

chiometry of the complex.¹⁸ Interestingly with 4 equiv of SnCl₄, 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 SnCl₄·2L which we assign to SnCl₄·L. This assignment is supported by the experiment with 10 equiv of SnCl₄ 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 SnCl₄, (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 SnCl₄: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 SnCl₄·2L 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.

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Supplementary Material Available: Listing of atomic coordinates, bond lengths, bond angles, and positional and thermal parameters for SnCl₄·2L (43 pages); tables of structure factors for SnCl₄·2L (11 pages). Ordering information is given on any current masthead page.

(18) Theoretically with 0.25 equiv of SnCl₄ the ratio of free to complexed L is 50:50 for SnCl₄·2L and 75:25 for SnCl₄·L.

(19) Percent relative intensity is defined with respect to the major peak for SnCl₄·2L = 100%.

An Unbridged Triple Bond Uniting d⁶ Mo(0) and d² Mo(IV) Atoms: Mo₂(O-*i*-Pr)₄(dmpe)₂

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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 d⁴ Mo(II)-d⁴ 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 ML₄ units as seen in the structures of Mo₂(O₂CR)₄ and Mo₂X₄(PR₃)₄ compounds, where X = Cl, Br, and I.¹ The use of the bidentate phosphine dppe (dppe = Ph₂PCH₂CH₂PPh₂) leads to α and β isomers for Mo₂Cl₄(dppe)₂ compounds.² In the α isomer, the dppe ligands chelate, one to each molybdenum atom, such that the near-eclipsed Mo₂Cl₄P₄ unit is achieved. In the β isomer, the dppe ligands span the Mo-Mo bond and impart a staggered arrangement of the two MoCl₂P₂ units.³ The latter

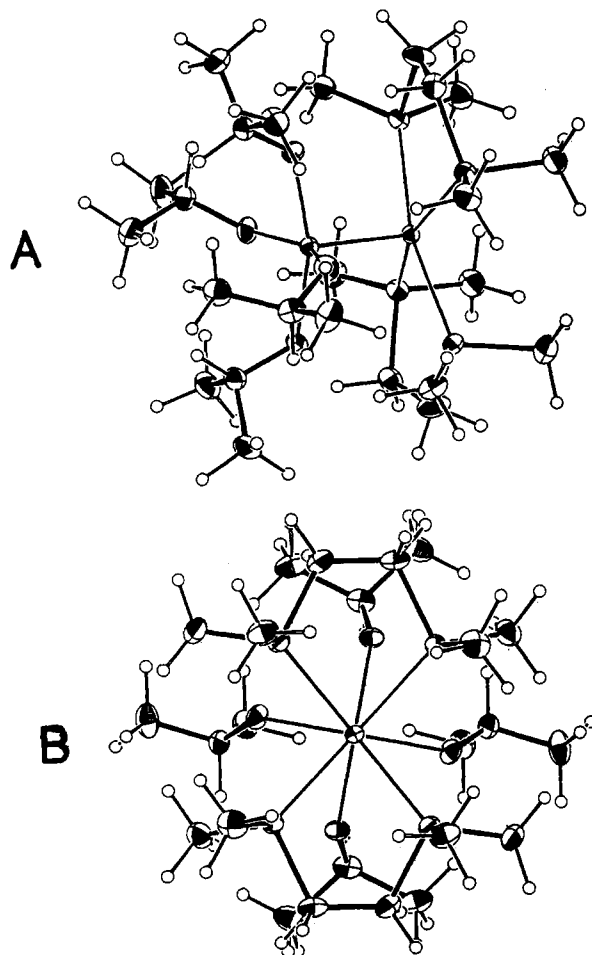
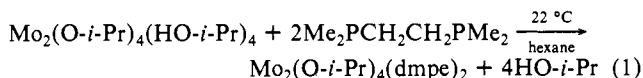


Figure 1. Two ORTEP views of the Mo₂(O-*i*-Pr)₄(dmpe)₂ molecule. The molecule has a crystallographically imposed C₂ axis coincident with the M-M bond. Pertinent distances (Å) and angles (deg) averaged where appropriate are Mo-Mo = 2.236 (1), Mo-O = 2.00 (1), Mo-P = 2.438 (1), Mo-Mo-O = 103.8 (1) and 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 d⁴-d⁴ 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 Mo₂(OR)₄L₄ (R = *i*-Pr, L = HO-*i*-Pr and py; R = Np, L = HNMe₂ and PMe₃).⁶ These compounds contain d⁴ Mo(II)-d⁴ Mo(II) centers with an essentially eclipsed Mo₂O₄L₄ skeleton. The π -donor alkoxides lengthen and labilize the Mo-Mo quadruple bond. We wished to compare the chemistry of the alkoxide-supported Mo₂⁴⁺ 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



essentially quantitative yield. A convenient alternate synthesis involves the reaction between Mo₂(*i*-Bu)₂(NMe₂)₄, *i*-PrOH (>4 equiv), and dmpe (2 equiv) in a hydrocarbon solvent. This obviates

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the isolation of $\text{Mo}_2(\text{O-}i\text{-Pr})_4(\text{HO-}i\text{-Pr})_4$, though it is likely that this compound or a dimethylamine-substituted derivative is a reactive intermediate.^{6,7}

$\text{Mo}_2(\text{O-}i\text{-Pr})_4(\text{dmpe})_2$ is a dark-brown, hydrocarbon-soluble, air-sensitive, crystalline compound.⁸ The NMR spectra in toluene- d_8 revealed a single ^{31}P signal and only one type of O- i -Pr ligand with equivalent isopropyl-methyl groups.⁹ A molecule having a staggered $\text{Mo}_2\text{O}_4(\text{P-P})_2$ unit similar to that seen in $\beta\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$ should have displayed diastereotopic methyl groups. The NMR data are consistent with expectations based on the molecular structure found in the solid state.¹⁰ See Figure 1. The dmpe ligands do not span the Mo-Mo bond but rather act as chelating ligands to one molybdenum atom. The four alkoxides are bonded to the other molybdenum atom. The $\text{Mo}_2\text{O}_4\text{P}_4$ unit adopts a staggered conformation as is evident from one of the views shown in Figure 1. This is the only example of an unsupported M-M multiple bond uniting Mo(0) and Mo(IV) atoms, though it should be recognized that M-M multiple bonds between metal atoms in different oxidation states have been known since the discovery of $\text{Re}_2\text{Cl}_5(\text{C}_4\text{H}_{10}\text{S}_2)_2$ in 1966 ($\text{C}_4\text{H}_{10}\text{S}_2$ is 2,5-dithiahexane).¹¹ The recent report of the Re(IV)-Re(II) dinuclear compound $\text{Re}_2(\text{OEt})_2\text{Cl}_4(\text{PPh}_3)_2$ is particularly worthy of note in that the Re(IV) center is supported by two alkoxide ligands.¹²

We propose that the M-M multiple bond in this molecule is a triple bond, $\sigma^2\pi^4$, uniting the d^2 Mo(IV) and d^6 Mo(0) metal atoms.¹³ This is consistent with the observed Mo-Mo distance which is comparable to those in $\text{Mo}_2(\text{OR})_6\text{L}_2$ compounds,¹⁴ e.g., Mo-Mo = 2.242 (1) Å in $\text{Mo}_2(\text{OSiMe}_3)_6(\text{HNMe}_2)_2$.¹⁵ Formation of a δ bond can be ruled out based on the staggered $\text{Mo}_2\text{O}_4\text{P}_4$ conformation, and the Mo(0) center will have two electrons residing in a metal-centered atomic orbital, namely, the d_{xy} orbital which otherwise could be involved in δ bonding. At the Mo(O- i -Pr)₄ center, the metal d_{xy} orbital is involved in Mo-O π bonding.¹⁶

Though we cannot rule out the possibility that the title compound represents a kinetic rather than the thermodynamic product of reaction 1, this seems unlikely. Why should a molecule of formula $\text{Mo}_2(\text{O-}i\text{-Pr})_4(\text{dmpe})_2$ favor the observed Mo(IV)-Mo(0) structure? Though it is clearly premature to venture any detailed explanation, we do note the following. (1) The introduction of RO ligands to the Mo_2^{4+} center weakens the M-M bonding, particularly the δ bond such that little, if any, M-M bonding is sacrificed in going from a Mo(II)-Mo(II) to the Mo(IV)-Mo(0) structure. (2) Metal-ligand bonding is optimized in the Mo(IV)-Mo(0) structure in that four hard alkoxide ligands coordinate to the Mo(IV) center and four soft phosphorus lone pairs coordinate to the Mo(0) center.

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(8) Anal. Calcd (Found) for $\text{Mo}_2\text{P}_4\text{C}_{24}\text{H}_{60}\text{O}_4$: C, 39.6 (39.4); H, 8.3 (8.2); P, 17.0 (16.8); N, 0.00 (<0.03).

(9) $^{31}\text{P}\{^1\text{H}\}$ NMR δ 43.2 (rel H_3PO_4); ^1H NMR (21 °C toluene- d_8 , 360 MHz) δ 4.22 (sept, $^3J_{\text{HH}} = 6$ Hz, CHMe_2), 1.34 (d, $^3J_{\text{HH}} = 6$ Hz, CHMe_2), 2.28, 0.30 (PMe_2), 2.79, 2.20, 1.27, 1.10 ($\text{PCH}_2\text{CH}_2\text{P}$).

(10) Crystal data for $\text{Mo}_2(\text{O-}i\text{-Pr})_4(\text{dmpe})_2$, at -155 °C: $a = 10.709$ (2) Å, $b = 18.902$ (5) Å, $c = 17.121$ (4) Å, $\beta = 92.05$ (1)°, $Z = 4$, $d_{\text{calc}} = 1.397$ g cm⁻³, and space group C2/c. Of the 2784 reflections collected (Mo K α , 6° < 2 θ < 45°), the 2006 having $F > 3\sigma(F)$ were used in the full least-squares refinement. All hydrogen atoms were located and refined isotropically; all non-hydrogen atoms were refined anisotropically. Final residuals were $R(F) = 0.027$ and $R_w(F) = 0.031$.

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(13) This will have a dative component as in $\text{Re}_2\text{Cl}_4(\text{OEt})_2(\text{PPh}_3)_2$; ref 12.

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(16) The Mo-O distance of 2.00 (1) Å (av) corresponds to a bond order of 1 $\frac{1}{4}$, and may be compared to an estimated single bond length of 2.06 Å and distances of 1.94 and 1.88 Å for Mo-OR bonds of order 1 $\frac{1}{3}$ and 1 $\frac{2}{3}$, respectively. See ref 6, 14, and: Chisholm, M. H.; Heppert, J. A.; Huffman, J. C. *Polyhedron* **1984**, *3*, 475.

Further studies are in progress.¹⁷

Supplementary Material Available: Listings of atomic positional parameters together with a VERSORT drawing giving the atom number scheme and a complete listing of bond distances and angles (3 pages). See any current masthead page for ordering information.

(17) We thank the National Science Foundation and the Wrubel Computing Center for support and L.R.S. Van Der Sluys for obtaining ^{31}P NMR spectra.

Non-Koopmans' Effects in the Outer Valence Ionizations of Polyenes

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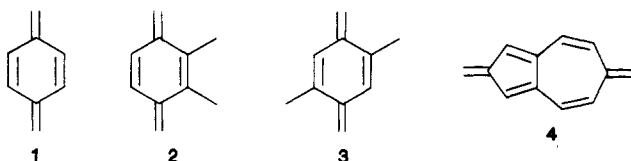
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We wish to describe the results of our investigations of polyenes 1-4 by our transient photoelectron (TPE) method.^{1,2} The data shed light on questions that have been raised³ concerning the original experimental observations of the photoelectron spectra of 1¹ and its 2,5-dimethyl derivative 3⁴ and the interpretational



differences in the Koopmans' theorem⁵ model (KTM)⁶ and non-Koopmans' models (NMK).⁶ The crucial factor that makes the present studies of 2 and 4 possible is the availability of sufficient quantities of (cyclophane) flash vacuum pyrolysis (FVP) precursors^{7,8} since 1-4 are not kinetically stable.

Existing data from photoelectron spectroscopy (PES) overwhelmingly support the position⁹ that the symmetry/energy sequence for the first several ionic states (IP_i) of molecules can be

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