Synthetic and Mechanistic Features of Dinuclear Reductive Elimination between $Re_2H_8(PMe_2Ph)_4$ and Several Tin(II) Reagents

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We have recently employed alcohol or amine elimination to synthesize a variety of heterometallic polyhydride clusters, including $[CuOsH_3(PMe_2Ph)_3]_3$,[1] $Re_2H_6(PMe_2Ph)_4(AuPPh_3)_2$,[2] $[CuRe_2H_7(PMe_2Ph)_4]_2$,[2] and $[MeC(CH_2PPh_2)_3]RhH_2[ZnN(SiMe_3)_2]$.[3] We report here the results of our attempts to incorporate a carbene-like tin(II) fragment into a rhenium polyhydride as a first step toward understanding the patterns of composition, structure, and reactivity of Pt/Re/Sn petroleum reforming catalysts.[4-7]

The two-coordinate monomeric compounds $Sn[N(SiMe_3)_2]_2$[8] and $Sn(OAr)_2$[9] (Ar = 2,4,6-*t*-$Bu_3H_2C_6$) react quantitatively in benzene at room temperature[10] with $Re_2H_8(PMe_2Ph)_4$ according to eq 1.[11] The dimeric alkoxide $[Sn(O\text{-}t\text{-}Bu)_2]_2$[12] reacts with $Re_2H_8(PMe_2Ph)_4$ to yield the same $SnRe_4H_{12}(PMe_2Ph)_8$ (eq 2), but this reaction proceeds according to a stoichiometry different

$$Re_2H_8(PMe_2Ph)_4 + SnX_2 \rightarrow \tfrac{1}{2}SnRe_4H_{12}(PMe_2Ph)_8 + 2HX + \tfrac{1}{2}Sn \quad (1)$$

$$2Re_2H_8(PMe_2Ph)_4 + \tfrac{1}{2}[Sn(O\text{-}t\text{-}Bu)_2]_2 \rightarrow SnRe_4H_{12}(PMe_2Ph)_8 + 2HO\text{-}t\text{-}Bu + H_2 \quad (2)$$

from that in eq 1. This reaction requires elevated temperature (110 °C for 45 min in toluene). Integration of the hydride and P–Me signals of $SnRe_4H_{12}(PMe_2Ph)_8$ at long (10 s) pulse delay times yielded a hydride-to-phosphine mole ratio of 6:4. The incorporation of one tin atom is indicated by the intensity of the $^{119/117}Sn$ satellites in the $^{31}P\{^1H\}$ NMR. In the case of $[Sn(O\text{-}t\text{-}Bu)_2]_2$, the H_2 evolved was identified by NMR and quantitated (93% yield of the amount shown in eq 2) by Toepler/volumetric methods. An X-ray diffraction study[13] of crystals of $SnRe_4H_{12}(PMe_2Ph)_8$ grown from toluene (Figure 1) reveals two Re_2P_4 units forming an elongated tetrahedron about the central tin atom. The resulting metallaspiropentane displays a curious distortion about the tin as demonstrated by Sn–Re distances ranging from 2.627 (2) to 2.793 (2) Å. The distortion may be due to hydride (not located) bridging of some of the Sn–Re vectors or may simply be due to steric congestion around the tin. The staggered $P_2Re\text{–}ReP_2$ conformations (Figure 1) render the molecule asymmetric. This distortion is not simply a solid-state phenomenon, since it persists in solution: six chemical shifts are resolved in the low-temperature $^{31}P\{^1H\}$ NMR[14] spectrum. As in $[CuRe_2H_7(PMe_2Ph)_4]_2$[2] and $[CuRe_2H_8(PMe_2Ph)_4]_2^{2+}$,[15] the high temperature or low field ^1H NMR[16] reveal that there is no rapid migration of hydrides from one Re_2 unit to the other.

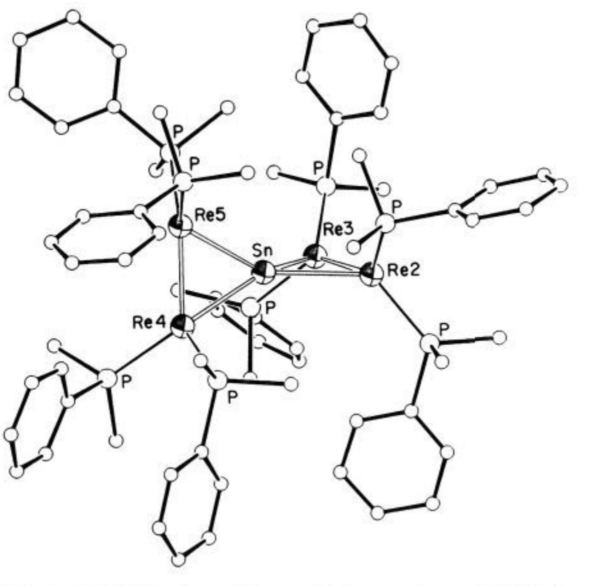

Figure 1. ORTEP drawing of the non-hydrogen atoms of $SnRe_4H_{12}(PMe_2Ph)_8$. Unlabeled atoms are carbon. Selected structural parameters are as follows: Re2–Re3, 2.5555 (19) Å; Re4–Re5, 2.5663 (22); Re2–Sn, 2.7330 (24); Re3–Sn, 2.7520 (23); Re4–Sn, 2.6265 (21); Re5–Sn, 2.7931 (22); Re2–Sn–Re3, 55.54 (5)°; Re4–Sn–Re5, 56.43 (6); Re–P distances range from 2.327 (6) to 2.344 (7) Å.

By monitoring the progress of eq 1 with ^1H and $^{31}P\{^1H\}$ NMR, intermediates of formula $XSnRe_2H_7(PMe_2Ph)_4$ can be detected.[17,18] The slower rate and the occurrence of H_2 evolution in eq 2 (cf. eq 1) speak for a different mechanism. We suggest a rate-determining step in which a lone pair of $[Sn(O\text{-}t\text{-}Bu)_2]_2$ displaces H_2 from $Re_2H_8P_4$ to form an adduct analogous to $[(OC)_3Ni \leftarrow Sn(O\text{-}t\text{-}Bu)(\mu\text{-}O\text{-}t\text{-}Bu)]_2$.[19] Such nucleophile-induced reductive elimination is consistent with the known[20] reaction of PMe_2Ph with $Re_2H_8(PMe_2Ph)_4$ to give H_2 and $Re_2H_6(PMe_2Ph)_5$. The mechanistic distinction is thus due to the fact that dimeric $[Sn(O\text{-}t\text{-}Bu)_2]_2$ lacks the empty orbital of monomeric SnX_2.

The results reported here provide facile synthetic procedures for incorporating tin into heterometallic polyhydride compounds. While the distinct mechanisms operative with monomeric and with dimeric Sn(II) reagents are explicable in terms of the presence and absence, respectively, of an empty tin orbital, it appears that

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(10) For X = –OAr, the reaction proceeds at 25 °C over a period of hours; for X = $-N(SiMe_3)_2$, the reaction takes a period of days to go to completion at 25 °C.

(11) Spectroscopic data for $SnRe_4H_{12}(PMe_2Ph)_8$: 360 MHz ^1H NMR (25 °C, toluene-d_8) 7.67 (t, 16 H), 7.14 (t, 16 H), 7.04 (t, 8 H), 1.95 (d, $J_{P\text{-}H}$ = 7.6 Hz, 48 H), –6.12 (br s, 12 H); 40.5 MHz $^{31}P\{^1H\}$ NMR (25 °C, toluene-d_8) –7.02 (s, with satellites with $J_{Sn\text{-}P}$ = 54 Hz); IR (Nujol) 1960 cm^{-1} (w, br), 1890 cm^{-1} (m, br).

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(13) Crystallographic data (–155 °C) for $SnRe_4H_{12}(PMe_2Ph)_8 \cdot C_7H_8$: space group $P2_1/a$ with $a = 23.802$ (15) Å, $b = 13.715$ (8), $c = 25.534$ (16), $\beta = 113.55$ (3)°, and $Z = 4$. $R(F) = 0.0740$ and $R_w(F) = 0.0693$ for 7369 reflections with $F > 2.33\sigma(F)$ using a model with thermal parameters isotropic for carbon and anisotropic for all other atoms. The data did not warrant inclusion of hydrogen atoms in the model. Positional and thermal parameters are available as Supplementary Material.

(14) 40.5 MHz or 146 MHz $^{31}P\{^1H\}$ NMR (–90 °C, C_7D_8) 0.18 (br, s, 1 P), –0.84 (br s, 1 P), –2.68 (s, 1 P), –7.53 (br s, 2 P), –9.88 (br s, 2 P), –11.60 (s, 1 P); 360 MHz ^1H NMR (–85 °C, C_7D_8) –3 to –9 (8 br signals observed).

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(16) 90 MHz ^1H NMR (25 °C, C_6D_6) –6.05 (quintet, $J_{P\text{-}H}$ = 12 Hz); 360 MHz ^1H NMR (75 °C, C_7D_8) –6.12 (~quintet, $J_{P\text{-}H}$ ~10 Hz).

(17) NMR of intermediates for X = OAr, 360 MHz ^1H NMR (25 °C, C_6D_6) 2.07 (s, 24 H), 1.55 (s, 18 H), 1.53 (s, 9 H), –5.38 (br s, 7 H); 40.5 MHz, $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6) –12.4 (s, $J_{^{117/119}Sn\text{-}P}$ ~ 60 Hz). For X = $-N(SiMe_3)_2$: 360 MHz ^1H NMR (25 °C, C_6D_6) 1.64 (d, $J_{P\text{-}H}$ = 7.2 Hz, 24 H), 0.60 (s, 18 H), hydrides too broad to detect; 40.5 MHz $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6) –10.6 (s).

(18) The NMR data for $XSnRe_2H_7(PMe_2Ph)_4$ resemble those of the structurally characterized $Ph_3PAuRe_2H_7(PPh_3)_4$. See: Moehring, G. A.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 1861.

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retention of unsaturated tin in the product is precluded either by conversion to four-coordinate Sn or by hydride bridging to tin. This is a conclusion also evident from our study[21] of the products of reductive elimination of methane from $AlMe_3$ and $ReH_m(PR_3)_n$. Our consistent finding that hydride ligands in heterometallic polyhydride clusters do not rapidly migrate past Cu, Ag, and now Sn centers suggests that hydrogen spillover,[22,23] the migration of hydrogen on a surface, may encounter significant activation barriers.[24]

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Supplementary Material Available: Listing of atomic positional and thermal parameters for $SnRe_4H_{12}(PMe_2Ph)_8{\cdot}C_7H_8$ (2 pages). Ordering information is given on any current masthead page.

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Titanium, Zirconium, and Hafnium Tetrahydroborates as "Tailored" CVD Precursors for Metal Diboride Thin Films

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In the last decade, there has been increasing interest in the use of group 4 diborides, MB_2 (where M = Ti, Zr, Hf), as coatings prepared by chemical vapor deposition (CVD).[1] This interest arises from their desirable properties: high hardness, high melting point, moderate strength, resistance to wear and corrosion, and good electrical conductivity.[2] Such properties are retained even at high temperature and make the diborides, particularly TiB_2, useful for such applications as coatings for metal cutting tools,[3] as crucibles and electrodes in metal-refining equipment such as aluminum reduction cells,[4] and potentially as coatings in rocket nozzles, valves, and the nose and leading edge of reusable re-entry vehicles in the aerospace industry.[5] There are currently four principal methods for preparing group 4 diborides: synthesis from the elements at over 2000 °C, reduction of the metal oxide and boron oxide by carbon at 2000 °C, reduction of the metal oxide by boron carbide and carbon at 2000 °C, and reduction of the metal halide and boron trihalide by hydrogen at 1200 °C; of these methods, only the last is suitable for the preparation of thin films.[1] An earlier publication dealth with the successful use of "tailored" molecular precursors to prepare thin films of TiC at 250 °C;[6] here we describe a remarkable extension of this CVD approach to the preparation of thin films of TiB_2, ZrB_2, and HfB_2 at exceptionally low temperatures (200 °C).

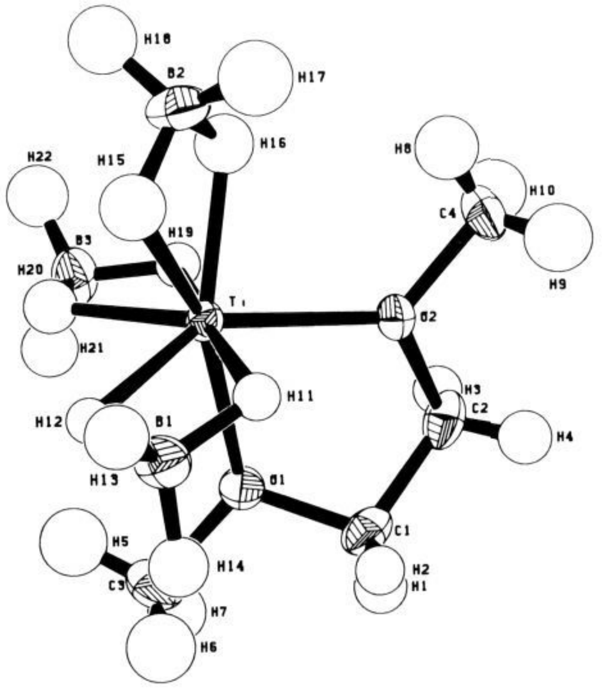

Figure 1. Molecular structure of $Ti(BH_4)_3(dme)$.

Transition-metal tetrahydroborates[7] should serve as excellent CVD precursors for metal borides, since they are often appreciably volatile and are known to thermolyze under mild conditions to give hydrogen and variable amounts of diborane. Unfortunately, binary titanium tetrahydroborates are poorly suited for CVD studies since $Ti(BH_4)_4$ is unknown (Ti^{IV} is reduced by BH_4^-) and $Ti(BH_4)_3$[8] is an exceedingly unstable species that decomposes well below room temperature. However, derivatives of $Ti(BH_4)_3$ are known,[9,10] and tris(tetrahydroborato)(1,2-dimethoxyethane)titanium(III) was chosen for CVD studies since it is one of the few Lewis base adducts of titanium tris(tetrahydroborate) that exhibits appreciable thermal stability and volatility. Light blue $Ti(BH_4)_3(dme)$ can be prepared by addition of dme to the thermally unstable adduct $Ti(BH_4)_3(OEt_2)$[10] or, more simply, by direct interaction of $TiCl_4$ with excess $NaBH_4$ in dme followed by crystallization from diethyl ether. $Ti(BH_4)_3(dme)$ is paramagnetic ($\mu_{eff} = 1.8\ \mu_B$), and its IR spectrum shows intense B–H stretches at 2412 cm^{-1} (terminal) and 2114 cm^{-1} (bridging) that are diagnostic of bidentate tetrahydroborate groups. This is confirmed by the X-ray crystal structure of $Ti(BH_4)_3(dme)$ which reveals a distorted trigonal bipyramidal geometry (Figure 1), considering the BH_4^- groups to occupy one site. The dme ligand bridges between an axial and an equatorial position, with Ti–O = 2.110 (1), 2.074 (1) Å. The Ti⋯B contacts are all equal at 2.411 (3)

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