is formed, the only possibly present byproduct being some unreacted $(R_3Sn)_2O$.

$$R_6Sn_2O + Mg \xrightarrow{THF} R_6Sn_2 + MgO \qquad (3)$$

Ditins are obtained as pure materials after distillation. For instance, for R = n-Bu, this reaction gives a better yield than the coupling of tri-n-butyltin chloride by magnesium.[12] The reaction occurs also in the absence of solvent, but the yield is lower. No reaction was observed with iron powder, and with aluminium, large amounts of tetraalkyltin, together with hexaalkylditins, are recovered.

In conclusion, we have shown that bis(triorganotin) oxides (often easily available from industrial sources) react readily with metals. This reduction provides a convenient new route to ditins. In particular, the preparation of hexa-n-butylditin from bis(tri-n-butyltin) oxide and magnesium is an especially attractive method on the laboratory scale.

Experimental Procedure. A solution of bis(tri-n-butyltin) oxide (59.6 g, 100 mmol) in 60 mL of dry THF was added dropwise to a suspension of magnesium powder (98%, 70 mesh) (3.6 g, 150 mmol), activated by a few drops of 1,2-dibromoethane (or a crystal of iodine) in 20 mL of dry THF. The mixture was heated at reflux for 15 h. At this time the characteristic Sn–O–Sn IR absorption at 755 cm^{-1} has disappeared. An ^{119}Sn NMR spectrum of the crude hexa-n-butylditin showed only one signal at −83.2 ppm (C_6D_6, Me_4Sn as external standard). Then, after addition of 200 mL of petroleum ether, filtration, and evaporation of the solvents, the product was recovered by distillation: yield 47 g (81%); bp 145 °C (0.05 torr) (i-Bu_6Sn_2, bp 136–138 °C (0.05 torr); n-Oct_6Sn_2, bp 180–185° (0.01 torr)).

Registry No. n-Bu_6Sn_2, 813-19-4; i-Bu_6Sn_2, 3750-18-3; n-Pen_6Sn_2, 21227-23-6; n-Oct_6Sn_2, 21227-24-7; n-Bu_6Sn_2O, 56-35-9; i-Bu_6Sn_2O, 6208-26-0; n-Pen_6Sn_2O, 25637-27-8; n-Oct_6Sn_2O, 2787-93-1.

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Facile Activation of Hydrogen by an Unsaturated Metal Carbonyl Cluster. The Addition of H_2 to $Os_4(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}HC_2CO_2Me)$

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Summary: The unsaturated cluster $Os_4(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}HC_2CO_2Me)$ (**1**) has been synthesized and structurally characterized. Compound **1** readily adds hydrogen to form two isomeric hydride containing clusters of formula $Os_4(CO)_{11}(\mu_3\text{-}S)(\mu\text{-}HC_2CO_2Me)(\mu\text{-}H)_2$ (**2a** and **2b**). These will subsequently add CO to form $Os_4(CO)_{12}(\mu_3\text{-}S)(\mu_3\text{-}HC_2CO_2Me)(\mu\text{-}H)_2$ (**3**). Compounds **1**, **2b**, and **3** have been characterized structurally.

The inability of metal carbonyl cluster complexes to add and activate hydrogen under mild conditions has been a major impediment in the development of these compounds as hydrogenation catalysts.[1,2] Unsaturated clusters would seem to offer a potential solution to the problem, but the number of fully characterized unsaturated clusters is very small.[2] An important class of unsaturated clusters are the polyphosphine complexes of rhodium and platinum.[3,4] These compounds activate hydrogen very readily and even serve as hydrogenation catalysts.[3,5] We wish to report that we have synthesized the new unsaturated *carbonyl* cluster $Os_4(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}HC_2CO_2Me)$ (1) and have found that it activates hydrogen, reversibly, under unusually mild conditions.

When the compound $Os_4(CO)_{12}[\mu_4\text{-}SC(CO_2Me)CH]$[6] is refluxed in octane solvent for 40 min, it loses 1 mol of CO and is transformed into the new cluster $Os_4(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}HC_2CO_2Me)$ (1) in 88% yield.[7] The molecular structure of 1 was determined by a single-crystal X-ray diffraction analysis, and an Ortep diagram of the molecule

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