monomer $TaCl_2H_2(PMe_3)_4$,[16] **2**, in ca. 80% recrystallized ($PhCH_3/PMe_3$, −40 °C) yield (eq 2). The room-temperature

$$\underset{\mathbf{1}}{\mathrm{TaCl_2(PMe_3)_4}} + \mathrm{H_2} \xrightarrow[\mathrm{PMe_3}]{\mathrm{OEt_2}} \underset{\mathbf{2}}{\mathrm{TaCl_2H_2(PMe_3)_4}} \qquad (2)$$

^1H NMR spectrum of **2** (toluene-d_8) shows a single, very broad ($\Delta\nu_{1/2}$ = 160 Hz) PMe_3 resonance at δ −0.96. The latter does not split on cooling to −80 °C, and we were unable to locate the hydride resonance at either temperature. The IR spectrum of **2** (Nujol) shows a strong terminal metal–hydride stretch at 1690 cm^{-1}, which shifts to 1212 cm^{-1} in the IR spectrum of $TaCl_2D_2(PMe_3)_4$. The ESR spectrum of the *deuteride* ($PhCH_3$ solution, 25 °C, 9.64 GHz) is an octet (^{181}Ta, $I = {}^7/_2$, 100% abundance) of quintets: $\langle g \rangle = 1.960$, $\langle a \rangle_{Ta} = 139.4$ G, $\langle a \rangle_P =$ 33.8 G. Hydride coupling in the ESR spectrum of **2** was not resolved, but from the increase in line width we can estimate $\langle a \rangle_H$ to be ca. 6–7 G.

Reaction 2 is a rare example of an oxidative addition reaction connecting paramagnetic monomers[17] and the only one we know of that involves dihydrogen. In addition to **2**, the following *isolable* paramagnetic hydrides have been claimed: $HFe(dppe)_2$,[18] $[HFeCl(dppe)_2]BF_4$,[18] and $HCoL_4^{+}$.[19] None of these systems has been structurally characterized.

An ORTEP drawing[20] of **2** is shown in Figure 1 (center). The terminal hydride ligands were located directly from difference Fourier maps and were well behaved during least-squares refinement: Ta–H1, 1.94 (11); Ta–H2, 1.85 (11) Å; H1–Ta–H2, 77 (6)°. The overall geometry is best described as dodecahedral with the chloride and hydride ligands in the sterically less demanding "A" sites[21] of the dodecahedron. Selected structural data are as follows: Ta–Cl2, 2.542 (5); Ta–Cl3, 2.563 (5); Ta–P4, 2.633 (6); Ta–P5, 2.567 (5); Ta–P6, 2.559 (5); Ta–P7, 2.628 (6) Å; Cl2–Ta–Cl3, 81.8 (1); P5–Ta–P6 123.6 (1); P4–Ta–P7, 158.9 (1)°.

The solution thermolysis of **2** (cyclohexane, 81 °C, 1 h) provides a single tantalum-containing product in quantitative yield (eq 3).

$$\underset{\mathbf{2}}{\mathrm{TaCl_2H_2(PMe_3)_4}} \xrightarrow[\mathrm{C_6H_{12}}]{\Delta} 0.5\underset{\mathbf{3}}{[\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-}\mathrm{H})_4} + 2\mathrm{PMe_3} \qquad (3)$$

The yellow-green product was identified as the quadruply hydrogen-bridged tantalum(IV) dimer $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_4$, **3**, by spectral comparison (IR, ^1H and ^{31}P NMR) with an authentic sample prepared by an independent and more difficult route.[3b,22]

The reduction of **2** with 1 equiv of sodium amalgam in ether containing free PMe_3 gave, after workup and recrystallization (toluene/PMe_3, −40 °C) green air-sensitive crystals of the diamagnetic tantalum(III) monomer $TaClH_2(PMe_3)_4$,[23] **4**, in ca. 50% yield (eq 4). The IR spectrum (Nujol) of **4** shows a terminal metal–hydride stretch at 1662 cm^{-1}, which shifts to 1191 cm^{-1} in the deuterium analogue. The proton NMR of **4** (benzene-d_6) shows two resonances at δ 1.46 (36 H) and 0.23 (2 H).[24] The latter disappears in the proton NMR spectrum of $TaClD_2(PMe_3)_4$.

$$\underset{\mathbf{2}}{\mathrm{TaCl_2H_2(PMe_3)_4}} + \mathrm{Na/Hg} \xrightarrow[\mathrm{PMe_3}]{\mathrm{OEt_2}} \underset{\mathbf{4}}{\mathrm{TaClH_2(PMe_3)_4}} + \mathrm{NaCl} \qquad (4)$$

An ORTEP drawing of **4**[25] is shown in Figure 1 (bottom). Unfortunately, the hydride ligands were not located by difference Fourier methods, but they must be located in the cavity above the four PMe_3 ligands. Selected structural data are as follows: Ta–Cl2, 2.472 (4); Ta–P3, 2.490 (4); Ta–P4, 2.555 (4); Ta–P5, 2.545 (4); Ta–P6, 2.479 (4) Å; P3–Ta–P6, 140.8 (1); P4–Ta–P5, 157.8 (1)°. Several other monomeric tantalum(III) hydride complexes are known[26,27] in addition to **4**, but only one has been structurally characterized, i.e., pentagonal-bipyramidal $TaH(PPh_2)_2(dmpe)_2$.[27]

Other aspects of the chemistry of **1**, **2**, and **4** are currently under investigation as well as an attempt to develop niobium chemistry along similar lines.

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Registry No. 1, 85923-35-9; **2**, 85939-38-4; **4**, 85923-36-0; $TaCl_5$, 7721-01-9; PMe_3, 594-09-2; H_2, 1333-74-0.

Supplementary Material Available: Fractional coordinates and thermal parameters for **1**, **2**, and **4** (5 pages). Ordering information is given on any current masthead page.

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(16) Anal. Calcd for $TaCl_2H_2(PMe_3)_4$ ($TaCl_2P_4C_{12}H_{38}$): C, 25.82; H, 6.86. Found (Galbraith): C, 25.63; H, 6.68. Magnetic moment: μ_{eff} (298 K) = 1.74 μ_B (Guoy method).

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(19) Sander, J. R. *J. Chem. Soc., Dalton Trans.*, **1973**, 748–749.

(20) $TaCl_2H_2(PMe_3)_4$ crystallizes (from $PhCH_3$, −40 °C) in the acentric monoclinc space group *Cc* with a = 15.127 (3) Å, b = 12.005 (3) Å, c = 12.410 (2) Å, β = 92.49 (1)°; V = 2251.59 $Å^3$, and ρ(calcd) = 1.647 g cm^{-3} for M_r 558.18 and z = 4. Diffraction data were collected at −160 °C,[13b] and the structure was solved by direct methods (MULTAN), difference Fourier syntheses, and full-matrix least-squares refinement. Final discrepancy indices were R_F = 2.85% and R_{wF} = 2.93% for those 2418 reflections with $F_o > 2.33\sigma(F_o)$. The limits of data collection were $6° < 2\theta < 45°$ (Mo Kα).

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(22) The solution thermolyses of complexes **1** and **4** are considerably more complex than that of **2**. Both reactions provide multiple products and are still under investigation.

(23) Anal. Calcd for $TaClH_2(PMe_3)_4$ ($TaClP_4C_{12}H_{38}$): C, 27.57; H, 7.33; Cl, 6.78. Found (Schwartzkopf): C, 27.63; H, 7.28; Cl, 6.77.

(24) Variable-temperature ^1H and $^{31}P\{^1H\}$ NMR studies are currently in progress and will be reported in detail elsewhere.

(25) $TaClH_2(PMe_3)_4$ crystallizes (from $PhCH_3$, −40 °C), in the monoclinic space group $P2_1/a$ with a = 18.617 (5) Å, b = 9.428 (2) Å, c = 12.528 (3) Å, β = 97.92 (1)°; V = 2178.04 $Å^3$, and ρ(calcd) = 1.594 g cm^{-3} for M_r 522.73 and z = 4. Diffraction data were collected at −160 °C.[13b] The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares. Final discrepancy indices were R_F = 5.70% and R_{wF} = 5.47; for those 2232 reflections with $F_o \geq 2.33\sigma(F_o)$. The limits of data collection were $6° < 2\theta < 45°$ (Mo Kα).

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Reaction of Acyl Halides with Organotin Hydrides. Mechanism of Aldehyde Formation[1]

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In 1966 Kuivila and Walsh reported that when an acid chloride was mixed at room temperature with tri-*n*-butyltin hydride, there was frequently an exothermic reaction.[4] The major products were the corresponding aldehyde and ester, the relative yields of which depended on both the nature of the acyl moiety and the experimental conditions (eq 1). Kuivila and Walsh carried out a rather

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$$\mathrm{RCOCl} \xrightarrow{n\text{-}\mathrm{Bu_3SnH}} \mathrm{RCHO} + \mathrm{RC(O)OCH_2R} + n\text{-}\mathrm{Bu_3SnCl} \quad (1)$$

detailed mechanistic study of these reactions[4,5] and concluded that both aldehyde[4] and ester[5,6] were produced by free-radical chain processes involving acyl radicals as intermediates. The formation of aldehyde was suggested to be mechanistically analogous to the formation of alkane in the alkyl halide–tin hydride reaction,[7] i.e., eq 2 and 3. Although this mechanism has been generally accepted, we can now report that for at least one acyl chloride at temperature ≤60 °C the aldehyde is actually formed by a facile, nonradical process.

$$\mathrm{RCOCl} + n\text{-}\mathrm{Bu_3Sn\cdot} \rightarrow \mathrm{R\dot{C}{=}O} + n\text{-}\mathrm{Bu_3SnCl} \quad (2)$$

$$\mathrm{R\dot{C}{=}O} + n\text{-}\mathrm{Bu_3SnH} \rightarrow \mathrm{RCHO} + n\text{-}\mathrm{Bu_3Sn\cdot} \quad (3)$$

As supporting evidence for reactions 2 and 3 Kuivila and Walsh went to some trouble to find an acyl chloride that, on reaction with tin hydride, showed one of the distinguishing features of acyl radical chemistry, namely, decarbonylation:

$$\mathrm{R\dot{C}{=}O} \rightarrow \mathrm{R\cdot} + \mathrm{CO} \quad (4)$$

However, only triphenylacetyl chloride yielded any CO, and then only small amounts under conditions specifically designed to encourage decarbonylation (T = 100–110 °C, slow addition of hydride).[4] Room-temperature kinetic data are now available for H abstraction from tin hydride by some alkyl radicals[8,9] (e.g.,[9] $k \sim 2 \times 10^6$ M s^{-1} for primary, secondary, and tertiary alkyls) and for some decarbonylations (e.g., $k_4 \sim 1 \times 10^5$ s^{-1} for $\mathrm{Me_3C\dot{C}{=}O}$[10] and $\sim 9 \times 10^6$ s^{-1} for $\mathrm{PhCH_2\dot{C}{=}O}$[11]). The Kuivila and Walsh data[4] imply that reaction 3 is sufficiently rapid to prevent decarbonylation of the pivaloyl and the phenylacetyl radical—*if* they were actually intermediates in the reaction of the corresponding acyl chloride with tin hydride. This seems highly improbable[12] and, as the following experiment demonstrates, is certainly untrue for the pivaloyl radical.[13]

A mixture containing 53 μL of n-$\mathrm{Bu_3SnD}$ (1 M), 150 μL of $\mathrm{Me_3CCHO}$ (10 M), and 9 mg of $\mathrm{Me_3CONNOCMe_3}$ (0.25 M) was heated to 50 °C under vacuum for 16 h (ca. 8 half-lives of hyponitrite), cooled to −80 °C, and opened, and cold (−30 °C) toluene was added (to trap isobutane). Immediate analysis by GC/MS gave the isobutane concentration as ca. 1.5 M (there is some radical chain decarbonylation). This isobutane contained ca. 16% $\mathrm{Me_3CD}$ (≈25% of D initially present, much of the remainder was probably present as $\mathrm{Me_3COD}$). There was *no* detectable incorporation of D into the remaining aldehyde. Clearly, $\mathrm{Me_3C\dot{C}{=}O}$ were produced, but they underwent decarbonylation in preference to D abstraction from n-$\mathrm{Bu_3SnD}$, i.e., for this acyl radical reaction 3 does not compete with reaction 4.

This conclusion received independent support from the products formed by reaction of 0.6 M $\mathrm{Me_3CCOCl}$ with 0.6 M n-$\mathrm{Bu_3SnH}$ in octane at 60 °C for 9 h in the absence of and in the presence of 0.01 M $\mathrm{Me_3CONNOCMe_3}$.[14] The uninitiated reaction gave 0.62 M $\mathrm{Me_3CCHO}$, 0.02 M $\mathrm{Me_3CH}$, and 0.006 M $\mathrm{Me_3C(O)OCH_2CMe_3}$, and the free-radical-initiated reaction gave 0.06 M $\mathrm{Me_3CCHO}$, 0.54 M $\mathrm{Me_3CH}$, and 0.003 M $\mathrm{Me_3C(O)OCH_2CMe_3}$. (In both reactions trace amounts of $\mathrm{Me_3CCH_2OH}$ and $\mathrm{Me_3C(O)OCHClCMe_3}$ were also produced.) It is obvious that providing the system with a source of free radicals causes a dramatic change in products—the direction of this change ruling out the Kuivila and Walsh mechanism for aldehyde formation.

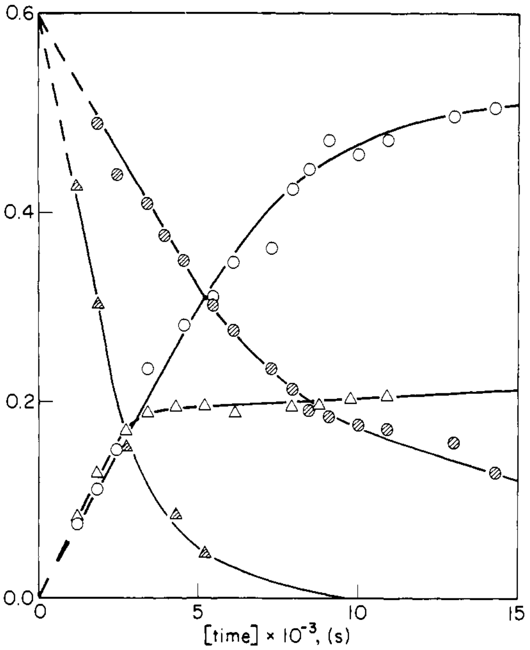

Figure 1. Reaction of 0.6 M $\mathrm{Me_3CCOCl}$ with 0.6 M $\mathrm{Bu_3SnH}$ in $\mathrm{C_6D_6}$ at 28 °C followed by NMR. ○ $\mathrm{Me_3CCHO}$, ● $\mathrm{Bu_3SnH}$: uninitiated reaction. △ $\mathrm{Me_3CCHO}$, ▲ $\mathrm{Bu_3SnH}$: in presence of 0.1 M $\mathrm{Me_3CONNOCMe_3}$.

Further evidence against the intermediacy of free radicals in an uninitiated reaction was obtained by monitoring the kinetics of the reaction of 0.6 M $\mathrm{Me_3CCOCl}$ with 0.6 M n-$\mathrm{Bu_3SnH}$ in $\mathrm{C_6D_6}$ at 28 °C by NMR in the absence of and in the presence of 0.1 M $\mathrm{Me_3CONNOCMe_3}$ (which would generate $\mathrm{Me_3CO\cdot}$ radicals at a rate of $\sim 3 \times 10^{-7}$ M s^{-1}).[15] As can be seen in Figure 1, the initial rate of formation of $\mathrm{Me_3CHO}$ is identical in the two experiments (6×10^{-5} M s^{-1}), but the initial rate of destruction of n-$\mathrm{Bu_3SnH}$ (and presumably of $\mathrm{Me_3CCOCl}$) was increased from 6×10^{-5} M s^{-1} to 17×10^{-5} M s^{-1} by the radical initiator.[16] It is evident that the deliberate introduction of free radicals into the mixture initiates a radical-chain reaction that proceeds in parallel to the "normal" reaction, consuming reagents but producing isobutane rather than pivaldehyde. The normal reaction cannot, therefore, be a radical-chain process. We suggest that aldehyde is formed either in a concerted bimolecular reaction or via an unstable α-chloroalkoxytin:

$$n\text{-}\mathrm{Bu_3SnH} + \mathrm{Me_3CCOCl} \rightarrow (n\text{-}\mathrm{Bu_3SnOCH(Cl)CMe_3}) \rightarrow n\text{-}\mathrm{Bu_3SnCl} + \mathrm{Me_3CCHO} \quad (5)$$

Although our results do not rule out a Kuivila and Walsh radical-chain route to aldehyde for chlorides that could yield acyl radicals having low k_4 values, we see no reason why aldehyde should be formed in this way *unless* radicals are generated in the system. Indeed, the room-temperature uninitiated reaction of 0.6 M 5-hexenoyl chloride with 0.6 M n-$\mathrm{Bu_3SnH}$ (which yields mainly the $\mathrm{C_5H_9C(O)OC_6H_{11}}$ ester and is much slower than the $\mathrm{Me_3CCOCl}$ reaction) produces only minute traces of 5-hexenoyl radical derived cyclized products, 2-methylcyclopentanone and cyclohexanone. This result, which indicates that 5-hexenoyl

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radicals are not involved[17] in the uninitiated reaction, contrasts sharply with the results of others on the radical-initiated reaction at higher temperatures.[18-21] Moreover, it indicates that acyl radicals are *not* involved in ester formation, as originally postulated.[5,6] This last conclusion receives further support for our observation that absolutely no $Me_3C(O)OCH_2CMe_3$ was produced when 0.2 M $Me_3CONNOCMe_3$ was completely decomposed in 7.4 M Me_3CCHO in benzene at 30 or 60 °C.[23] The detected decrease in the aldehyde concentration was 2 M at both temperatures, but the only aldehyde derived product was isobutane. We are currently investigating the mechanism of ester formation.

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Registry No. *n*-Bu_3SnD, 688-73-3; Me_3CCHO, 630-19-3; $Me_3CONNOCMe_3$, 14976-54-6; Me_3CCOCl, 3282-30-2; Cl_2, 7782-50-5; H_2, 1333-74-0; $Me_3C\dot{C}{=}O$, 50694-27-4.

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Rapid Incorporation of Copper(II) in Porphyrin Derivatives

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The mechanism by which metal ions are incorporated into porphyrins and substituted porphyrins has been intensively investigated without establishing a definitive mechanism[1-4] It has been suggested that the mechanism includes an association between the free or complexed metal ion and the porphyrin.[5-7] Normally, these reactions are quite slow, with the rate-determining step being variously attributed to deformations of the rigid porphyrin plane,[7,8] proton dissociation by an active metal complex,[5,6] or complex formation with the porphyrin[4] or porphyrin substituents.[7]

Table I. Observed Rate Constants for Incorporation of Cu(II) into Tetraphenylporphine (TPP) and Several *meso*-$\alpha,\alpha,\alpha,\alpha$-Tetrakis(*o*-acylamidophenyl)porphine ($\alpha^4H_2T_{acyl}PP$) Derivatives[a]

compd	K_{obsd}, h^{-1}	compd	K_{obsd}, h^{-1}
TPP	0.040	$\alpha^4H_2T_{lauroyl}PP$	1.019
$\alpha^4H_2T_{palmitoyl}PP$	0.999	$\alpha^4H_2T_{decanoyl}PP$	1.119
$\alpha^4H_2T_{myristoyl}PP$	1.074		

[a] $[Cu^{2+}] = 0.04$ M.

We have investigated the incorporation of Cu(II) into derivatives of *meso*-tetraphenylporphine (TPP) in nondetergent microemulsions over a nominal pH range of 1.00–4.00. The kinetic data for a number of coordinating and noncoordinating ligands clearly show that very fast rates of metal incorporation depend on the formation of a reactive metal complex as previously postulated.[3,4,6,8] The slow step apparrently involves an outer-sphere association between the reactive intermediate and the porphyrin followed by rapid metal incorporation.

Under pseudo-first-order conditions the reaction is first order in Cu(II) concentration. Plots of $-\ln (A_\infty - A_t)$ vs. time were linear, and varying initial concentrations gave the same slope.

The reaction is zero order in $[H^+]$ over a pH range of 2.00–4.00 but inverse half order below pH 2.00. The rates of metal incorporation for the 10–16 carbon derivatives, *meso*-$\alpha,\alpha,\alpha,\alpha$,-tetrakis(*o*-acylamidophenyl)porphine, $\alpha^4H_2T_{acyl}PP$, are approximately 25 times faster than that for TPP itself (Table I). Observed rate constants for several ligands have been obtained. These rates correlate approximately with E_n, the ligand nucleophilicity parameter described by Edwards.[10]

Metalation reaction between $\alpha^4H_2T_{pal}PP$ (pal = palmitoyl) and various cupric salts have been examined in a detergent-free microemulsion. A composition of toluene, 2-propanol, and water (mole fractions 0.36, 0.44, and 0.20, respectively) exhibits characteristics similar to detergent-stabilized microemulsions.[11] The acylated TPP derivative is a surface-active porphyrin possessing four 16-carbon chains preferentially solubilized in the toluene-rich continuum and an aromatic porphyrin ring with four imine nitrogens solubilized in the 2-propanol-rich region.

meso-$\alpha,\alpha,\alpha,\alpha$-Tetrakis(*o*-aminophenyl)porphine[11] was acylated with palmitoyl chloride, which upon subsequent workup and crystallization produced the surface-active porphyrin in 90% yield.. These violet crystals show a single spot on TLC (1:1 benzene-ether) and exhibit maxima at 645, 587, 543, 519, and 450 nm (Soret). The aqueous phase was adjusted to pH 3.00 prior to forming the microemulsion. At pH 3.00 and a concentration of 8.50×10^{-5} M in toluene the porphyrin exists primarily as the free base.

All kinetic studies were run under pseudo-first-order conditions where Cu(II) concentrations ranged from 0.01 to 0.10 M, with the Cu(II) concentrations always in approximately 100-fold excess with respect to porphyrin. Spectra were followed over at least 7 half-lives on a Varian Cary 219 recording spectrophotometer for the slower reactions or a stopped-flow spectrophotometer interfaced to an Amino-Morrow storage and retrieval system for faster reactions. The kinetic runs were carried out by rapid mixing of two solutions: the first contained appropriate amounts of 2-propanol, water, Cu(II), and anion; the second contained toluene and porphyrin. Kinetic data were obtained by following the appearance of the Cu(II)-porphyrin band at 540 nm. The temperature was held to 25.0 ± 1.0 °C.

Previous studies have suggested that the controlling feature of porphyrin metalation is the nature of the porphyrin itself. More recently, evidence has been presented that the nature of the reactive

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