were not located, they are probably bridging the basal osmium atoms since observed Os–Os distances are appropriate for such an arrangement: Os(1)–Os(2) = 2.913 (1) Å, Os(1)–Os(3) = 2.917 (1) Å, Os(2)–Os(3) = 2.919 (1) Å.[13-18]

A nearly linear BCO unit [∠178.0 (2)°] is present in I and the CO distance, 1.145 (15) Å, is typical for a carbonyl group. The BC distance, 1.469 (15) Å, is short compared to the B–C distances in BH_3CO, $B_2H_4(CO)_2$, and B_3H_7CO (1.52–1.57 Å),[19-21] compounds that tend to lose CO with relative ease compared to I. This could reflect significant back bonding between the e orbitals of boron and the e* orbitals of CO, with electron density being furnished by the Os_3B cluster unit. However, if such back bonding is significant, it is not reflected in the CO stretching frequency of the unique carbonyl on boron, 2120 cm^{-1} (tentatively assigned), since this value is larger than expected[19] but is below the stretching frequencies observed in the borane carbonyls (2163–2140 cm^{-1}) cited above.

Work on $(\mu\text{-}H)_3(CO)_9Os_3BCO$ with respect to examining its derivative chemistry is in progress.

Acknowledgment. We thank NSF for support of this work (Grant CHE79-18149). We also thank J. R. Shapley for helpful conversations.

Supplementary Material Available: Tables of selected bond distances, bond angles, positional parameters, thermal parameters, and observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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$Mo_2(SC_6H_2Me_3)_6$. The First Example of a Compound Containing a Mo–Mo Triple Bond Supported by Six Mercaptido Ligands

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Homoleptic compounds of formula $X_3Mo\equiv MoX_3$ are known for X = bulky β-elimination-stabilized alkyls (CH_2CMe_3, CH_2SiMe_3), NMe_2, and OR (R = a bulky alkyl or trialkylsilyl group, e.g., *t*-Bu, *i*-Pr, CH_2-*t*-Bu, $SiMe_3$, $SiEt_3$, etc.).[1,2] We have wondered for some time whether this series could be extended to include mercaptido, SR, ligands. Though there was no reason to believe that such compounds could not exist, our initial synthetic attempts were thwarted by problems arising from molybdenum's high affinity toward sulfur, facile C–S bond cleavage, polymerization by μ-SR formation, and oxidation of the Mo_2^{6+} center.[3]

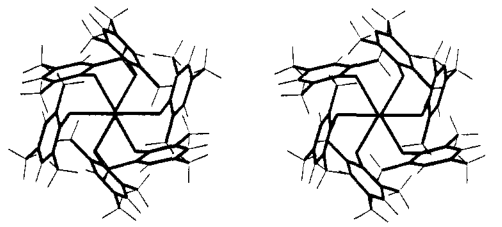

Figure 1. Stereoview of the $Mo_2(SC_6H_2Me_3)_6$ molecule viewed down the Mo–Mo bond. Pertinent distances (Å) and angles (deg) are Mo–Mo = 2.228 (1), Mo–S = 2.325 (2), S–C = 1.792 (5), ∠Mo–Mo–S = 96.6 (1), ∠Mo–S–C = 110.1 (2), and the torsion angle Mo–Mo–S–C = 25.5 (2).

We wish here to report a successful synthesis and our characterization of the first mercaptido member of the $X_3Mo\equiv MoX_3$ class.

Recognizing the problems associated with facile C–S bond cleavage and μ-SR formation, we chose to work with the bulky aromatic thiol, 2,4,6-trimethylbenzenethiol.[4] Reaction between hydrocarbon solutions of $Mo_2(NMe_2)_6$ and $C_6H_2Me_3SH$ (≥6 equiv) at room temperature gives an orange crystalline compound of formula $Mo_2(NMe_2)_2(SC_6H_2Me_3)_4$. Similarly, $Mo_2(OR)_6$ and $C_6H_2Me_3SH$ (≥6 equiv) yield $Mo_2(OR)_2(SC_6H_2Me_3)_4$, where R = *t*-Bu and *i*-Pr.[5] The inability to replace completely the dimethylamido and alkoxy groups is interesting and could be due to steric factors, electronic factors or both. However, we find that by first introducing two *t*-BuS ligands to the dimetal center, 1,2-$Mo_2Cl_2(NMe_2)_4$ + 2LiS-*t*-Bu → 1,2-Mo_2(S-*t*-Bu)$_2$(NMe_2)$_4$,[6] followed by reaction with $C_6H_2Me_3SH$ (≥6 equiv), we obtain the orange-red crystalline compound $Mo_2(SC_6H_2Me_3)_6$, along with an as yet uncharacterized yellow powder that is insoluble in all common hydrocarbon solvents. The latter shows bands in the IR spectrum characteristic of the $SC_6H_2Me_3$ ligand.

The compound $Mo_2(SC_6H_2Me_3)_6$ is diamagnetic and hydrocarbon soluble and shows a simple ^1H NMR spectrum.[7] The molecular structure deduced from an X-ray study[8] confirmed that this compound is a member of the $X_3Mo\equiv MoX_3$ class of compounds.[9] There is an unbridged Mo–Mo bond of distance 2.228 (1) Å, essentially the same as that found in $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$, 2.222 (1) Å.[10] The molecule has crystallographically imposed symmetry, S_6, which yields a beautiful view down the Mo–Mo bond as shown in Figure 1. The Mo–S distance, 2.325 (2) Å, is similar to that seen in Mo_2(S-*t*-Bu)$_2$(NMe_2)$_4$.[6]

We conclude that by appropriate choice of thiol and synthetic strategy, it should be possible to prepare $Mo_2(SAr)_6$ compounds in sufficient number and quantity so that their chemistry may be explored in a manner akin to that for $Mo_2(OR)_6$ compounds.[11] Further studies are in progress.[12]

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Registry No. $Mo_2(SC_6H_2Me_3)_6$, 86350-27-8; 1,2-Mo_2(S-*t*-Bu)$_2$-(NMe_2)$_4$, 83312-38-3.

Supplementary Material Available: Table of atomic coordinates for the $Mo_2(SC_6H_2Me_3)_6$ molecule (1 page). Ordering information is given on any current masthead page.

Stereochemical Control of Yeast Reductions. 1. Asymmetric Synthesis of L-Carnitine

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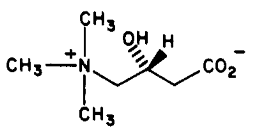
L-Carnitine (**1**) plays an important role in the human metabolism and transport of long-chain fatty acids.[1] Because D-carnitine



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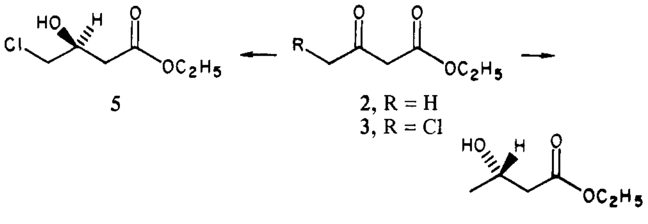
is a competitive inhibitor of L-carnitine acyl transferases[2] and can deplete the L-carnitine level of heart tissue, L-carnitine has been recommended for replacement therapy.[3] We herein describe an efficient chemomicrobiological synthesis of L-carnitine, which obviates the tedious expensive resolution methods that are currently being used in its chemical synthesis.[4] The salient feature of this approach resides in our ability to direct the sterochemical course of yeast reduction of β-keto esters.

Ethyl acetoacetate (**2**) is reduced by bakers' yeast (*Saccharomyces cerevisiae*) to give ethyl (*S*)-(+)-3-hydroxybutanoate[5] (**3**) of high optical purity. Hence, we envisaged that ethyl γ-chloroacetoacetate (**4**) perhaps would be similarly reduced to yield ethyl (*R*)-4-chloro-3-hydroxybutanoate, which could then be easily transformed into L-carnitine by known methodology.[6] However, when **4** was exposed to bakers' yeast, ethyl (*S*)-4-chloro-3-hydroxybutanoate[7a] (**5**), $[\alpha]^{23}_D$ −11.7° (*c* 5.75, $CHCl_3$) (ee = 55%),[7b] was preferentially formed.



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2, R = H
3, R = Cl

3

It is generally assumed that the stereoselectivity of yeast reductions of acyclic ketones may be predicted by the Prelog rule.[8-11]

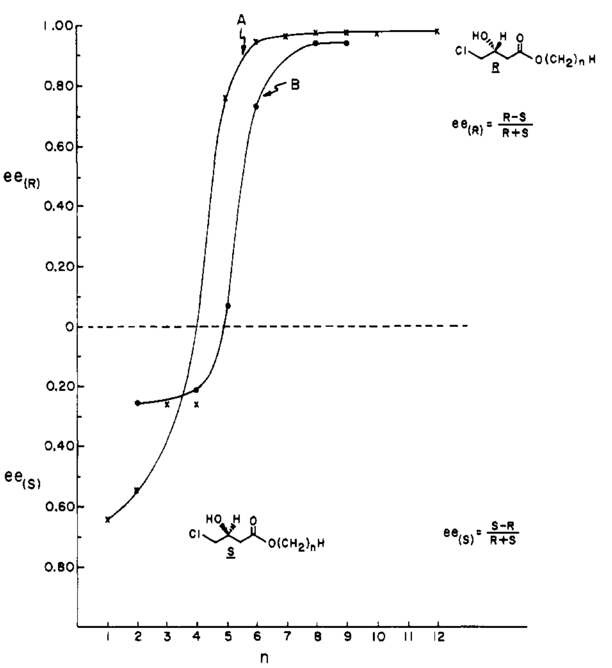

Figure 1. Plot of enantiomeric excess (ee) vs. the size of ester grouping: (A) Red Star bakers' yeast (4 g), tap water (20 mL), 23 °C; γ-chloroacetoacetic esters (0.91 mmol); (B) Red Star bakers' yeast (12 g), tap water (20 mL), 23 °C; γ-chloroacetoacetic esters (2.7 mmol). Usual workup after 48 h.

However, the applicability of the Prelog rule to yeast reduction of β-keto carbonyl derivatives has not been closely examined. We noted that while ethyl acetoacetate[12] and acetoacetic acid[13] were reduced predominantly to their *S* isomers, ethyl β-ketovalerate[14] (**6**) and caproic[13] (**7**), caprylic[13] (**8**), and β-keto-6-heptenoic[15] (**9**) acids were all preferentially converted into their respective *R* isomers. Consequently, if the stereochemistry of yeast reduction of γ-chloroacetoacetic esters could also be altered, i.e., from *S* → *R*, by modifying the size of the ester grouping, (*R*)-γ-chloro-β-hydroxybutyrate could then be obtained for L-carnitine synthesis.

To test our hypothesis, we synthesized a homologous series of γ-chloroacetoacetic esters[16] ranging from C_1 to C_{16} and exposed them to bakers' yeast (Figure 1). Although there was no significant difference in the rates of yeast reduction of γ-chloroacetoacetic esters containing one–eight carbons (n = 1–8), there was a drastic decrease in the reduction rate for the C_{12} ester, which resulted in low product yield. No reduction was observed for the C_{16} ester. More importantly, contrary to the current view,[17] there was indeed a dramatic shift in the stereochemistry of the carbinols formed as the size of the ester grouping is enlarged (Figure 1).

If these β-keto esters are reduced by a single oxidoreductase, this enzyme is able to interact with both faces of the carbonyl group to form two competing *R* and *S* transition states, one of which is more favored than the other. A second possibility is that yeast contains more than one oxidoreductase, which generates carbinols of opposite configurations but at different rates.

Since the optical purities of the various esters change with concentration (curve B, Figure 1), this demonstrates[18] that bakers' yeast contains at least two oxidoreductases producing γ-chloro-

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