

Table II. Barriers to Rotation, ΔG^\ddagger_T (T_c) (kcal/mol (K)) about M-N and M-P Bonds in *gauche*-1,2- $M_2(P(t-Bu)_2)_2(NMe_2)_4$

bond	M = Mo	M = W
M-NMe ₂	11.5 ± 0.1 (260)	11.3 ± 0.1 (256)
M-N'(Me) ₂	8.2 ± 0.1 (185)	7.5 ± 0.1 (170)
M-P(<i>t</i> -Bu) ₂	8.6 ± 0.1 (190)	9.7 ± 0.1 (212)

2.477 (1) Å, is close to that expected for a Mo-P single bond based on the covalent radii r_{Mo} (for $(M\equiv M)^{6+}$) = 1.40 Å⁹ and r_P = 1.10 Å.¹⁰ Furthermore, the geometry at phosphorus is distinctly pyramidal, as evidenced by (i) the sum of the angles about P, 348.5°, and (ii) the deviation of the P atom from the MoC₂ plane of the Mo-PC₂ moiety, 0.41 Å. The W-P distance is shorter than the Mo-P distance by 0.08 Å, and the distortion of the W-PC₂ moiety from planarity is smaller. This is shown in the sum of the angles about P, 355.6°, and the deviation of P from the WC₂ planes, 0.25 Å.

Important structural comparisons can be made as follows. In Mo(NMe₂)₄¹¹ and Mo(PCy₂)₄,¹² both of which contain planar (at N and P), 4-electron-donor ($\sigma + \pi$) ligands, the Mo-N and Mo-P distances are 1.926 (6) and 2.265 (2) Å, respectively. A parameter can be calculated, $\Delta = d(Mo-P) - d(Mo-N) = 0.339$ Å, to represent the difference in bond lengths of M-NR₂ vs. M-PR₂ double bonds. For 1,2- $M_2(P(t-Bu)_2)_2(NMe_2)_4$, two NMe₂ and one P(*t*-Bu)₂ ligand compete for two metal acceptor orbitals ($d_{x^2-y^2}$, d_{xy}). The larger Δ values in I, $\Delta = 0.502$ Å, and II, $\Delta = 0.429$ Å, reflect the preference for M←NR₂ π bonding over M←PR₂ π bonding in the mixed-ligand compounds. Of further interest are the M-P distances in Cp₂Hf(PEt₂)₂ of 2.682 (1) and 2.488 (1) Å for the pyramidal and planar PR₂ ligands, respectively.¹³ Formally, the difference of 0.194 Å corresponds to the difference in M-P single- and double-bond distances. Clearly, the Mo-P bonds in I have little if any π character while the W-P bonds in II have substantially more.¹⁴

These conclusions based on structural data are supported by the barriers to rotation about M-NMe₂ and M-P(*t*-Bu)₂ bonds in the 1,2- $M_2(P(t-Bu)_2)_2(NMe_2)_4$ compounds. Low-temperature ¹H NMR spectra reveal that rotations about M-N and M-P bonds are frozen out on the NMR time scale; NMe and P(*t*-Bu) proximal and distal resonances are well separated (by 1.9-1.2 and 0.7-0.6 ppm, respectively) as a result of the diamagnetic anisotropy of the $(M\equiv M)^{6+}$ units.¹⁵ Barriers calculated from coalescence temperatures¹⁶ are listed in Table II for the *gauche* conformers, which predominate in solution: *gauche:anti* = 2:1 (M = Mo) and 4:1 (M = W). We observe that proximal-to-distal exchange in the P(*t*-Bu)₂ ligands is more rapid for M = Mo than for M = W, while proximal-to-distal exchange rates for NMe₂ ligands follow the inverse order.¹⁷ If P inversion was also slow at temperatures for which M-N and M-P rotations are frozen out, the observation

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(14) (a) Other M=P bond distances of relevance: Mo-P = 2.382 (1) Å in [Mo(P(*t*-Bu)₂)(μ -P(*t*-Bu)₂)₂]₂,^{14b} W-P = 2.345 (4) Å in [W₂(PCy₂)₂(μ -PCy₂)₂]₂,¹² and W-P = 2.284 (4) Å in (η^5 -C₅H₅)W(CO)₂(P(*t*-Bu)₂).^{14c} (b) Jones, R. A.; Lasch, J. G.; Norman, N. C.; Whittlesey, B. R.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 6184. (c) Jorg, K.; Malisch, W.; Reich, W.; Meyer, A.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 92.

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of several stereoisomers resulting from the various relative configurations at phosphorus might be expected. Specifically, anti conformers could exist as a mesolike isomer (*C*₂ symmetry as in I) or as an enantiomeric pair having *C*₂ symmetry. A set of three diastereomers would be expected for *gauche* conformers, each representing an enantiomeric pair. Our failure to detect such invertomers suggests that inversion at phosphorus in the phosphido ligands is facile¹⁸ and not frozen out on the NMR time scale.

We conclude that amido ligands are stronger π donors than phosphido ligands in 1,2- $M_2(P(t-Bu)_2)_2(NMe_2)_4$ compounds and that tungsten has a greater propensity to π bond with the PR₂ ligands than molybdenum does. The latter is unlikely due to differences in Mo-P vs. W-P overlap, since the covalent radii r_{Mo} and r_W in $(M\equiv M)^{6+}$ compounds are nearly identical,¹⁹ but might be rationalized by orbital energetics. The energy difference in the valence levels for Mo vs. W in $(M\equiv M)^{6+}$ and $(M-M)^{4+}$ compounds is ca. 0.5 eV, as determined by PES data.²⁰ The higher energy of tungsten valence orbitals may provide a better energy match with the phosphido 3p orbital, resulting in a stronger π interaction.²¹

Supplementary Material Available: Selected NMR data and tables of atomic positional parameters (4 pages). Ordering information is given on any current masthead page.

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Transition Structures for Hydride Transfers

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Received June 17, 1986

Hydride transfers are ubiquitous organic and biochemical reactions.¹⁻² The degenerate hydride transfer from methoxide to formaldehyde, a prototype for such reactions, has been observed with labeled compounds in the gas phase by Nibbering et al.³ We have investigated this reaction theoretically in various geometries and with metal counterions.⁴ All structures were optimized with gradient methods, and the stationary points on the potential energy surfaces were characterized by harmonic vibrational frequency calculations, using the GAUSSIAN 80 and GAUSSIAN 82 programs of Pople et al.⁵

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Table I. Geometries (Å and deg) and Energies (kcal/mol, relative to **1**) of **6** Optimized at Various Levels^a

	r_{CO}	$r_{\text{C-H}}$	$\angle\text{C-H-C}$	$\angle\text{O-C-H}$	ΔE		r_{CO}	$r_{\text{C-H}}$	$\angle\text{C-H-C}$	$\angle\text{O-C-H}$	ΔE
3-21G	1.261	1.463	152	118	7.8	6-31+G*	1.245	1.396	147	115	14.4
6-31G*	1.236	1.452	142	116	11.5 ^b	MP2/6-31+G	1.321	1.360	159	115	1.5
6-31+G	1.284	1.364	159	115	16.3						

^aThe absolute energies (au) (basis set, CH₂O, CH₃O⁻, C₂H₅O⁻ (C_{2v})): 3-21G, -113.221 82, -113.724 80, -226.934 12; 6-31G*, -113.866 33, -114.384 47, -228.232 41; 6-31+G, -113.812 69, -114.366 03, -228.152 71; 6-31+G*, -113.871 16, -114.411 12, -228.259 37; MP2/6-31G*///6-31G*,^b-114.165 25, -114.701 62, -228.860 92; MP2/6-31+G -114.040 67, -114.609 50, -228.647 80. ^bThe MP2/6-31G*///6-31G* activation energy is 3.7 kcal/mol.

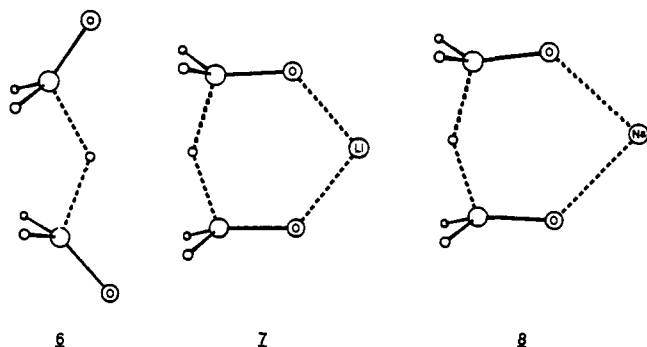
Table II. Geometries (Å and deg) and Energies (kcal/mol) of **7** and **8** Relative to the Reactants

species	basis set	r_{CO}	$r_{\text{C-H}}$	$r_{\text{O-M}}$	$\angle\text{C-H-C}$	$\angle\text{O-C-H}$	ΔE
7 (Li ⁺)	3-21G	1.293	1.369	1.721	145	109	1.2
	6-31G*	1.262	1.371	1.780	147	110	5.9
8 (Na ⁺)	3-21G	1.287	1.376	2.047	148	111	-1.2
	6-31G*	1.257	1.382	2.112	153	111	5.9

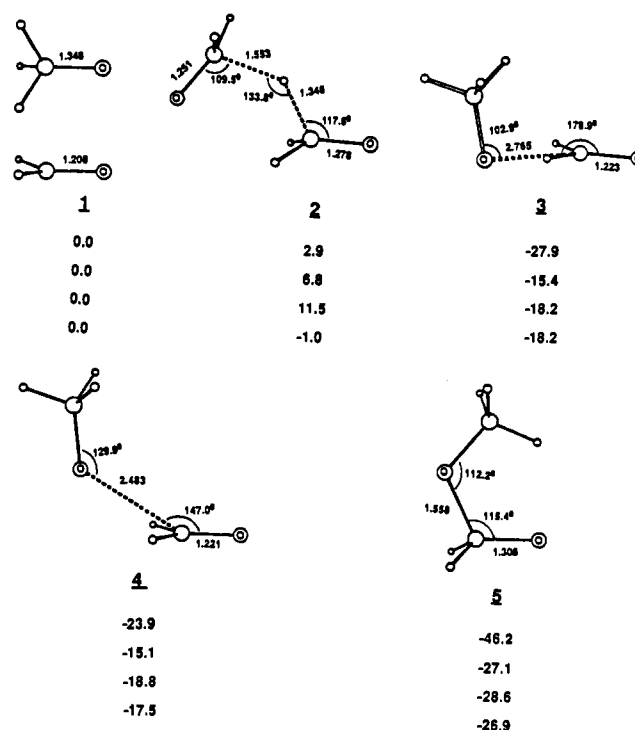
The stationary points on the methoxide-formaldehyde surface are shown in Figure 1. Structures were optimized at the 3-21G level, and additional single-point calculations on these geometries were carried out at the 6-31G*, 6-31+G, and MP2/6-31+G levels. There are two pathways from reactants **1** to the ion-molecule complex **3**. One is a barrierless process, while the other involves hydride transfer through the unsymmetrical transition structure **2**. This transition structure is very unsymmetrical, as indicated by the difference in the lengths of the two C-H bonds and the two H-C-O angles. Transition structure **2** involves hydride transfer with some added stabilization afforded by the electrostatic interaction of the developing alkoxide oxygen with the carbonyl carbon. The negative activation energy at the MP2 level is not unreasonable, since ion-dipole complexes such as **3** will all be more stable than reactants **1**, and hydride transfer from these will be an activated process.

There is a very low barrier for conversion of complex **3** to the stable tetrahedral addition product **5** at all computational levels. The transition structure for this process, **4**, has a very large attack angle of 147° and a very long forming CO bond. Madura and Jorgensen have found similar results for the addition of hydroxide to formaldehyde.⁶

We have also studied the C_{2v} structure, **6**, for hydride transfer.⁷ At the 3-21G level, **6** has two imaginary vibrational frequencies.



The larger (1308i cm⁻¹) corresponds to hydride transfer motion along the reaction coordinate, while the smaller (95i cm⁻¹) corresponds to a rotation of one formaldehyde moiety with respect to the other, the result of the repulsion between the two partially negative oxygens. The potential surface is very flat in this region, and reliable characterization of transition structures will require more extensive calculations. Higher level optimizations give similar structures, as shown in Table I. Each of these structures

**Figure 1.** Stationary points on the methoxide plus formaldehyde surface. Geometries are 3-21G, and relative energies are (top to bottom) 3-21G, 6-31G*, 6-31+G, and MP2/6-31+G.

has a bent (142–159°) C-H-C angle. The angle of attack on the carbonyl is a relatively consistent 115–118°, similar to the larger angle in **2**. Although not a transition state, **6** is a good model for the intramolecular hydride transfers observed in various 4-hydroxycyclohexanones,^{8,9} where the C₁-C₄ distances are 2.6–2.7 Å, close to the distance of 2.6–2.8 Å in **6**. We also used the C_{2v} structure to assess computational levels. As shown in Table I, the activation energies generally increase as the quality of the basis set is increased, but they drop when correlation energy corrections are made. At all comparable levels, the C_s structure, **2**, is 4–5 kcal/mol more stable than the C_{2v} structure, **6**.

The 3-21G and 6-31G* transition structures and activation energies for the reactions of metal methoxides with formaldehyde are summarized as **7** and **8** and in Table II. There are similarities in the angle of hydride attack and the length of C-H

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bond, but now the oxygens are syn, due to electrostatic attraction for the metal cations.

All previous semiempirical and ab initio calculations have predicted a preference for linear hydride transfer.^{4,11} By contrast, all of our transition structures are bent but with rather easy bending of the C-H...C angle. Our results are consistent with the ease of hydride transfer in polycyclic 4-hydroxycyclohexanones⁸⁻¹⁰ and with experimental isotope effects in NAD-(P)⁺/NAD(P)H models.^{12,13}

Another interesting feature revealed by these calculations is the attack angle of hydride on the carbonyl (109-118°), consistent with the Dunitz-Bürgi¹⁴ predictions.¹⁵ In the transition structures for hydride transfer, the negative charge on the transferring hydride is only -0.1 to -0.2, similar to the charge found on hydrogen for concerted sigmatropic hydrogen shifts.¹⁶ That is, there is little hydride character on the migrating hydrogen and the transition state is "tight". Additional transition structures for hydride transfers by amines and NAD(P)H models will be reported shortly.

Acknowledgment. We are grateful to the National Science Foundation for research and supercomputer grants and the Harris Corporation for a computer grant. This study was initiated as the result of stimulating discussions with Professors Gordon Hamilton and Steven Benkovic at Pennsylvania State University.

Registry No. Methoxide, 3315-60-4; formaldehyde, 50-00-0.

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Electronic and Conformational Effects on π -Facial Stereoselectivity in Nucleophilic Additions to Carbonyl Compounds

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Received August 18, 1986

Since the early 1950's, when Cram proposed a rule to rationalize the stereoselectivities of nucleophilic additions to acyclic chiral carbonyl compounds¹ and Dauben proposed an unrelated rationale for these reactions of cyclohexanone derivatives,² many other rules and explanations have been proposed for these phenomena.³⁻⁸ We

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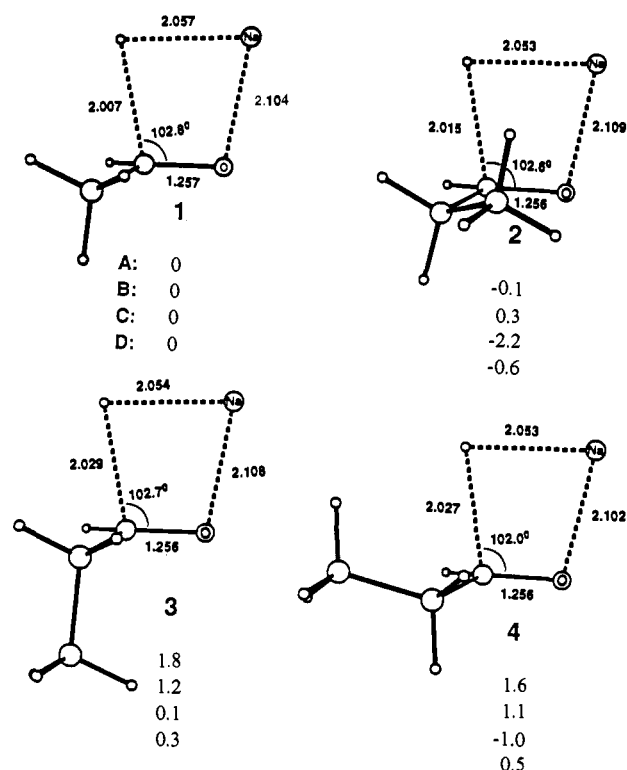


Figure 1. 3-21G transition structures and relative activation energies for reactions of NaH with acetaldehyde and propionaldehyde: A, 3-21G; B, 6-31G**/3-21G; C, 6-31G**/3-21G (Na⁺ removed); D, 6-31G**/3-21G relative energies of distortion of aldehydes into transition-state geometries.

have studied these reactions computationally⁹ and report quantitative support for the Felkin model⁴ for both acyclic and cyclic carbonyl compounds.

The transition structures for NaH addition to acetaldehyde (1) and propionaldehyde (2-4) are shown in Figure 1.¹⁰ The relative activation energies obtained by ab initio calculations with the 3-21G (A) and 6-31G* (B) basis sets show that an inside methyl has little effect on the activation energy, relative to acetaldehyde, while anti or outside methyl groups raise the activation energy. Removal of Na⁺ gives relative energies, C, indicating that anti is disfavored, while removal of NaH gives relative energies, D, indicating that the anti methyl is disfavored even in the distorted ground states.¹¹ The anti methyl group is disfavored relative to anti CH, because the former is a better donor and destabilizes the electron-rich transition structure. An outside methyl is disfavored relative to anti methyl for steric reasons. This conclusion differs from that of Anh and Eisenstein, whose calculations predicted that an anti methyl stabilizes such transition states.⁵ Cieplak proposed that an anti CH stabilizes nucleophilic transition states by electron donation and that CH is a better donor than CC,⁶ contrary to much experimental evidence which shows that CC is a better donor.¹² We conclude that an anti methyl destabilizes the electron-rich transition state because it is a better donor than a CH bond.¹³

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