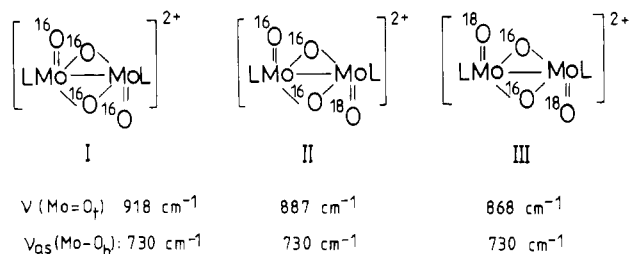


increases from 4.8×10^{-3} to $7.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. We cannot offer at present a reasonable explanation for this effect, since in this range of $[\text{H}^+]$ the Mo(III) dimer is fully protonated (aqua ligands) whereas the nitrate anion is fully deprotonated.

The kinetic data suggest that substitution of a coordinated aqua ligand of the Mo(III) dimer by NO_3^- is the rate-determining step (rds) of the redox reaction.¹⁰ An associative mechanism (I_a) is most probably operative.⁹

In order to gain insight into what happens after the rds we have investigated the reaction using ^{18}O -enriched potassium nitrate (60% and 90%) as oxidant.¹¹ After the reaction of the Mo(III) dimer with NO_3^- in unlabeled water was complete the very insoluble salt, *anti*- $[\text{L}_2\text{Mo}_2\text{O}_4]\text{I}_2$, was rapidly precipitated by addition of sodium iodide to the reaction mixture. The solid material was analyzed by infrared spectroscopy. This was readily accomplished because the terminal $\text{Mo}=\text{O}_t$ stretching frequency and the $\nu_{\text{as}}(\text{Mo}-\text{O})$ of the bridging oxo groups in the unlabeled Mo(V) dimer are observed as strong, sharp bands at 918 and 730 cm^{-1} , respectively. The IR spectrum of the Mo(V) dimer obtained from such a reaction mixture using ^{18}O -enriched NO_3^- (60%) exhibits then two additional strong bands at 887 and 868 cm^{-1} which are assigned to $\nu(\text{Mo}=\text{O}_t)$ stretching frequencies. Most importantly, no additional bands are observed at wavenumbers $<730 \text{ cm}^{-1}$. This indicates that during the course of the redox reaction no bridging oxygen atoms are incorporated that stem from the nitrate anion; i.e., terminal oxo groups only are transferred from the nitrate to the molybdenum centers. Thus three different products were obtained.

The semiquantitative analysis of respective relative intensities of these $\nu(\text{Mo}=\text{O})$ stretching frequencies reveals that the amount of ^{18}O -labeled products (II and III) is always 1.4 times more than



that of I. By use of 90% ^{18}O -enriched nitrate only small amounts of I and II were detected whereas III represents the dominating species. These results can most readily be accounted for if it is considered that only the two terminal oxo groups in *anti*- $[\text{L}_2\text{Mo}_2\text{O}_4]^{2+}$ are transferred from ^{18}O -enriched nitrate and that all the oxygens of the terminal $\text{Mo}^{\text{V}} = \text{O}$ groups stem from the nitrate; i.e., at least 90% (as a lower limit) of the reduction of NO_3^- by $[\text{L}_2\text{Mo}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_2]^{4+}$ in acidic aqueous solution in the presence of an NO_2^- scavenger, proceeds via an oxo-group transfer.

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(10) Kinetic data for the anation reaction of $[\text{L}_2\text{Mo}^{\text{III}}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_2]^{4+}$ and chloride ions⁹ are comparable.

(11) ^{18}O -Labeling experiments: In a typical experiment an aqueous solution (10 mL) of $\text{H}_2\text{NSO}_3\text{H}$ (0.19 g, 1.8 mmol) and $[\text{L}_2\text{Mo}_2(\mu\text{-OH})_2(\text{HO})_2](\text{PF}_6)_3$ (0.05 g, 0.06 mmol) was reacted with ^{18}O -enriched (60% or 90%) potassium nitrate (0.096 g, 0.9 mmol) under strictly anaerobic conditions (argon atmosphere) at room temperature. Within 40 min the original green color of the solution turned red. Addition of sodium iodide (0.08 g) initiated the precipitation of *anti*- $[\text{L}_2\text{Mo}_2\text{O}_4]\text{I}_2$, which was recovered in 96% yield with respect to Mo(III) dimer substrate.

(12) Under our experimental conditions both the oxo groups of the nitrate¹³ and of the product *anti*- $[\text{L}_2\text{Mo}_2\text{O}_4]^{2+}$ do not undergo oxygen-exchange reactions with the solvent water. The latter observation is in excellent agreement with Murman's ^{18}O -exchange studies on syn- $[\text{Mo}_2\text{O}_4(\text{edta})]^{2-}$.¹⁴

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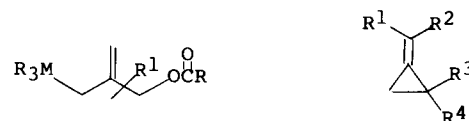
On the Nucleophilic Nature of a TMM-PdL₂ Intermediate: A Direct Palladium-Catalyzed Addition of Trimethylenemethane to Heteroatom Unsaturation

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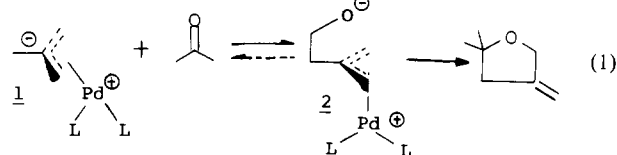
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Received July 2, 1985

The chemistry of trimethylenemethane, an intensely studied area from a mechanistic and theoretical point of view,¹ appears poised to have an impact on complex synthesis. Two seemingly related approaches use a metal-catalyzed cycloaddition—one employing 2-[(trimethylsilyl)- or 2-[(trialkylstannyl)methyl]allyl carboxylates² and the other alkylidenecyclopropanes.³ Such



reactions are, however, quite different in many respects such as chemo- and regioselectivity. Clearly the same intermediates cannot be involved in both reactions. In order to try to determine which reaction, if either, proceeds through a TMM-PdL₂ species, we have been examining the reactivity profile of the intermediate in the silyl and stannyl carboxylate reaction. Theory indicates that a TMM-PdL₂ intermediate should behave as a zwitterion as illustrated in 1.⁴ While the known behavior of the silyl-carboxylates seemingly are in accord with a zwitterionic intermediate,^{2,5} carbonyl additions (see eq 1), a classic test of nucleophilicity, have heretofore given poor results.



In analogy to the Diels-Alder reaction which can cycloadd to both olefins and carbonyl groups, the extension of the $[3 + 2]$ cycloaddition reaction to carbonyl groups would greatly expand its scope in an important direction since (1) substituted tetrahydrofurans are important structural units of many natural products, especially ionophores, (2) the exocyclic methylene group serves as a versatile handle for structural elaboration, and (3) the 3-methylenetetrahydrofuran is easily oxidized to α -methylene- γ -butyrolactones,⁶ another important structural feature of many natural products. The obvious importance of such a process led us to develop a two-step approach using a Lewis acid catalyzed addition of 2-[(trialkylstannyl)methyl]allyl acetate (3) followed by cyclization.⁷ We wish to report that such tin conjunctive reagents directly add to aldehydes with excellent chemo- and regioselectivity mediated by a Pd catalyst.

The reaction involves mixing approximately equimolar amounts of an aldehyde and the tin acetate 3 in dioxane with 3 mol % of

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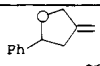
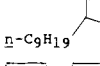
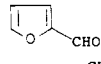
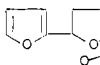
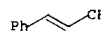
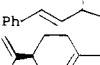
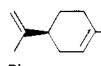
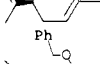
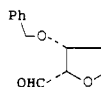
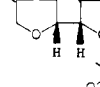
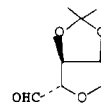
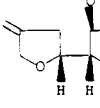
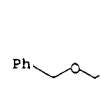
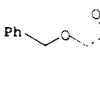
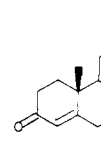
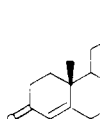
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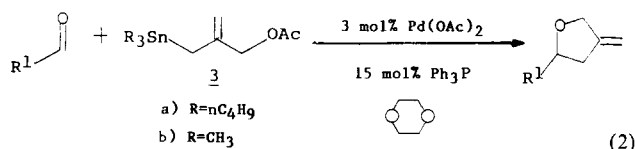
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Table I. Pd-Mediated Cycloaddition of **2** to Aldehydes^a

entry	aldehyde	reagent	temp	product	yield ^b
1	PhCHO	2a,b	reflux, 40 °C		100%, 92%
2	<i>n</i> -C ₉ H ₁₉ CHO	2a,b	reflux, 40 °C		68%, 66%
3		2a,b	reflux, 40 °C		77%, 81%
4		2a	reflux		65% ^c
5		2a	reflux		59%
6		2a	reflux		74%
7		2a	reflux		81%
8		2a	reflux		66%
9		2b	40 °C		80%

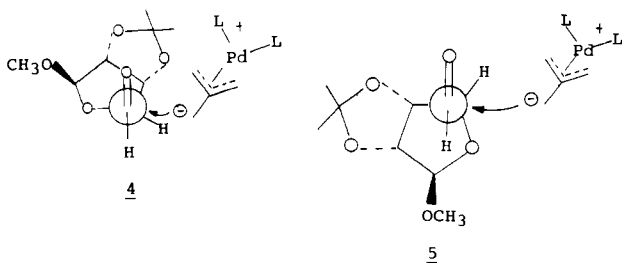
^a All reactions performed according to the general procedure. ^b Yields are for isolated pure products which have been fully characterized. ^c A small amount of product in which the double bond isomerized to an endocyclic position was visible in the NMR spectrum.

a catalyst formed by simply mixing triphenylphosphine with palladium acetate (P: Pd ratio = 5:1). Equation 2 and Table I



summarize the results. Remarkably, reaction proceeds at or near room temperature (entries 1–3, 6, 9) although normally we found it convenient and more general to use refluxing dioxane. The chemoselectivity is excellent. Most surprising is the lack of cycloaddition to the double bond of α,β -unsaturated aldehydes (entries 4 and 5). The steroid (entry 9) shows the compatibility of other carbonyl functionalities. Apparently, our previous observations of these species serving as a base toward ketones does not complicate the desired cycloaddition.²

The diastereoselectivity is also excellent (entries 6–9). It follows the Felkin–Anh model as depicted in **4** for entry 7. An alternative,



5, which better minimizes dipole–dipole and nonbonded interactions predicts the same diastereoselectivity. The lack of normal Lewis acids⁷ facilitates the use of highly oxygenated substrates. The carbohydrate substrates (entries 6–8) suggest this cycloaddition should prove valuable in the synthesis of ionophores, a task under current investigation. The exocyclic methylene group is a particularly useful handle for further elaboration in such tasks.

A general procedure follows. A solution of 3 mol % Pd(OAc)₂ and 15 mol % Ph₃P in 2 mL of dioxane is stirred 15–25 min. Sequential addition of 1 equiv of aldehyde and 1.05–1.10 equiv of **3** either neat or in 2–3 mL of dioxane (for a final concentration of >0.1 M) causes lightening of the yellow color within minutes. After refluxing overnight, the bulk of the dioxane is removed by distillation at atmospheric pressure and the residue purified by chromatography.

Synthetically, this one-step procedure represents an improvement in yield, cleanliness, and convenience in comparison to the earlier two-step synthesis of methylenetetrahydrofurans.^{8,9} On the other hand, whereas the one-step method is limited to aldehydes, the two-step approach is much more general. Mechanistically, it verifies the nucleophilic nature of the intermediate in the palladium-catalyzed reaction of the bifunctional conjugative reagents—an important piece of evidence in support of the formulation of **1** as the structure of this intermediate. The product of nucleophilic addition, i.e., **2** (eq 1), is trapped by external acetate faster than it cyclizes as evidenced by the observation of such adducts (which have been independently synthesized) by TLC. The rather unfavorable 5-endo-trig type of cyclization and the oxygen nucleophile, a rather poor one in palladium reactions,¹⁰ probably account for the sluggishness of the cyclization step. While the reactions of methylenecyclopropanes with CO₂ catalyzed by palladium are known,¹¹ a cooligomerization rather than a TMM–PdL₂ reaction may be operative. Their reaction with aldehydes is not known. Clearly, much more work will be required

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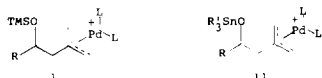
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before a fuller understanding of the different intermediates in the two processes will emerge. The ability of the bifunctional reagents **2** to be coaxed to react with the highly polarized heteroatom unsaturation of an aldehyde, even in preference to cycloaddition to an electron-deficient double bond, agrees with the theoretical description of a TMM-PdL₂ species.¹²

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their generous support of our programs. We thank Johnson Matthey and Englehard Industries for supplies of palladium salts.

(12) Control experiments demonstrates no carbonyl addition in the absence of Pd(0) catalysts with these silicon or tin conjunctive reagents. The silicon reagent can also cycloadd to aldehydes under these conditions but the yields are inferior, many cases fail, and much more drastic conditions are required. We attribute the differences to the ability of i vs. ii, which form as a result



of trapping the initial carbonyl-TMM-PdL₂ adduct by TMSOAc or R₃'SnOAc, to cyclize. In the former case, products derived from **i** can be isolated, but we have not been able to detect the products derived from **ii** which suggests its cyclization must be efficient. Alternatively, R₃'SnOAc may be sufficiently unreactive that **2** cyclizes directly and **ii** never forms. **Note Added in Proof:** 1,3-Diyl trapping by benzaldehyde has recently been reported. Little, R. D.; Bode, H.; Stone, K. J.; Wallquist, O.; Dannecker, R. *J. Org. Chem.* **1985**, 50, 2400.

First Examples of Polynuclear, Sulfur-Containing, Zirconium Compounds. The Synthesis and Structural Characterization of the Trinuclear Zr₃S₃(S-*t*-Bu)₂(BH₄)₄(THF)₂ and the Hexanuclear Zr₆S₆(S-*t*-Bu)₄(BH₄)₈(THF)₂ Clusters

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Recent interest in Zirconium chemistry derives to a considerable extent from the demonstrated importance of certain low-valent Zr compounds in CO activation and reduction.¹ The rarity of soluble polynuclear Zr clusters and the potential importance of such molecules in small-molecule activation prompted us to examine the methodology for the synthesis of such species. We have focused our attention on Zr-S clusters, with the anticipation that once obtained such molecules will be thermodynamically unstable relative to O, N, or halide ligands and consequently well suited as synthons for future studies. Furthermore, reduction of polynuclear Zr-S clusters or their derivatives may well lead to low-valent Zr clusters with unusual catalytic properties.

The coordination chemistry of Zirconium with sulfur ligands is limited to that of the octahedral dithiolene, (Zr(L)₃)³⁻, complexes,² the eight-coordinate dithiocarbamate complexes,³ Zr(R₂Dtc)₄, and the pentagonal-bipyramidal (Cp)Zr(Me₂Dtc)₃ complex.⁴ To our knowledge aliphatic thiolate complexes of Zr are virtually unknown, and only a brief report on the synthesis of the blue Zr(SPh)₄ complex has appeared in the literature.⁵ In this paper we report on the synthesis of two new Zr clusters that

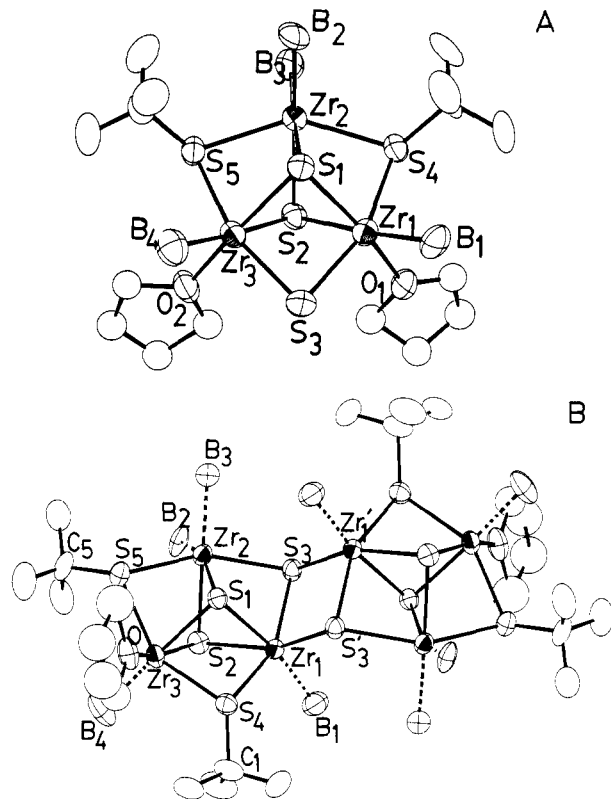
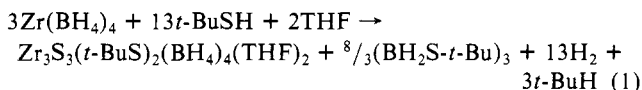


Figure 1. Structure and labeling of Zr₃S₃(S-*t*-Bu)₂(BH₄)₄(THF)₂ (A) and Zr₆S₆(S-*t*-Bu)₄(BH₄)₈(THF)₂ (B). Thermal ellipsoids as drawn by ORTEP (Johnson, C. K. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965) represent the 40% probability surfaces. In A and B above only the B atoms of the BH₄⁻ ligands are drawn.

contain BH₄⁻, *t*-BuS⁻, S²⁻, and THF ligands.

The trinuclear Zr₃S₃(*t*-BuS)₂(BH₄)₄(THF)₂ cluster, **I**, is obtained from the reaction between Zr(BH₄)₄ and *t*-BuSH, in 70% yield (based on Zr(BH₄)₄), according to the stoichiometry. This



reaction (eq 1) proceeds in THF at ambient temperature with a steady evolution of H₂ for about 30 min and goes to completion when the pale yellow solution is further heated to ~50 °C for 4–6 h. Crystals of **I** are obtained following dilution with diethyl ether and *n*-hexane and cooling to -20 °C.⁶ After the isolation of **I** from solution, the very soluble (BH₂S-*t*-Bu)₃ byproduct is obtained in 90% yield (based on eq 1) by concentrating the filtrate to near dryness. The structure of this cyclic thioetherane has been determined.⁷

A concentrated solution of **I** in CD₂Cl₂ upon standing for ca. 24 h at ambient temperature deposited yellow crystals of a compound (**II**) with a powder diffraction pattern different than that of **I**. The single-crystal X-ray structures of **I** and **II** were determined⁸ and reveal the trimeric nature of **I** and the hexameric

(6) Anal. Calcd for C₁₆H₅₀B₄O₂S₃Zr₃: C, 25.66; H, 6.68; B, 5.88; S, 21.39; Zr, 36.09. Found: C, 26.69; H, 7.31; B, 5.87; S, 19.10; Zr, 35.33. Infrared spectra (KBr, cm⁻¹): ν(B-H), 2527 (s), 2465 (s), 2414 (s); ν(B-H₂), 2182 (s), 2111 (s), 2050 (sh), 1986 (s); δ(Zr-H-B) 1232 (vs); ν(C-S) 838 (vs).

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(8) Crystal and refinement data for Zr₃S₃(*t*-BuS)₂(BH₄)₄(THF)₂ (**I**): *a* = 11.545 (3) Å, *b* = 16.481 (4) Å, *c* = 18.118 (4) Å, β = 91.123 (2)°; space group P2₁/c, *Z* = 4; *d*_{calcd} = 1.45 g/cm³; μ = 11.4 cm⁻¹, 2θ_{max} = 40 (Mo K_α, 0.710 69 Å); Unique Reflections 3248, used in refinement 2169 (*F*_o² > 3σ(*F*_o²)); parameters 235; final *R* = 0.06. Crystal and refinement data for Zr₆S₆(*t*-BuS)₄(BH₄)₈(THF)₂ (**II**): *a* = 12.443 (1) Å, *b* = 15.197 (2) Å, *c* = 18.365 (2) Å, β = 70.214 (7)°; space group P2₁/c, *Z* = 2; *d*_{calcd} = 1.55 g/cm³; μ = 12.5 cm⁻¹; 2θ_{max} = 45 (Mo K_α, 0.710 69 Å); unique reflections 4275; used in refinement 3102 (*F*_o² > 3σ(*F*_o²)); parameters 278; final *R* = 0.04.

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