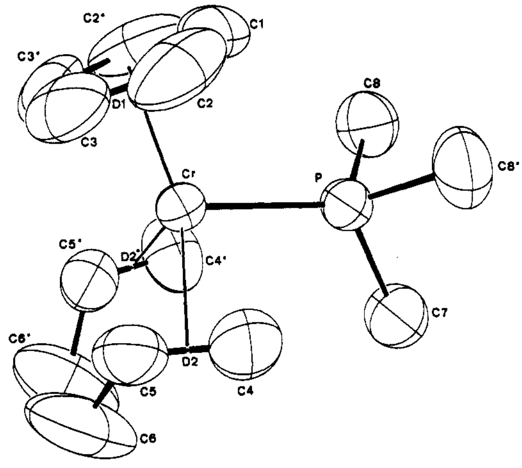


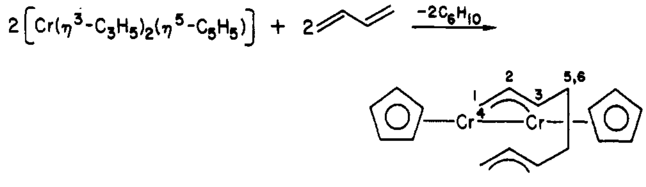
Figure 2. The molecular structure of $[Cr(PMe_3)(\eta^2,\ \eta^2\text{-}1,5\text{-}C_6H_{10})(\eta^5\text{-}C_5H_5)]$ (3).

organic ligands are ca. 0.1 Å closer to the metal in the case of the chromium complex, and the meso H atoms (C7–H, C10–H) are separated by only 2.05 Å (2.17 Å for Mo). The $\eta^5\text{-}C_5H_5$ ring is essentially symmetrical whereas in the case of the Mo complex the Cp C–C bond distances vary between 1.410 (4) and 1.373 (5) Å.

2 reacts readily with inorganic and organic nucleophiles. A number of donor ligands induce reductive coupling of the allyl groups to give dark green, paramagnetic, η^2, η^2-1,5-hexadiene chromium complexes (**3**) in high yield.[10] The crystal structure of the PMe_3 adduct has been established by X-ray diffraction (Figure 2).

$$[Cr(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)] + L \xrightarrow[-10\ ^\circ C]{\text{pentane}} \underset{\mathbf{3}\ (L = CO,\ P(OMe)_3,\ PMe_3)}{[Cr(L)(\eta^2,\ \eta^2\text{-}1,5\text{-}C_6H_{10})(\eta^5\text{-}C_5H_5)]}$$

Unsaturated organic compounds displace the allyl groups to give mono- and binuclear chromium complexes. For example, the product of the reaction with butadiene is a yellow, diamagnetic binuclear complex, $[\{Cr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}\eta^3,\ \eta^3\text{-}C_8H_{12})]$ (**4**), whose ^1H NMR spectrum indicates that an octadienediyl moiety bridges the metal atoms.[11] Alkynes react to give both mononuclear, e.g., $[Cr(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$, and binuclear, e.g., $[\{(Cr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}C_6Et_6)]$, species which are presumably related to the η^5-pentamethylcyclopentadienyl chromium complexes reported by Wilke et al.[12] Details will be reported later.



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Acknowledgment. C.C.R. thanks the Alexander von Humboldt Stiftung for the award of a stipend (1983–1984).

Registry No. 1, 90636-08-1; 2, 89922-80-5; 3 (L = PMe_3), 101860-22-4; 3 (L = $P(OMe)_3$), 101860-23-5; 3 (L = CO), 101860-24-6; 4, 101860-25-7; $CrCl_2(\eta^5\text{-}C_5H_5)$, 54235-50-6; $Cr(\eta^5\text{-}C_5H_5)_2$, 1271-24-5; butadiene, 106-99-0; allylmagnesium chloride, 2622-05-1.

Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal papameters, atomic coordinates, interatomic distances, and bond angles (31 pages). Ordering information is given on any current masthead page.

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[10] 3, L = PMe_3: yield 95%. Anal. Found (Calcd): Cr, 18.75 (18.99); P, 11.29 (11.25); c, 60.95 (61.08); H, 9.04 (8.79). MS: *m/e* 275 (M^+). Paramagnetic: 1.9 μ_B. X-ray diffraction data for $C_{14}H_{24}CrP$ (3, L = PMe_3): dark green; crystal size (mm) 0.36 × 0.72 × 0.36, crystal system orthorhombic; space group *Pnma* (no. 62); a = 13.937 (2) Å, b = 11.540 (2) Å, c = 9.136 (2) Å; V = 1469.4 Å^3; Z = 4; d_{calcd} = 1.24 g/cm^3; $\mu(\text{MoK}\alpha)$ = 8.4 cm^{-1}; no absorption correction; $F(000)$ = 588; Enraf-Nonius CAD-4 diffractometer; graphite-monochromated Mo radiation (λ = 0.71069 Å); Zr filter; scan mode = θ–2θ; T = 293 K, θ range = 1.5–30.8° measured reflections 4182 ($\pm h,\pm k,\pm l$); unique reflections 2416, observed reflections 1558 ($I \geqslant 2\sigma(I)$); structure solved by heavy-atom method; hydrogen atom positions calculated; number of variables 79; R = 0.055, R_w = 0.076 ($w = 1/\sigma^2(F_o)$); EOF = 3.6; residual electron density = 0.57 e Å^{-3}. Cl, Cr, and $P_{(\text{average})}$ located on a mirror plane. Some distances (C6,C6* (1.277 (9) Å) and Cp–ring distances) are artificially shortened by thermal motion (or disorder in $Pn2_1a$): Cr–P = 2.316 (2), C4–C5 = 1.370 (7), C5–C6 = 1.470 (7), C6-C6* = 1.277 (9), Cr–D1 = 1.900 (8), Cr–D2 = 2.047 (9) Å; P–Cr–D1 = 113.5 (2), P–Cr–D2 = 97.1 (2), D2–Cr–D2* = 99.5 (2), C4–C5–C6 = 122.3 (5)°. 3, L = $P(OMe)_3$: dark green (90% yield). Anal. Found (Calcd): Cr, 16.03 (16.08); P, 9.54 (9.58). MS: *m/e* 323 (M^+). Paramagnetic: 1.9–2.0 μ_B. Structure confirmed by X-ray diffraction study (disorder prevented refinement). 3, L = CO: dark green (85% yield). Anal. Found (Calcd): Cr, 22.82 (22.88); C, 65.10 (63.42); H, 7.13 (6.65). MS: *m/e* 227 (M^+). Paramagnetic: 1.61–1.58 μ_B. IR (KBr): ν(CO) 1870 vs, 1830 sh cm^{-1}.

[11] Anal. Found (Calcd); Cr, 30.24 (30.37); C, 63.16 (63.15); H, 6.47 (6.48). MS: *m/e* 342 (M^+). Diamagnetic. ^1H NMR (THF-d_8, −80 °C): δ 5.31, 5.25 (s, C_5H_5), 3.83 (H_1), 2.44 (H_2), 3.04 (H_3), 2.17 (H_4), 2.49 (H_5), 2.01 (H_6) (provisional assignment, all signals broad). ^{13}C NMR (toluene-d_8, −80 °C): δ 56.08 (C-1, J(CH) = 156 Hz), 72.96/75.79 (C-2/3, J(CH) = 150/156 Hz), 32.05 (C-4, J(CH) = 125 Hz), 98.30 (C_5H_5, J(CH) = 171 Hz).

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Alkylation of Osmium(VI) Nitrido Complexes: Reaction of $[Os(N)R_4][N\text{-}n\text{-}Bu_4]$ with $[Me_3O][BF_4]$ and the X-ray Crystal Structures of $[Os(N)(CH_2SiMe_3)_4][N\text{-}n\text{-}Bu_4]$ and $[Os(NMe)(CH_2SiMe_3)_4]$

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Received January 8, 1986

Summary: The nitridoosmium(VI) anion $[Os(N)(CH_2SiMe_3)_4][N\text{-}n\text{-}Bu_4]$ can be methylated by Me_3OBF_4, $MeOSO_2CF_3$, or MeI to give $Os(NMe)(CH_2SiMe_3)_4$ in high yield. The structures of both $[Os(N)(CH_2SiMe_3)_4][N\text{-}n\text{-}Bu_4]$ and $Os(NMe)(CH_2SiMe_3)_4$ were determined by X-ray diffraction. The alkyl complexes $[Os(N)R_4][N\text{-}n\text{-}Bu_4]$, where R = Me or $CH_2C_6H_5$, also react 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 $[Os(NSiMe_3)(CH_2SiMe_3)_4]$.

Reactions of unsaturated nitrogen ligands bound to transition metals are of interest as models for steps in the ammoxidation of olefins[1] and the reduction of dinitrogen.[2]

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[1] Chang, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420–3426. Grasselli, R. K.; Burrington, J. D.; Brazdil, J. F. *Faraday Dis.* **1981**, *72*, 203–223. Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073–2074.

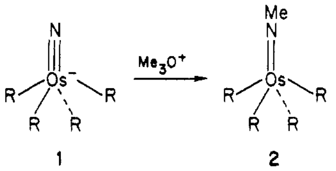
[2] Chatt, J.; Leigh, G. H. *Chem. Soc. Rev.* **1972**, *1*, 121–144. Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625.

0276-7333/86/2305-1269$01.50/0

A key step in the ammoxidation reaction, alkylation of an unsaturated nitrogen ligand on the metal, has been proposed to proceed by a radical mechanism on heterogeneous catalysts and by migration of an alkyl to an imide ligand in a soluble catalyst.[1,3]

The metal nitride unit, particularly for the group VIII (8–10[18]) metals, is quite chemically unreactive. For osmium complexes, oxo groups are more readily attacked than nitrides.[4] The nitrido ligands in transition-metal nitrido complexes are seldom nucleophilic enough to react with electrophiles.[5] There are exceptions to this. The nitrogen atom in the electron-rich molybdenum nitrido complex $Mo(N)(S_2CNR_2)_3$ can be protonated by acids or alkylated by $[Me_3O][BF_4]$,[6] and the nitrogen atom in *trans*-$[Mo(N)X(dppe)_2]$ can be protonated.[7] The nitrogen atom of the rhenium nitrides $ReNY_2(PEt_2Ph)_3$, where Y = Cl, and Br, acts as a Lewis base, forming adducts with the boron trihalides BX_3(X = F, Cl, Br).[8]

We have recently reported the synthesis of a series of nitrido–alkyl complexes of osmium(VI), $[Os(N)R_4][N\text{-}n\text{-}Bu_4]$, where R = Me, CH_2SiMe_3, CH_2CMe_3, and CH_2Ph.[9] We now report that these anionic complexes can be alkylated with R'_3OBF_4 or $R'OSO_2CF_3$ (where R′ = Me or Et).



$[Os(N)(CH_2SiMe_3)_4][N\text{-}n\text{-}Bu_4]$ (1) reacts with 1 equiv of $[Me_3O][BF_4]$ in methylene chloride at room temperature. ^1H NMR spectroscopy of the reaction mixture shows that one organometallic product is formed. This product 2, which analyzes correctly for $OsNSi_4C_{17}H_{47}$, can be crystallized in 79% yield from concentrated pentane solutions at −30 °C. The methylation of 1 with $MeOSO_2CF_3$ or CH_3I occurs more slowly than with $[Me_3O][BF_4]$. The product 2 is formed quantitatively by NMR in all cases. The ^1H and ^{13}C NMR spectra of 2 show four equivalent (trimethylsilyl)methyl groups and one methyl group.[10] With ^{15}N-labeled compound, the ^{15}N nucleus is coupled to the methyl protons, J = 2 Hz, but not to the methylene protons. There are examples of both two-bond and three-bond ^{15}N–^1H couplings of this magnitude.[11] Assignments of methyl and methylene protons in the ^{13}C NMR spectrum were confirmed by use of the DEPT NMR pulse sequence.[12] The IR spectrum of 2 shows a strong band at 1246 cm^{-1} which is characteristic of an (alkylimido)metal stretching vibration. An X-ray crystal structure showed this product to be $[Os(NMe)(CH_2SiMe_3)_4]$. The structure of the nitrido complex 1 was also determined by X-ray diffraction.[13]

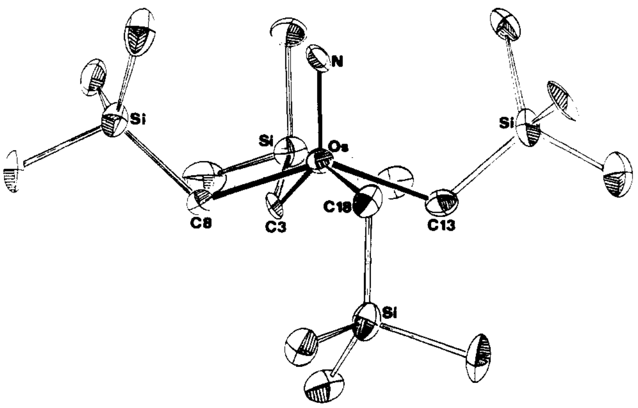


Figure 1. Ortep diagram for $[Os(N)(CH_2SiMe_3)_4][NBu_4]$. Selected bond distances (Å) are as follows: Os–N = 1.631 (8); Os–C(3) = 2.120 (9); Os–C(8) = 2.144 (10); Os–C(13) = 2.142 (10); Os–C(18) = 2.115 (10). Selected bond angles (deg) are as follows: N–Os–C(3) = 108.8 (4); N–Os–C(8) = 107.1 (4); N–Os–C(13) = 108.0 (4); N–Os–C(18) = 107.0 (4); C(3)–Os–C(8) = 86.2 (3); C(3)–Os–C(13) = 84.6 (3); C(8)–Os–C(18) = 84.3 (4); C(13)–Os–C(18) = 83.6 (4). Hydrogen atoms are not shown.

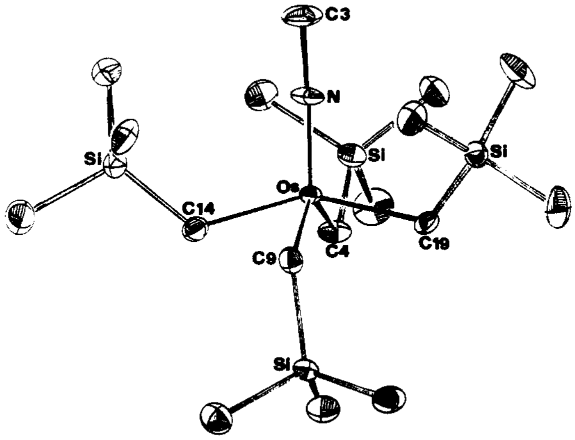


Figure 2. Ortep diagram for $[Os(NMe)(CH_2SiMe_3)_4][NBu_4]$. Selected bond distances (Å) are as follows: Os–N = 1.686 (5); N–C(3) = 1.430 (8); Os–C(4) = 2.069 (6); Os–C(9) = 2.085 (6); Os–C(14) = 2.1312 (6); Os–C(19) = 2.132 (6). Selected bond angles (deg) are as follows: N–Os–C(4) = 108.8 (3); N–Os–C(9) = 122.8 (3); N–Os–C(14) = 105.02 (26); N–Os–C(19) = 103.78 (27); C(4)–Os–C(14) = 85.68 (26); C(4)–Os–C(19) = 85.92 (25); C(9)–Os–C(14) = 81.86 (25); C(9)–Os–C(19) = 81.98 (24); Os–N–C(3) = 163.6 (6). Hydrogen atoms are not shown.

The five ligands in compound 1 are arranged in a square pyramid around the osmium with the nitride in the apical position. This is similar to the structure reported for $[Os(N)Cl_4][AsPh_4]$.[14] The four Os–C bonds vary between

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(3) Chan, D. M.-T.; Nugent, W. A. *Inorg. Chem.* **1985**, *24*, 1422–1424.

(4) Griffith, W. P. *Coord. Chem. Rev.* **1972**, *8*, 369–396.

(5) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175.

(6) Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Motevalle, M. *J.-Less Common Met.* **1977**, *54*, 487–493.

(7) Chatt, J.; Dilworth, J. R. *J. Indian Chem. Soc.* **1977**, *54*, 13–18.

(8) Chatt, J.; Heaton, B. J. *J. Chem. Soc. A* **1971**, 705. Danton, R.; Schweda, E.; Strahle, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 733.

(9) Belmonte, P. A.; Own, Z.-Y. *J. Am. Chem. Soc.* **1984**, *106*, 7493–7496.

(10) ^1H NMR (200 MHz, 298 K, C_6D_6): δ 3.49 (s, 8 H, $OsCH_2SiMe_3$), 1.59 (s, 3 H, CH_3N), 0.17 (s, 36 H, $SiMe_3$). $^{13}C\{H\}$ NMR (50 MHz, 298 K, C_6D_6): δ 46.2 (MeN), 42.6 ($OsCH_2SiMe_3$), 3.18 ($SiMe_3$). Anal. ($OsNSi_4C_{17}H_{47}$) C, H, N.

(11) Levy, G. C.; Lichter, R. L. *^{15}N NMR Spectroscopy*; Wiley-Interscience: New York, 1979.

(12) Bendall, M. R.; Doddrell, D. M.; Pegg, D. T.; Hull, W. E. *DEPT Bruker Information Bulletin*; Bruker Analytische Messtechnik: Karlesruhe, 1982.

(13) Data were collected on a diffractometer designed and constructed at Indiana University. The structures were solved by a combination of direct methods (MULTAN78) and Fourier techniques. Crystallographic data for $[Os(N)(CH_2SiMe_3)_4][N\text{-}n\text{-}Bu_4]$ (−160 °C): space group $C2/c$; molecules/per unit cell (Z) = 8; cell dimensions a = 40.063 (15) Å, b = 10.483 (2) Å, c = 21.521 (6) Å; β = 107.52 (2)°; R_F = 4.62%, R_{wF} = 4.52% for 4518 observed reflections with $F > 3.00\sigma$. One of the terminal methyl groups on the *n*-butyl ammonium ion was disordered with two apparently equivalent sites. Hydrogen atoms were not clearly visible in a difference Fourier phased on non-hydrogen atoms and were included only as fixed atom contributors in the final cycles. Crystallographic data for $[Os(NMe)(CH_2SiMe_3)_4]$ (−159 °C): space group $P2_1/c$; molecules/per unit cell (Z) = 4; cell dimensions a = 10.341 (2) Å, b = 14.829 (4) Å, c = 17.725 (5) Å; β = 96.16 (2)°; R_F = 3.38%, R_{wF} = 3.35% for 4113 observed reflections with $F > 3.00\sigma$. All hydrogen atoms were located in a difference synthesis phased on the non-hydrogen atoms and were included in the final least squares.

(14) Phillips, F. L.; Skapski, A. C. *J. Cryst. Mol. Struct.* **1975**, *5*, 83–92.

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.

Acknowledgment. We gratefully acknowledge the financial support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corp., and the University of Illinois at Chicago Research Board. We would also like to thank Eugene DeRose for his help and advice on NMR.

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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[15] Bright, D.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 709, 1078.

[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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[1] Verlhac, J. B.; Chanson, E.; Jousseaume, B.; Quintard, J. P. *Tetrahedron Lett.* **1985**, *26*, 6075. Chanson, E.; Jousseaume, B. *Synthesis*, in press.

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