SnCl₄(4-t-BuC₆H₄CHO)₂. X-ray Crystal Structure, Solution NMR, and Implications for Reactions at Complexed Carbonyls[1a]

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Received November 28, 1986

The reaction of allylic organometallic reagents with aldehydes (eq 1) has emerged as one of the more synthetically useful methods

for acyclic steroselection.[2] It is also a reaction that has aroused considerable interest in mechanistic detail since it shows divergent behavior depending upon the metal, double-bond geometry, and reaction conditions. We have recently reported the results of studies with models 1a and 1b which were desigened to clarify the origins of stereoselectivity in these reactions[3] (Scheme I). Specifically, those models allowed an unambiguous correlation between product stereochemistry and transition-state geometry. Thus, the syn alcohol 2 and the anti alcohol 3 arise from synclinal and antiperiplanar transition states, respectively. For 1a we noted variable syn selectivity (47–99%) with a strong dependence on the nature of the Lewis acid. This was interpreted in terms of the bulk of the Lewis acid–aldehyde complex (assumed to be of E configuration). We describe herein several studies on the effects of experimental variables (concentration, stoichiometry, and "spectator groups") on the stereoselectivity of cyclization. These data support our earlier hypothesis on the nature of Lewis acid–aldehyde complexation (and its importance in stereocontrol) with evidence from X-ray crystallography and NMR.[4]

All of the studies were carried out on model 1a with SnCl₄ as the Lewis acid. We were puzzled by the poor selectivity with this reagent (syn/anti 47/53) in our earlier work and suggested that the well-known 1:2 complexation stoichiometry (SnCl₄/Lewis base)[5] was responsible for the greater "effective steric bulk" of the Lewis acid. Given this hypothesis we investigated the effects

(1) (a) Presented at the 20th Great Lakes Regional Meeting, Milwaukee, WI, June 1986, ORGN 322. (b) Fellow of the Alfred P. Sloan Foundation (1985–1987); NSF Presidential Young Investigator (1985–1990). (c) Taken in part from: Weber, E. J. Ph.D. Thesis, University of Illinois, Urbana, 1985.

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(5) That benzaldehyde forms a 1:2 complex with SnCl₄ was first documented by Pfeiffer. The generality of this mode of complexation with neutral Lewis bases is well established. (a) Pfeiffer, P. Annalen 1910, 376, 285. (b) Filippini, F.; Susz, B.-P. Helv. Chim. Acta 1971, 54, 835. (c) Dumas, J. M.; Gomel, M. Bull. Soc. Chim. Fr. 1974, 10, 1885. (d) Beattie, I. R. Quart. Rev. 1963, 17, 382.
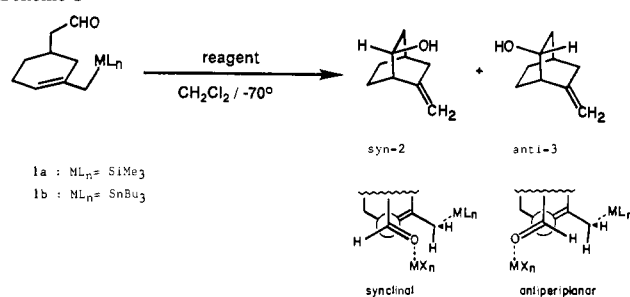
Scheme I

1a : MLₙ= SiMe₃
1b : MLₙ= SnBu₃

Table I. Concentration Effects on Stereochemistry in Conversion of 1a → 2/3[a]

entry	Lewis acid	concn of 1a, M	% convsn[b]	syn (2)/ anti (3)[c]
1	SnCl₄	0.25	89	44/56
2	SnCl₄	0.05	82	56/44[d]
3	SnCl₄	0.005	85	64/36
4	SnCl₄	0.0005	100	86/14
5	BF₃·OEt₂	0.28	89	82/18
6	BF₃·OEt₂	0.05	87	79/21
7	BF₃·OEt₂	0.005	93	84/16

[a] All reactions employed 1.1 equiv of Lewis acid in CH₂Cl₂ solution at −78 °C. [b] The conversions are calculated for products by comparison to decane as an internal standard. 1a was completely consumed in all runs. [c] Averages of at least three runs with ratios ±3%. [d] This measurement was less reproducible ranging from 46/54 to 63/37.

Table II. Stoichiometry Effects on Stereochemistry of Conversion of 1a → 2/3[a]

entry	Lewis acid	equiv	% convsn[b]	syn (2)/ anti (3)[c]
1	SnCl₄	0.25	83	51/49
2	SnCl₄	0.55	89	42/58
3	SnCl₄	1.10	82	56/44[d]
4	SnCl₄	10.0	93	60/40
5	SnCl₄	25.0	90	75/25
6	BF₃·OEt₂	0.55	85	92/8
7	BF₃·OEt₂	1.00	87	79/21
8	BF₃·OEt₂	10.0	86	80/20

[a] All reactions were run at 0.05 M in 1a in CH₂Cl₂ at −78 °C. [b] Calculated for products by comparison to decane as an internal standard. [c] See Table I. [d] See Table I.

Table III. Dummy Ligand Effects on Stereochemistry of Conversion of 1a → 2/3[a]

entry	equiv	time, min	% convsn[b]	syn (2)/ anti (3)[c]
1	1.1	10	41	90/10
2	1.1	60	80	87/13
3	1.1	360	88	72/28
4	5.0	360	97	70/30

[a] The Lewis acid used was SnCl₄·(SMe₂)₂ (1.0 M in CH₂Cl₂). All reactions were run at 0.05 M concentration in CH₂Cl₂ at −78 °C. [b] Calculated for products by comparison to decane as an internal standard. [c] See Table I.

of those experimental factors which might be expected to influence the nature of that complex and observed the changes in stereoselectivity. The results of concentration effects on stereochemistry are summarized in Table I. As the solution became more dilute, we noted than an increasing proportion of the syn product 2 was forming in preference to 3 to the point where SnCl₄ and BF₃·OEt₂ gave the same ratio. We interpret this trend in terms of the expected increase in the relative amount of the 1:1 complex at higher dilution. This complex should be kinetically competent and significantly less bulky.[6] The lesser bulk provides for a less

(6) (a) The "effective bulk" of the 1:2 vs. 1:1 complexes clearly depends on the geometry of complexation around oxygen and tin. (b) Zahrobsky, R. F. J. Am. Chem. Soc. 1971, 93, 3313.
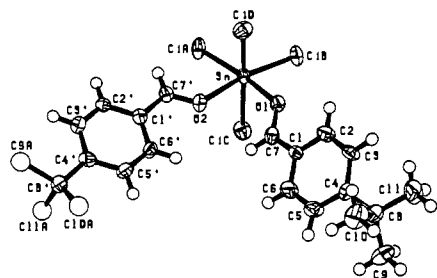
Communications to the Editor

J. Am. Chem. Soc., Vol. 109, No. 8, 1987 2513

Figure 1. ORTEP plot of SnCl$_4$·2L at the 35% probability level.

encumbered synclinal transition state (MX$_n$ is smaller). Thus, the product ratio reflects the weighted average of stereochemical profiles for both 1:2 and 1:1 complexes. In support of this hypothesis, BF$_3$·OEt$_2$ showed no concentration effects on stereochemistry over a 55-fold range. This is expected since BF$_3$ can only form 1:1 complexes.[7]

Other variables that influence complexation stoichiometry were investigated. The effects of reagent-to-substrate stoichiometry were studied and the results appear in Table II. At substoichiometric levels of SnCl$_4$ (entry 1) which assume saturation of the SnCl$_4$ (i.e., 1:2 complexation, vide infra), little change in reaction stereochemistry compared to 1 equiv (entry 3) was noted. However, with increasing amounts of SnCl$_4$ (entries 4 or 5) the proportion of isomer **2** again increased. This further supports the hypothesis that the 1:1 complex (expected to exist at high SnCl$_4$:**1a** ratios) has a more syn-selective profile than the 1:2 complex. Again, BF$_3$·OEt$_2$ showed no such dependence, as would be expected.

In a final series of experiments we investigated the use of a "dummy ligand" on SnCl$_4$ to replace the other **1a** in the 1:2 complex. We chose SnCl$_4$·(SMe$_2$)$_2$ since Merbach has shown Me$_2$S to be a better ligand than acetone.[8] The results of these experiments (Table III) again show an increase in the selectivity for the syn diastereomer **2**. This observation is in line with expectation for the heterogeneous complex[9] which should be less sterically demanding than SnCl$_4$·2(**1a**). Due to the much weaker Lewis acidity of SnCl$_4$·(SMe$_2$)$_2$, these reactions were much slower. As a result we detected an interesting change in selectivity as a function of time, suggesting that the nature of the reactive complex changes during the reaction.[10]

The interpretation of the data from these experiments implicates a special significance to the 1:2 nature of complexation with SnCl$_4$ and requires that we know more about the structural details. Despite the considerable body of crystallographic data on Sn-(IV)/Lewis base pairs,[11] we found no example of 1:2 complexes of aldehydes to SnCl$_4$ or any other Lewis acids.[12] Figure 1 shows an ORTEP drawing of the complex SnCl$_4$·(4-t-BuC$_6$H$_4$CHO)$_2$ (SnCl$_4$·2L).[13] Several features of the structure are noteworthy.[14]

(7) (a) Landolf, M. C. *Acad. Sci.* **1878**, *86*, 671. (b) Lombard, R.; Stephan, J.-P. *Bull. Soc. Chim. Fr.* **1957**, 1369. (c) Rabinovitz, M.; Grinvald, A. *J. Am. Chem. Soc.* **1972**, *94*, 2724. (d) Reetz, M. T.; Hullman, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *Ibid.* **1986**, *108*, 2405.

(8) (a) Ruzicka, S. J.; Merbach, A. E. *Inorg. Chim. Acta* **1976**, *20*, 221. (b) Ruzicka, S. J.; Merbach, A. E. *Ibid.* **1977**, *22*, 191. (c) Ruzicka, S. J.; Favez, C. M. P.; Merbach., A. E. *Ibid.* **1977**, *23*, 239. (d) Knight, C. T. G.; Merbach, A. E. *J. Am. Chem. Soc.* **1984**, *106*, 804. (e) Knight, C. T. G.; Merbach, A. E. *Inorg. Chem.* **1985**, *24*, 576.

(9) We assume that, at least initially, cyclization is proceeding via a complex SnCl$_4$·**1a**·Me$_2$S. The slow step may be either cyclization or displacement of Me$_2$S.

(10) All control experiments on reversibility have demonstrated that these reactions are under kinetic control.

(11) A search of the Cambridge Crystallographic Data Center Database for compounds containing Sn and Cl produced 238 hits, many of which were salts of SnCl$_6^{2-}$. Nine structures with carbonyl ligands were found. See also: Britton, D.; Dunitz, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2971.

(12) We are aware of only two other X-ray crystal structures of aldehyde–Lewis acid complexes both of which are 1:1. BF$_3$·benzaldehyde: ref 7d. (CH$_3$)$_2$SnCl$_2$-salicylaldehyde: Cunningham, D.; Douek, I.; Frazer, M. J.; McPartlin, M.; Matthews, J. D. *J. Organomet. Chem.* **1975**, *90*, C23.

(13) This compound was fully characterized by ¹H, ¹³C, and ¹¹⁹Sn NMR, IR, MS, and elemental analysis. It is indefinitely stable at <0 °C but decomposes slowly even in the solid state under argon at 20 °C.

Table IV. VT ¹³C NMR with L and SnCl$_4$[a]

	δ(C-1),[b] SnCl$_4$:L			
T, °C	0:1	1:2[c]	1:4	4:1
20	191.71	198.77	198.79	195.79
0	191.82	198.92		
−20	191.97	198.99		195–196[d]
−40	192.11	199.05		e
−60	192.38	199.69	199.51	193.20/199.79
−80	192.57	199.74	199.79	193.40/199.79

[a] All experiments were run at 0.25 M in CDCl$_3$/CD$_2$Cl$_2$ 3:5. [b] δ are given in ppm relative to CDCl$_3$ (77.05). [c] Analytically pure complex was used. [d] Broad signal. [e] No signal observed due to exchange.

Table V. VT ¹H NMR with L and SnCl$_4$[a]

	δ[H-C(1)],[b] SnCl$_4$:L				
T, °C	0:1	1:2[c]	1:4	4:1	10:1
20	9.968	10.041	10.010	9.852	9.788
0	9.971	10.047	10.011	9.881	9.809
−20	9.978	10.050	10.013	9.913	9.848
−40	9.982	10.050	10.015	9.946	9.880
−60	9.988	10.052	10.018	9.983	9.920
−80	9.997	10.056	9.992/10.054[d]	10.049[e]	10.029[f]

[a] All experiments were run at 0.25 M in CDCl$_3$/CD$_2$Cl$_2$ 3:5. [b] δ are given in ppm relative to (CH$_4$)$_4$Si (0.00). [c] Analytically pure complex was used. [d] Integrated ratio (54:46). [e] New signal at δ 9.7, 14% of major peak. [f] New signal at δ 9.7, 25% of major peak.

First, the two aldehyde units are not identically oriented with respect to the tin core; nonetheless, the Sn atom resides very nearly in the plane of each carbonyl group (2° and 4° torsional angles). Second, the C–O–Sn array is decidedly bent, suggesting coordination through an sp²-type lone pair on oxygen (128.0° and 126.2).[15] *Third, the two aldehydes are cis on the Sn octahedron, describing an acute O–Sn–O angle of 78.9°.*[16] The preference for the cis configuration of SnCl$_4$·2L can be understood in view of the electronegativity of the sp²-oxygen ligand. Merbach[8b] and Drago[17a] have explained the tendency toward the cis orientation in complexes with ligands of similar electronegativity by invoking d²sp³ hybridization (equivalent s character). The cis isomer minimzes the splitting between d$_z^2$ and d$_{x-y}^2$ orbitals.[17b] This information illustrates the significance of the presence of the second ligand on the chemical environment of the other complexed aldehyde.

To gain information about the structure of the complex in solution we have carried out extensive, variable-temperature ¹H and ¹³C NMR experiments with SnCl$_4$ and L. The ¹³C NMR data is highlighted in Table IV which shows only the shift of the carbonyl carbon at various temperatures and with varying ratios of SnCl$_4$ to L. The most striking features are (1) the presence of a single complexed species below the exchange limit (−40 °C), (2) the lack of a strong temperature dependence of chemical shift for 1:2 or 4:1 mixing (1.5% and 1.9% change over a 100 °C range), and (3) the presence of only free L and SnCl$_4$·2L below −60 °C with substoichiometric amounts of SnCl$_4$. The VT ¹H NMR data (Table V) are in agreement and also provided additional insights. The aldehydic proton, H–C(1), shifts downfield upon complexation and the 1:2 complex shows little tendency to dissociate. With 0.25 equiv of SnCl$_4$ both free L and the SnCl$_4$·2L could be detected at −80 °C, and the integrated ratio (54:46) confirms the stoi-

(14) A complete detailed report of the crystallographic parameters, data collection and reduction, and structure solution and refinement along with structural parameters is provided as supplemental material.

(15) This is consistent with picture of complexation with the other two complexed aldehyde crystal structures[12] but is in contrast to the π-type complexation observed for ethyl acryloyl lactate with TiCl$_4$: Poll, T.; Metter, J. O.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 112.

(16) This is in contrast to the 1:2 complex of SnCl$_4$ and ethyl cinnamate which is trans. Lewis, F. D.; Oxman, J. D.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 466.

(17) (a) Hill, J. C.; Drago, R. S.; Herber, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 1644. (b) Ballhausen, L. J. *Introduction to Ligand Field Theory*; McGraw-Hill: New York, 1962; pp 106–107.

chiometry of the complex.[18]   Interestingly with 4 equiv of $SnCl_4$, H–C(1) moved upfield at 20 °C. Cooling to –80 °C revealed the presence of a new signal at δ 9.7 (14% of relative intensity)[19] in addition to $SnCl_4$·2L which we assign to $SnCl_4$·L. This assignment is supported by the experiment with 10 equiv of $SnCl_4$ in which the signal at δ 9.7 increased to 25% relative intensity. Taken together these data suggest that (1) L is fully complexed at 20 °C with 0.5 equiv of $SnCl_4$, (2) the complexation equilibrium is temperature independent, (3) 1:2 complexation is preferred in solution, and (4) the 1:1 complex is in equilibrium with the 1:2 complex at high $SnCl_4$:L ratios and is detectable at –80 °C in significant concentration.

In summary we have established that the structure of the Lewis acid–aldehyde complex is playing a stereochemically significant role in allylmetal aldehyde condensations. Furthermore, we have demonstrated that the observed dependence of stereochemistry on experimental variables can be understood by the change in structure of the reactive intermediates and suggest that the cis coordination geometry in $SnCl_4$·2L is responsible for the stereochemical variability. The unambiguous structural determination of the species in solution and identification of the 1:1 complex are currently under investigation.

Supplementary Material Available: Listing of atomic coordinates, bond lengths, bond angles, and positional and thermal parameters for $SnCl_4$·2L (43 pages); tables of structure factors for $SnCl_4$·2L (11 pages). Ordering information is given on any current masthead page.

(18) Theoretically with 0.25 equiv of $SnCl_4$ the ratio of free to complexed L is 50:50 for $SnCl_4$·2L and 75:25 for $SnCl_4$·L.

(19) Percent relative intensity is defined with respect to the major peak for $SnCl_4$·2L = 100%.

An Unbridged Triple Bond Uniting d^6 Mo(0) and d^2 Mo(IV) Atoms: $Mo_2(O\text{-}i\text{-}Pr)_4(dmpe)_2$

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Received January 15, 1987

Probably of all the metals, molybdenum shows the greatest propensity to form M–M multiple bonds, and there are now scores of structurally characterized compounds containing the central d^4 Mo(II)–d^4 Mo(II) unit with the M–M MO bonding configuration $\sigma^2\pi^4\delta^2$.[1] The formation of the M–M quadruple bond requires an eclipsed or near-eclipsed conformation of two square-planar ML_4 units as seen in the structures of $Mo_2(O_2CR)_4$ and $Mo_2X_4(PR_3)_4$ compounds, where X = Cl, Br, and I.[1] The use of the bidentate phosphine dppe (dppe = $Ph_2PCH_2CH_2PPh_2$) leads to α and β isomers for $Mo_2Cl_4(dppe)_2$ compounds.[2] In the α isomer, the dppe ligands chelate, one to each molybdenum atom, such that the near-eclipsed $Mo_2Cl_4P_4$ unit is achieved. In the β isomer, the dppe ligands span the Mo–Mo bond and impart a staggered arrangement of the two $MoCl_2P_2$ units.[3] The latter
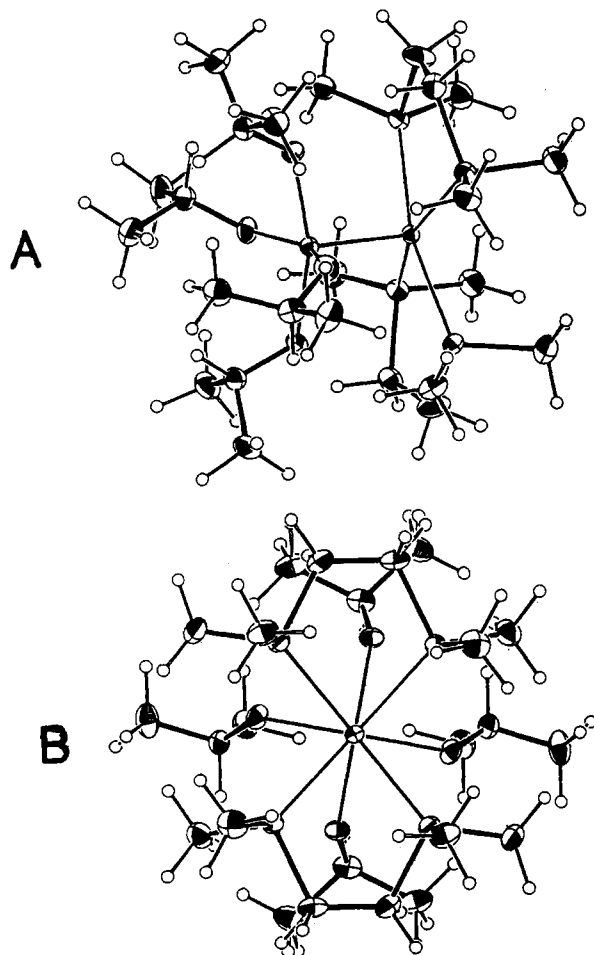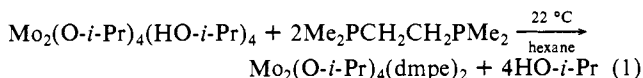

Figure 1. Two ORTEP views of the $Mo_2(O\text{-}i\text{-}Pr)_4(dmpe)_2$ molecule. The molecule has a crystallographically imposed C_2 axis coincident with the M–M bond. Pertinent distances (Å) and angles (deg) averaged where appropriate are Mo–Mo = 2.236 (1), Mo–O = 2.00 (1), Mo–P = 2.438 (1), Mo–Mo–O = 103.8 (1) and 98.9 (1), Mo–Mo–P = 98.0 (1) and 100.8 (1), Mo–O–C = 128 (1).

geometry has a profound effect on the δ orbital since for a perfectly staggered arrangement (P–Mo–Mo–P torsion angle = 45°) d–d overlap goes to zero for the δ bond. Recently these types of staggered d^4–d^4 dinuclear compounds have been the subjects of considerable interest in terms of assignments of the $\delta \rightarrow \delta^*$ transition, their magnetic properties, and the relationship between M–M distance and δ overlap.[3-5]

We have prepared and characterized compounds of formula $Mo_2(OR)_4L_4$ (R = i-Pr, L = HO-i-Pr and py; R = Np, L = $HNMe_2$ and PMe_3).[6] These compounds contain d^4 Mo(II)–d^4 Mo(II) centers with an essentially eclipsed $Mo_2O_4L_4$ skeleton. The π-donor alkoxides lengthen and labilize the Mo–Mo quadruple bond. We wished to compare the chemistry of the alkoxide-supported Mo_2^{4+} unit in both its eclipsed and staggered forms. In an attempt to prepare an example of the latter, we carried out the reaction shown in eq 1, which gave the title compound in

$$Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4 + 2Me_2PCH_2CH_2PMe_2 \xrightarrow[\text{hexane}]{22\ °C}$$
$$Mo_2(O\text{-}i\text{-}Pr)_4(dmpe)_2 + 4HO\text{-}i\text{-}Pr \quad (1)$$

essentially quantitative yield. A convenient alternate synthesis involves the reaction between $Mo_2(i\text{-}Bu)_2(NMe_2)_4$, i-PrOH (>4 equiv), and dmpe (2 equiv) in a hydrocarbon solvent. This obviates

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(2) Best, S. A.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 99.

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(4) Campbell, F. L.; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1985**, *24*, 177.

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(6) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 1153.