in Table V. The results of a calculation using this model spectrum are displayed graphically in Figure 10. Each free molecule transition generates one allowed and one forbidden crystal state. No mixing occurs between the $A_1 \rightarrow A_1$ and $A_1 \rightarrow B_2$ transitions; however, modest mixing occurs between the two $A_1 \rightarrow B_2$ transitions. The result here is to shift ~10% of the intensity of I into III. The crystal field effects are therefore of little consequence in the basic interpretation of the crystal spectra and the assignments of the transitions.

Adduct-Hydrocarbon Spectrum. No absorption that is attributable to the hexadecane molecule in the urea adduct spectra can be definitely discerned. Based on the neat urea data, there is about 35% "extra" absorption over that expected in the vicinity of 60000 cm^{-1} for the $\|c$ spectrum of the adduct, and this intensity could conceivably arise from transitions based on the hydrocarbon. The molar concentration of the hydrocarbon in the adduct crystal is 1.3 mol/L compared to a value of 15.4 for the urea presence. We then estimate that if the extra intensity is attributable to the hydrocarbon, then the molar extinction coefficient for hexadecane would have a magnitude ~2000 cm^{-1} M^{-1}, and its polarization would be transverse to the hydrocarbon long axis. In fact, absorption of long *n*-alkanes begins at about 60000 cm^{-1} and rises more or less continuously toward higher energy.[18] A positive identification, however, is not possible here. We thank Professor B. Hudson (University of Oregon) for alerting us to this interesting type of crystal system.

Summary

Polarized reflection spectra from single crystals of urea and urea-hexadecane adduct have been used to identify the excited-state symmetries of three valence shell transitions in the vacuum ultraviolet. The results from an oriented gas analysis of the data unambiguously give the three transitions as I (56000 cm^{-1}, f = 0.21, $A_1 \rightarrow B_2$), II (62000 cm^{-1}, f = 0.23, $A_1 \rightarrow A_1$), and III (65000 cm^{-1}, f = 0.09, $A_1 \rightarrow B_2$). Crystal field induced shifts and mixing are of minor significance in urea. The observed urea crystal spectra can be closely fit by a model spectrum with but minor energy shifts (+800, +1400, +300 cm^{-1} for I, II, and III) from those given above. The lowest energy $A_1 \rightarrow B_2$ transition is assigned as an electron transition between predominantly the antibonding combination of $2p_\pi$ nitrogen orbitals and π^* of the carbonyl, while the $A_1 \rightarrow A_1$ transition must be essentially the $\pi \rightarrow \pi^*$ of the carbonyl. No assignment of the third observed band ($A_1 \rightarrow B_2$) can be made.

(18) Raymonda, J.; Simpson, W. T. *J. Chem. Phys.* **1967**, *47*, 430.

On the Mechanism of $SnCl_4$-Promoted Additions of Allylstannanes to Aldehydes: A Response to Denmark, Wilson, and Willson

Gary E. Keck,* Merritt B. Andrus, and Stephen Castellino[†]

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. *Received November 2, 1987*

Abstract: The reaction of allyltri-*n*-butylstannane with the complexes formed from three aldehydes (**1-3**) with $SnCl_4$ has been investigated via variable-temperature ^{119}Sn NMR spectroscopy under carefully controlled conditions. With aldehyde **1**, which forms a tight bidentate chelate with $SnCl_4$, addition products are produced without the intermediacy of the transmetalation product allyltrichlorostannane at 1:1 stoichiometry, as revealed by appropriate control experiments with this reagent. The same is true of 2:1 (aldehyde:$SnCl_4$) complexes derived from **1** and **2** provided that such complexes are formed stoichiometrically at low temperature and free $SnCl_4$ is not present. With **3**, free $SnCl_4$, chelate, and 2:1 complex are all in equilibrium at -80 to -90 °C at 1:1 $SnCl_4$:aldehyde stoichiometry, and transmetalation with free $SnCl_4$ is an important component of the overall reaction pathway. Competition experiments between the chelate and the 2:1 complex derived from **1** reveal that the chelate is more reactive but that the rate difference is modest. In addition, a mechanistic/spectroscopic study of allylstannane additions to aldehydes reported recently by Denmark, Wilson, and Willson has been reinvestigated, and results contrary to those reported are presented. In particular, it is shown that transmetalation pathways involving conversion of allyltri-*n*-butylstannane to allyltrichlorostannane or diallyldichlorostannane prior to reaction with aldehydes **5** and **6** do not occur from stable 2:1 $(RCHO)_2 \cdot SnCl_4$ complexes at low temperature. The sensitivity of such experiments to experimental details is emphasized.

Previous studies in our laboratories[1] have revealed that the preferred solution structures of complexes derived from β-alkoxy aldehydes and various Lewis acids (e.g., $MgBr_2$ and $TiCl_4$) are an extremely sensitive function of aldehyde structure and that the most complex behavior is observed with $SnCl_4$. This case provides an opportunity to assess the mechanistic consequences of such structural variations in allylstannane addition reactions, particularly issues involving transmetalation reactions,[2] which are relevant both to synthetic applications and to other mechanistic investigations.[3] We record herein the results of a study of the dynamics of such reactions as revealed by ^{119}Sn NMR.[4,5]

Shown in Figure 1 are selected data points for the reaction of allyltri-*n*-butylstannane with the bidentate chelate formed from the β-benzyloxy aldehyde **1** and $SnCl_4$, as observed by ^{119}Sn NMR at -90 °C. The resonances for the chelate at -577 ppm and

[†]Department of Chemistry, North Dakota State University, Fargo, ND 58102.

(1) (a) Keck, G. E.; Castellino, S. *J. Am. Chem. Soc.* **1986**, *108*, 3847. (b) Keck, G. E.; Castellino, S.; Wiley, M. R. *J. Org. Chem.* **1986**, *51*, 5478. (c) Keck, G. E.; Castellino, S. *Tetrahedron Lett.* **1987**, *28*, 281. (d) Keck, G. E.; Castellino, S., unpublished results.

(2) (a) Tagliavini, G.; Peruzzo, V.; Plazzogna, G.; Marton, D. *Inorg. Chem. Acta* **1977**, *24*, L47. (b) Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* **1978**, *162*, 37. Gambaro, A.; Marton, D.; Tagliavini, G. *Ibid.* **1981**, *210*, 57. (c) Gambaro, A.; Marton, D.; Peruzzo, V.; Tagliavini, G. *Ibid.* **1982**, *226*, 149. (d) Gambaro, A.; Boaretto, A.; Marton, D.; Tagliavini, G. *Ibid.* **1983**, *231*, 307. (e) Tagliavini, G. *Rev. Silicon, Germanium, Tin, Lead Cmpds.* **1985**, *8*, 237. (f) Fishwick, M. W.; Wallridge, M. G. H. *J. Organomet. Chem.* **1977**, *136*, C46. (g) Yamamoto, Y.; Maeda, N.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1983**, 742. (h) Keck, G. E.; Abbott, D. E.; Boden, E. P.; Enholm, E. J. *Tetrahedron Lett.* **1984**, *25*, 3927. (i) Denmark, S. E.; Wilson, T.; Willson, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 984.

0002-7863/89/1511-8136$01.50/0

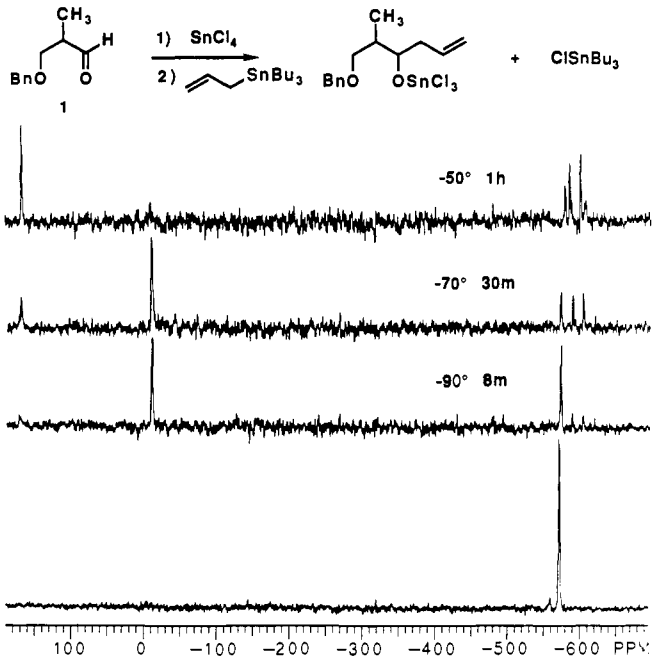

Figure 1. Reaction of allyltri-*n*-butylstannane with $SnCl_4$–β-(benzyloxy)propanal (**1**) chelate monitored by ^{119}Sn NMR.

allyltri-*n*-butylstannane (−14 ppm) smoothly decrease as signals for tri-*n*-butyltin chloride (+173 ppm) and addition products (−594 and −607 ppm) appear.[6] Also shown (Figure 2) are the results obtained in an "inverse" experiment in which allyltrichlorostannane (−36 ppm) was first generated by transmetalation between allyltri-*n*-butylstannane and $SnCl_4$ at −90 °C and then allowed to react with **1**. It is clear from such experiments that both reactions are sufficiently slow at −90 °C to be followed by ^{119}Sn NMR, that transmetalation is not involved in the reaction of the bidentate chelate formed from **1** and $SnCl_4$, and that no long-lived intermediates resulting from complexation or chelation of allyltrichlorostannane with **1** are present, as the chemical shift for this material is unchanged in the presence of the aldehyde.

On the basis of the results obtained with β-benzyloxy aldehyde **1** by ^1H and ^{13}C NMR[1] as well as the ^{119}Sn NMR results given above, one might expect that a bidentate chelate of **1** with $SnCl_4$ represents a free energy minimum at −80 to −90 °C. However, this is not the case, and the nature of the thermodynamically favored complex *is stoichiometry dependent*. Shown in Figure 3 are selected data points for the results of an experiment in which $SnCl_4$ is titrated with aldehyde **1** at −90 °C as observed by ^{119}Sn NMR. With 0.5 equiv of **1** relative to $SnCl_4$, both free $SnCl_4$ and chelate are observed (as expected), and only chelate is observed with 1.0 equiv of **1**. However, with 1.5 equiv of **1**, a new signal at −563 ppm appears, which increases in intensity with increasing equivalents of **1** in the range of 1.0–2.0 equivalents. This signal is assigned to the 2:1 complex between **1** and $SnCl_4$, in which only carbonyl complexation occurs, as in observed with aldehydes structurally incapable of forming bidentate chelates.

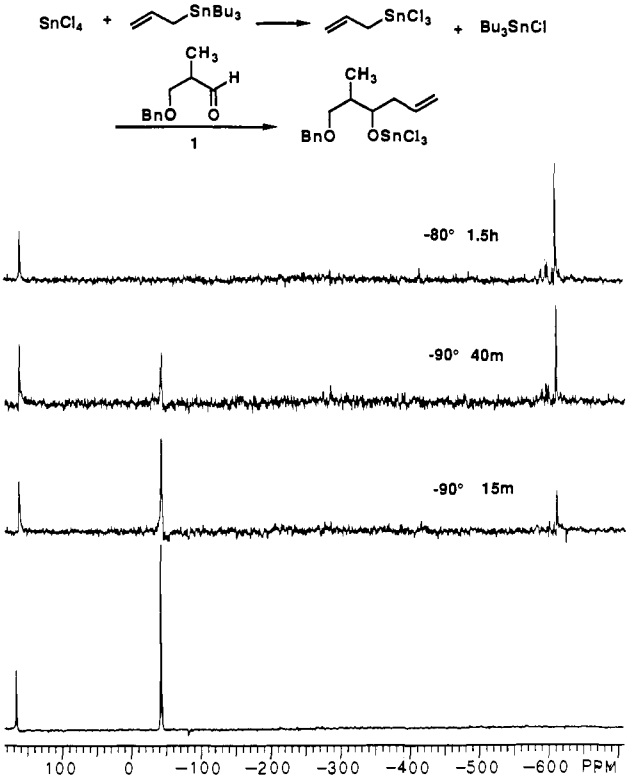

Figure 2. Trichloroallylstannane addition to aldehyde **1** at −90 °C monitored by ^{119}Sn NMR.

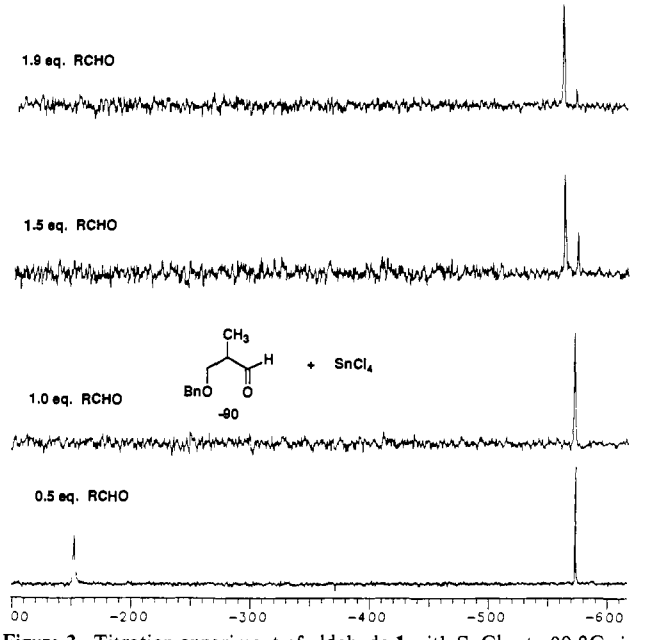

Figure 3. Titration experiment of aldehyde **1** with $SnCl_4$ at −90 °C via ^{119}Sn NMR.

(3) Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970.

(4) For ^{119}Sn NMR characterization of a chiral α-alkoxy ketone–$SnCl_4$ chelate, as well as an X-ray crystal structure of the complex, see: Reetz, M. T.; Harms, K.; Reif, W. *Tetrahedron Lett.* **1988**, *29*, 5881. These authors also report the ^{119}Sn chemical shift for a pentacoordinate adduct of $SnCl_4$ with di-*tert*-butyl ketone as −329.5 ppm.

(5) (a) All ^{119}Sn NMR spectra were recorded on a Varian XL-300 spectrometer at 112 MHz with a 16-mm broad-band probe. Chemical shifts are referenced to tetramethyltin as an external standard (0.00 ppm). Solutions were 0.1 or 0.4 M in $SnCl_4$. All materials were carefully purified and handled by techniques appropriate for air- and moisture-sensitive materials. The protocol employed for monitoring the addition reactions was as follows: To a flame-dried 16-mm NMR tube was added a solution of the substrate in 8 mL of dry methylene chloride or 1:1 methylene chloride–chloroform (via syringe under an argon atmosphere). The solution was cooled to −90 °C prior to the addition of $SnCl_4$ and mixing. The sample was then placed in the probe (−90 °C) and allowed to equilibrate for 10 min prior to acquisition of a spectrum. The sample was then removed from the probe and immediately placed in a −90 °C bath, and allyltri-*n*-butylstannane was then cautiously added in such a manner as to avoid mixing with the solution, and to form a second layer on top of the methylene chloride solution. The sample was then returned to the probe and equilibrated at −90 °C for 10 min without spinning prior to acquisition of a time-zero spectrum, again without spinning. The phases were then mixed by spinning to vortex the sample. After mixing, the spinning rate was reduced and acquisition begun. It should be noted that the peak areas of the ^{119}Sn NMR resonances are not quantified since variations in relaxation rates have not been accounted for. (b) The competition experiment shown in Figure 4 was done by using a minor variation of this protocol in which aliquots of allyltri-*n*-butylstannane were mixed in and the mixture was observed after the reaction of each aliquot was complete.

(6) These addition products must have a molecular composition corresponding to $ROSnCl_3$, although their exact structures are unknown. The chemical shifts suggest that they are not monomeric.

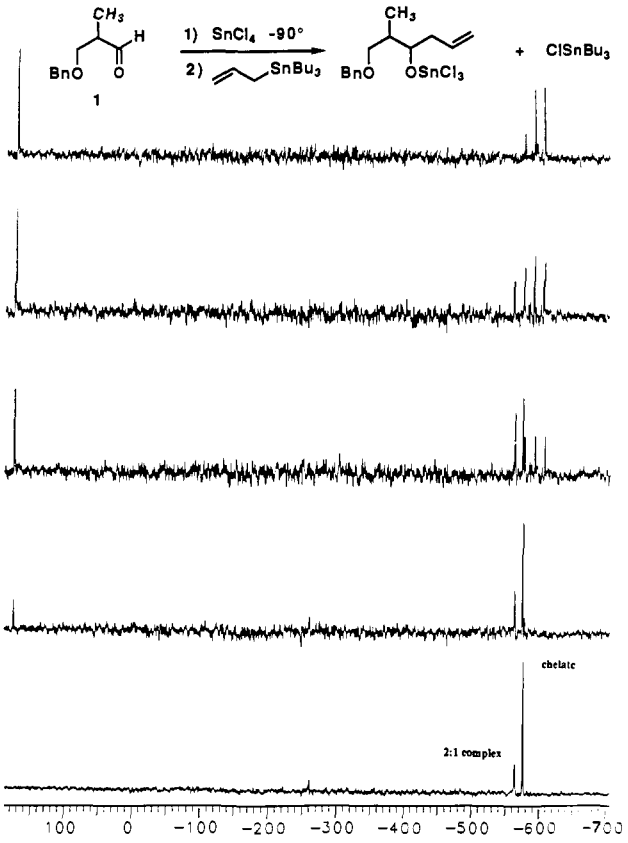

Figure 4. Competition experiment between 2:1 complex and chelate reacting with allylstannane observed by ^{119}Sn NMR at −90 °C.

Since equilibrium mixtures of chelate and 2:1 complex can be prepared from **1** simply by variations in stoichiometry, the relative reactivity of chelate and 2:1 complex can be be directly investigated with this substrate. Such competition experiments in which increments of allyltributylstannane are added to mixtures of chelate and 2:1 complex reveal that the chelate is in fact more reactive but that the rate difference is modest[7] (Figure 4).

The other extreme is represented by the OTBS derivative **2**, which forms only 2:1 complexes with $SnCl_4$.[1c] With an equimolar amount of $SnCl_4$, the 2:1 complex is observed at −566 ppm, and an equivalent amount of free $SnCl_4$ remains. Upon admixture with the allylstannane at −90 °C (note Figure 5), transmetalation with free $SnCl_4$ occurs very rapidly and is complete before any consumption of the 2:1 complex is observed. Products then grow in over time without any detectable transmetalation via the 2:1 complex.[8] Additional evidence that this is the case is shown in Figure 6. Thus, when the 2:1 complex of **2** is allowed to react with allyltri-*n*-butylstannane in the *absence* of free $SnCl_4$, no transmetalation products are observed.

The situation is somewhat intermediate with the β-benzyloxy aldehyde **3**, which is isomeric with **1**, but more sterically hindered at the ether oxygen. As is shown in Figure 7, three signals are observed in the ^{119}Sn NMR of a 1:1 mixture of $SnCl_4$ and **3** at −90 °C: free $SnCl_4$ (−155 ppm), a 2:1 aldehyde–$SnCl_4$ complex (−562 ppm), and a bidentate chelate (−580 ppm). Upon addition of allyltri-*n*-butylstannane, transmetalation with free $SnCl_4$ is virtually instantaneous, and the ratio of 2:1 complex to chelate changes significantly as $SnCl_4$ is removed from the equilibrium. Allyltrichlorostannane then disappears over time as addition products are produced. It is thus clear that much, if not all, of the reaction in this case proceeds via the transmetalated species and also that the 2:1 complex is present in significant concentration

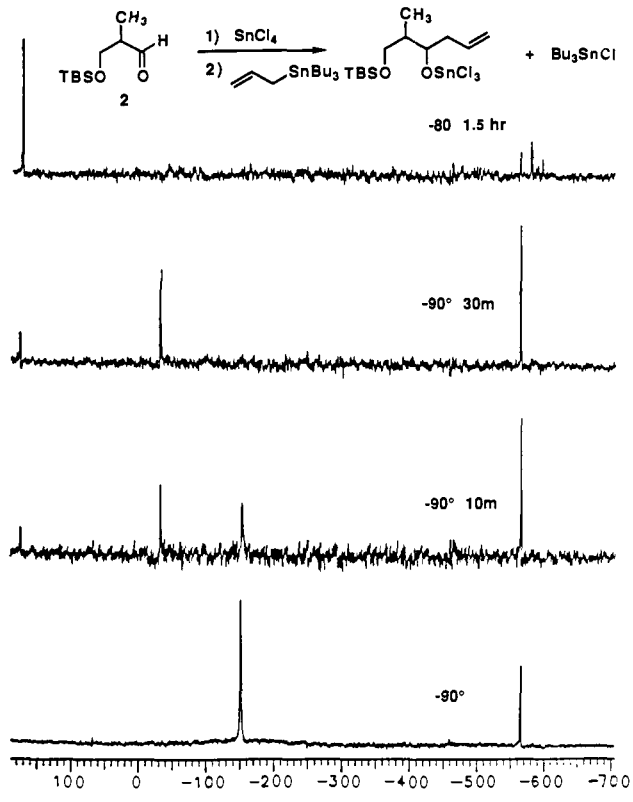

Figure 5. Reaction of $SnCl_4$ "complex" of aldehyde **2** with allyltri-*n*-butylstannane at 1:1 $SnCl_4$–aldehyde stoichiometry.

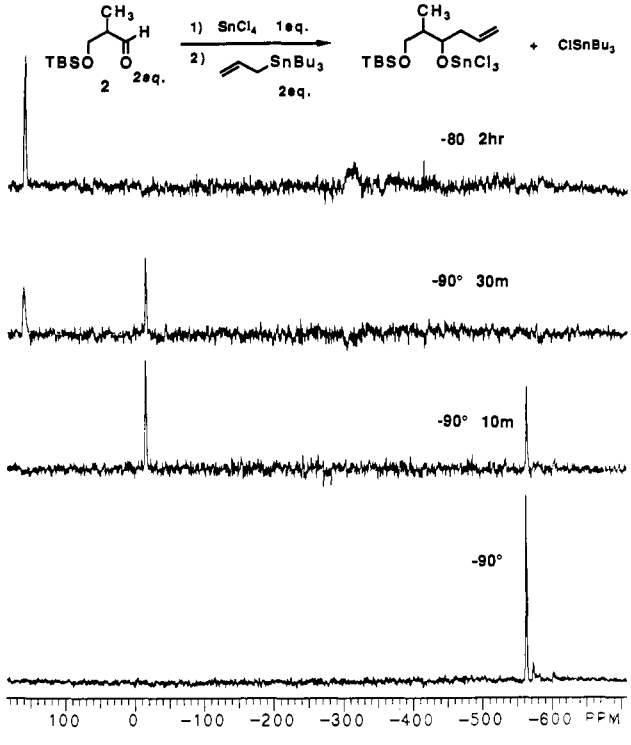

Figure 6. Reaction of 2:1 complex of β-silyloxy aldehyde **2** and $SnCl_4$ with allyltri-*n*-butylstannane observed by ^{119}Sn NMR.

(relative to chelate) as the addition reaction begins. The three substrates **1**, **2**, and **3** thus span a range of structure from "tight chelators" through "weak chelators" to "nonchelators".

Transmetalation is a phenomenon that depends critically upon the stability of complexed or chelated intermediates, which in turn depends upon aldehyde structure and temperature. The following experiment (Figure 8) nicely illustrates this point and also serves as a caveat regarding experimental technique in this area.[9] In

(7) A transient species (−578 ppm), presumably of the composition $RCHO{\cdot}SnCl_3{\cdot}OR$, is produced initially upon addition to the 2:1 complex. This material is then converted to the species that appear at −594 and −607 ppm.

(8) All additions to 2:1 complexes that we have studied show very low intensity peaks for the alkoxide addition products, with the exception of **1**.

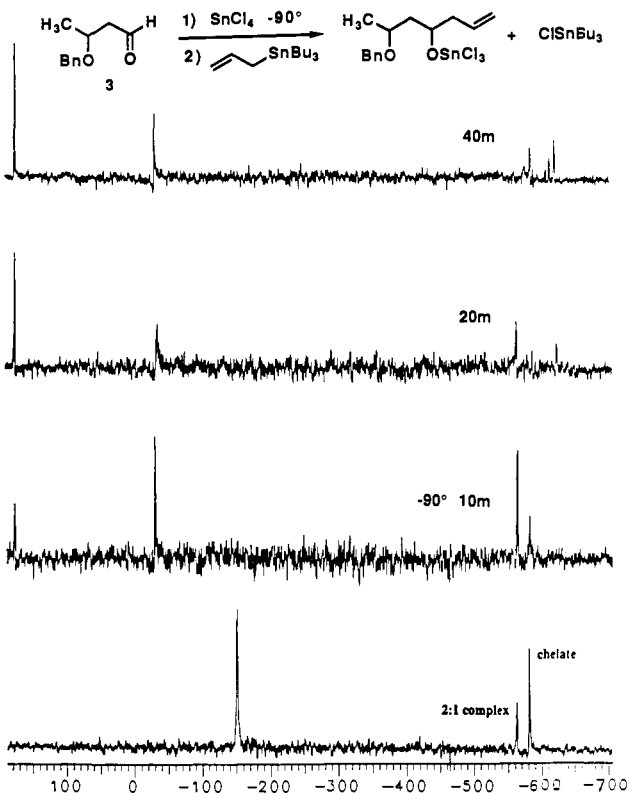

Figure 7. Reaction of 1:1 mixture of β-(benzyloxy)butanal (**3**) and $SnCl_4$ with allyltri-*n*-butylstannane at −90 °C observed by ^{119}Sn NMR.

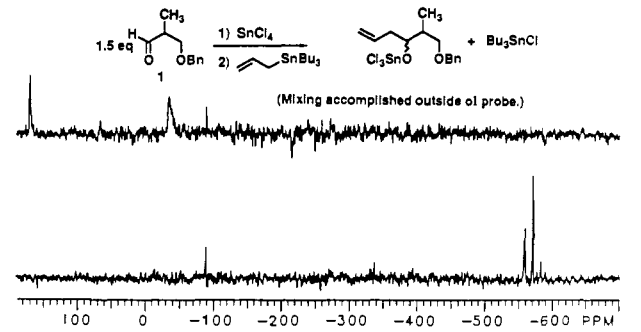

Figure 8. "Whoops experiment", NMR tube shaken outside the probe prior to acquisition.

this instance, the above experiment was repeated by using our normal protocol, except that mixing of the allylstannane with the reaction mixture was accomplished by ejecting the tube from the −90 °C probe, shaking briefly (which results in an increase in the temperature of the sample, since only the lower portion of the 16-mm tube is at −90 °C), wiping condensation from the tube, and reintroducing it into the −90 °C probe. After equilibration at −90 °C for 10 min and acquisition of data, the −567 and −573 ppm signals were completely absent, and only allyltrichlorostannane and tri-*n*-butyltin chloride were observed; hence complete transmetalation is observed in this experiment. Transmetalation reactions (*with free $SnCl_4$*) in all of these systems are much faster than additions to either chelates or 2:1 complexes.[10]

Thus, we have documented a broad range of mechanistic possibilities that can transpire in the $SnCl_4$-promoted reactions of allyltri-*n*-butylstannane with β-alkoxy aldehydes, based primarily upon stoichiometry and the ability of the β-alkoxy substituent to participate in the formation of a bidentate chelate. Similar experiments with acetaldehyde (**4**), 4-*tert*-butylbenzaldehyde (**5**), and pivaldehyde (**6**) have been reported by Denmark,[11] and their results and conclusions are in conflict with our own. In particular, these authors conclude that with 2:1 complexes $(RCHO)_2$·$SnCl_4$ metathesis with allyltrimethyl- or allyltri-*n*-butylstannane is essentially instantaneous at low (−90 °C) temperature and that addition products are formed only via the intermediacy of the transmetalated products so produced (e.g., allyltrichlorostannane or diallyldichlorostannane). Because their statements are in direct conflict with our own results, we have conducted an exhaustive reinvestigation using their substrates[12] *which clearly shows that no transmetalation with allyltri-n-butylstannane occurs directly from stable 2:1 $(RCHO)_2$·$SnCl_4$ complexes with these aldehydes.*

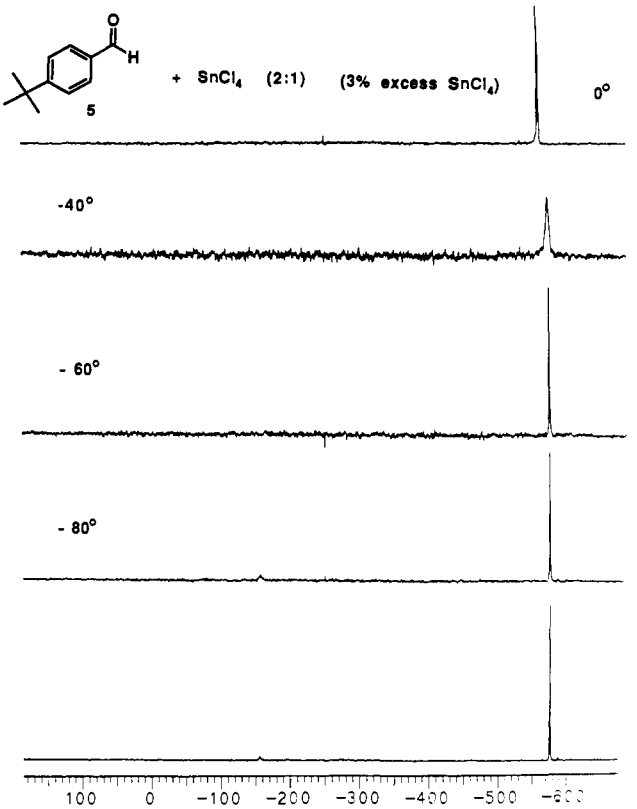

Figure 9. Spectra of the 2:1 complex of *tert*-butylbenzaldehyde (**5**) with 3% excess $SnCl_4$ from −90 to 0 °C.

We began with a study of complexation of 4-*tert*-butylbenzaldehyde (**5**) with $SnCl_4$ via ^{119}Sn NMR spectroscopy. We verify that this material forms very stable 2:1 complexes with $SnCl_4$ at 2:1 stoichiometry, and the ^{119}Sn NMR spectra are independent of temperature from −80 to 0 °C. However, in the presence of a trace of excess $SnCl_4$, ligand exchange is more rapid. Shown in Figure 9 is a VT ^{119}Sn NMR spectrum of the 2:1 complex of **5** with $SnCl_4$ (−578 ppm) in the presence of a 3% excess of $SnCl_4$. It can be seen that significant line broadening indicative of dynamic behavior is observed at −40 °C, while at 0 °C exchange is fast on the NMR time scale and the chemical shift observed for the 2:1 complex is averaged with that of the 3% of $SnCl_4$ that is present.

We next investigated the reaction of this complex with allyltri-*n*-butylstannane via ^{119}Sn NMR spectroscopy. The results of these experiments are shown in Figure 10. In contrast to the

(9) Given the relatively low thermal mass of typical NMR experiments, particularly those carried out with small volumes of solvent or at high concentrations, it is crucial that reactants be precooled to the temperature desired for the experiment prior to mixing and maintained at that temperature (or lower) during mixing. Our protocol ensures that this is the case.

(10) The work described to this point in this paper was first presented at the 193rd National Meeting of the American Chemical Society: Castellino, S.; Keck, G. E. Paper No. 16, April 5, 1987.

(11) Denmark, S. E.; Wilson, T.; Willson, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 984.

(12) We have not investigated reactions of acetaldehyde due to the expected difficulties of obtaining this material in highly pure (and anhydrous) form and since Denmark and co-workers were unable to reach meaningful mechanistic conclusions in this case.

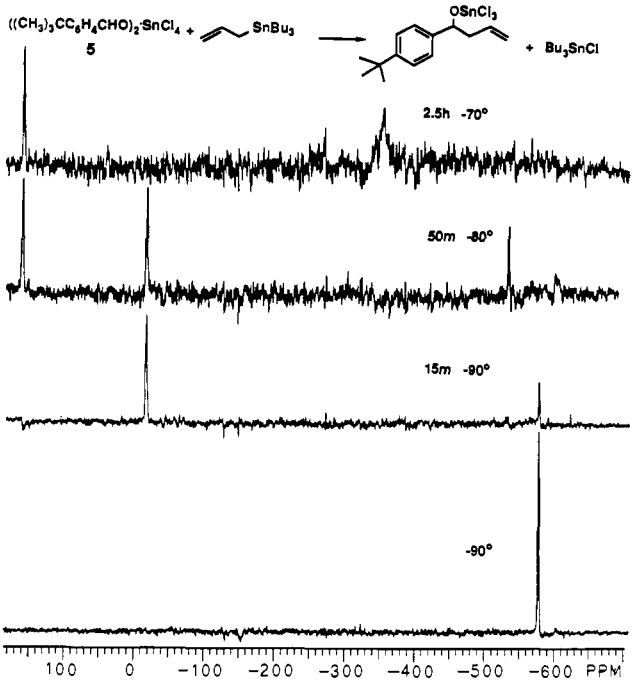

Figure 10. Reaction of 2:1 complex of *tert*-butylbenzaldehyde (**5**) and $SnCl_4$ with allyltri-*n*-butylstannane observed by ^{119}Sn NMR.

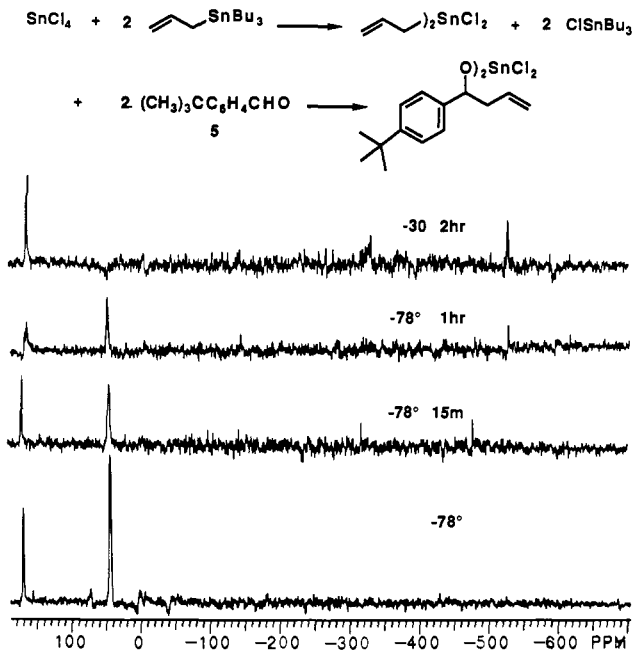

Figure 11. Reaction of diallyldichlorostannane with *tert*-butylbenzaldehyde (**5**).

claims of Denmark et al., who state that allyltri-*n*-butylstannane is consumed instantaneously (within 5 min) at −90 °C upon exposure to this complex, one can clearly see that allyltri-*n*-butylstannane (−14 ppm) *persists* in the spectrum and *is clearly evident even after 50 min at −80 °C*! No evidence for the generation of transmetalation products (e.g., allyltrichlorostannane (−36 ppm) or diallyldichlorostannane (+45 ppm)) is observed.

Denmark et al. claim that diallyldichlorostannane is produced instantaneously upon exposure of $(\mathbf{5})_2{\cdot}SnCl_4$ to allyltri-*n*-butylstannane at −90 °C. Our own control experiments clearly show that this is *not* the case and that in fact one could demonstrate the potential intermediacy of diallyldichlorostannane by rudimentary kinetics experiments. Shown in Figure 11 is the reaction of diallyldichlorostannane with **5** as monitored by ^{119}Sn NMR spectroscopy. It is clear that this substance is much less reactive than allyltri-*n*-butylstannane, as the resonance for diallyldichlorostannane is observed to persist even after ~1 h at −30 °C. *Thus this species can be discounted as an intermediate in the reaction of* $(\mathbf{5})_2{\cdot}SnCl_4$ *with allyltri-n-butylstannane, since we have documented that this material, if formed, is easily observable under the reaction conditions*, and, in fact, is considerably less reactive with respect to nucleophilic addition than is allyltri-*n*-butylstannane. Additional experiments have also been performed with allyltrichlorostannane (generated from allyltri-*n*-butylstannane and $SnCl_4$) and **5** with similar results: allyltrichlorostannane is easily observable under the reaction conditions and is considerably less reactive than allyltri-*n*-butylstannane in addition to aldehyde **5**. Thus, allyltrichlorostannane can still be observed after 2 h at −50 °C in the presence of stoichiometric amounts of **5**. *Thus, this material can also be discounted as an intermediate in the reaction of* $(\mathbf{5})_2{\cdot}SnCl_4$ *with allyltri-n-butylstannane.* Moreover, since the diallyldichloro reagent must be produced by reaction of allyltrichloro- with allyltri-*n*-butylstannane, it seems curious that this intermediate was not observed in the Denmark experiments.

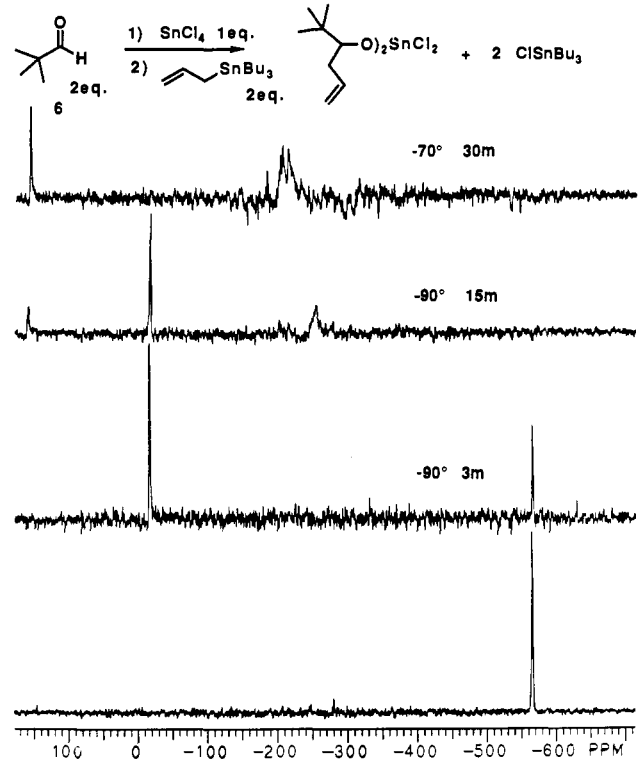

Figure 12. Reaction of 2:1 complex of pivaldehyde (**6**) and $SnCl_4$ with allyltri-*n*-butylstannane monitored by ^{119}Sn NMR.

A very simple and independent test of the Denmark mechanism (i.e., instantaneous and complete transmetalation prior to reaction with **5**) that does not rely on direct observation of reaction intermediates is possible via ^{119}Sn NMR simply by inclusion of an internal standard. Thus, the Denmark mechanism requires an immediate "burst" of Bu_3SnCl in the ^{119}Sn NMR spectrum, which then remains constant as addition products are produced. Thus, the reaction of allyltri-*n*-butylstannane with $(\mathbf{5})_2{\cdot}SnCl_4$ was repeated in the presence of tetrabutylstannane as internal standard. No "burst" of Bu_3SnCl was observed—allyltri-*n*-butylstannane disappears slowly over time and the signal for Bu_3SnCl grows in accordingly, consistent only with the production of Bu_3SnCl as a consequence of the formation of addition products. Again, resonances for allyltrichlorostannane and diallyldichlorostannane were not observed.

Parallel experiments with pivaldehyde (**6**) have also been conducted; again, no evidence for transmetalation from $(\mathbf{6})_2{\cdot}SnCl_4$ was observed (see Figure 12). Finally, we have also examined such reactions via ^{13}C NMR spectroscopy—the technique employed by Denmark.[11] Although this technique is not as straightforward as ^{119}Sn NMR due to some overlapping resonances

for allyltri-*n*-butylstannane and tri-*n*-butyltin chloride (and lower sensitivity—0.1% natural abundance vs 8.7% for ^{119}Sn), the chemical shift for the allylic carbon of allyltri-*n*-butylstannane is highly diagnostic (9.2 ppm). Again, this signal was observed to persist for more than 1 h at −90 °C upon reaction of $(5)_2$·$SnCl_4$ with allyltri-*n*-butylstannane, in marked contrast to the claims of Denmark and co-workers.

In summary, we find no evidence that transmetalation pathways intervene in the reactions of coordinatively saturated $SnCl_4$–aldehyde complexes with allyltri-*n*-butylstannane at low temperature, be they chelates or 2:1 complexes. We believe that our experiments demonstrate quite convincingly that transmetalation is only important under conditions where free $SnCl_4$ is present or where fast ligand exchange opens up vacant coordination sites on the metal, conditions that are identifiable via variable-temperature ^{119}Sn NMR spectroscopy of the complexes in the absence of allylstannane. The potential presence of free $SnCl_4$ cannot be addressed in the Denmark experiments which utilize ^{13}C observation. Although the reasons for the discrepancy between our results and those obtained by Denmark are not clear, we believe that differences in internal temperature are most probably responsible.

Acknowledgment. Financial support of this research by the National Institutes of Health through Grant GM-28961 is gratefully acknowledged. We also acknowledge the exchange of information between the Denmark group and our own on various occasions regarding the discrepancies between our results.

The Chemistry of Rhenium and Tungsten Porphyrin Complexes in Low Oxidation States. Synthesis and Characterization of Rhenium and Tungsten Porphyrin Dimers Containing Metal–Metal Multiple Bonds

James P. Collman,* James M. Garner, and L. Keith Woo

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received November 21, 1988*

Abstract: The coordination chemistry of rhenium and tungsten porphyrin complexes in low oxidation states is presented. $W^{IV}(Por)(Cl)_2$, $W^{II}(Por)(H_5C_6C{\equiv}CC_6H_5)$, and $W^{II}(OEP)(PEt_3)_2$ complexes [Por = 5,10,15,20-tetra(4-tolyl)porphyrin (TTP) or 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) dianions] were found to be similar to the analogous molybdenum porphyrin complexes by spectroscopic and magnetic measurements. The tungsten acetylene and phosphine complexes are suitable precursors to the diamagnetic, quadruply bonded $[W^{II}(OEP)]_2$ complex via the solid-state vacuum pyrolysis reaction previously developed for the $[Ru^{II}(Por)]_2$, $[Os^{II}(Por)]_2$, and $[Mo^{II}(Por)]_2$ complexes. The triply bonded $[Re^{II}(Por)]_2$ compounds were prepared by a similar pyrolysis reaction of the $Re^{II}(Por)(PEt_3)_2$ complexes. Population of a paramagnetic excited state for $[Re^{II}(OEP)]_2$ is postulated from solution ^1H NMR data but solid-state magnetic measurements indicate this dimer is diamagnetic. $[Re^{II}(OEP)]_2$ can be oxidized to yield mono- and dicationic dimeric complexes. UV–visible and vibrational spectroscopies indicate that these oxidations occur at the metal–metal bond rather than the porphyrin ligand.

Dimeric metalloporphyrin complexes joined by a metal–metal multiple bond represent a new class of binuclear metal complexes with M_2L_8 structures. As detailed earlier,[1] the porphyrin ligand allows opportunities and advantages to investigate the detailed nature of these bonds in ways that are unavailable with other classical inorganic ligands. Examples include the use of the porphyrin ligand to investigate the paramagnetism of the neutral ruthenium and osmium dimers by ^1H NMR,[2] as well as the use of meso-substituted porphyrins to obtain unique solution evidence for the existence of a δ bond in the molybdenum dimer.[3]

Our goal in this research has been to prepare an entire family of such compounds with all the formal metal–metal bond orders represented by substituting different divalent metal ions within the porphyrin macrocycle. Other classes of compounds that rival the dimetalloporphyrin family in terms of different metals, valence d electron counts, and bond orders are often supported with bridging bidentate ligands. An example of such a family is the dimetal tetracarboxylates. However, bridging ligands strongly influence the metal–metal bonding interaction, and systematic trends due solely to the metal–metal bonding are often masked by the ligand. The porphyrin ligand is more innocent in the metal–metal interaction by virtue of its nonbridging, rigid, square-planar geometry.[4] Hence, systematic trends of the structural, spectroscopic, and chemical properties within this family of compounds will likely be more salient, leading to new insights and questions concerning the nature of multiple bonds between metal atoms. Presently, the molybdenum,[1] ruthenium,[2] osmium,[1] rhodium,[5] and iridium[6] porphyrin dimers have been prepared; however, none of the divalent, four-coordinate, 3d metalloporphyrins show any tendency to form metal–metal bonded complexes. Therefore, completion of this family of compounds required the synthesis of the analogous rhenium and tungsten complexes.

Although rhenium and tungsten porphyrin complexes were first prepared 15 years ago, almost no low-valent complexes are described in the literature.[7] Herein, we report the coordination

(1) Collman, J. P.; Barnes, C. E.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7684.
(2) Collman, J. P.; Barnes, C. E.; Sweptson, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500.
(3) Collman, J. P.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 2592.
(4) Obviously, the macrocyclic ligand is not totally innocent in the metal–metal bonding interaction. Nonbonding repulsive forces between the two porphyrin moieties may indeed weaken the metal–metal bond to some degree.
(5) (a) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Am. Chem. Soc.* **1977**, *99*, 3869. (b) Wayland, B. B.; Newman, A. R. *Inorg. Chem.* **1981**, *20*, 3093.
(6) Del Rossi, K. J.; Wayland, B. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1653.

0002-7863/89/1511-8141$01.50/0