(3) The molybdenum compounds described here are all readily hydrolyzed in moist air. Standard precautions and manipulations for the handling of air-sensitive compounds were used. D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(4) ^{1}H NMR data, 40 °C, toluene-d_8, 60 MHz: $\delta(CH_2)$ 4.93, $\delta(CH_3)$ 1.08. δ parts per million relative to Me_4Si.
(5) ^{13}C NMR data, 38 °C, toluene-d_8, Varian XL 100 FT spectrometer: $\delta(O\mathit{C}H_2)$ 86.7; $\delta(\mathit{C}Me_3)$ 34.5, $\delta(C(\mathit{C}H_3)_3)$ 26.7; δ in parts per million relative to Me_4Si.
(6) NMR data for $Mo_2(OCH_2CMe_3)_6{\cdot}2HNMe_2$ recorded in toluene-d_8 at +38 °C; $\delta(C\mathit{H}_2)$ 4.40, $\delta(N(C\mathit{H}_3)_2)$ 2.40, $\delta(C(C\mathit{H}_3)_3)$ 1.05, $\delta(O\mathit{C}H_2)$ 82.9, $\delta(OCH_2\mathit{C}Me_3)$ 34.3, $\delta(OCH_2C(\mathit{C}H_3)_3)$ 27.3; $\delta(N(\mathit{C}H_3)_2)$ 40.3. δ in parts per million downfield from Me_4Si.
(7) Calcd. for $[Mo(OCH_2CMe_3)_3]_n$: C, 50.41; H, 9.33. Found: C, 50.33; H, 9.14. Cf. analysis of yellow-green crystals of $Mo_2(OCH_2CMe_3)_6$. Found: C, 50.08; H, 9.18.
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(9) Crystal data for $Mo_2(OCH_2CMe_3)_6$: space group, $P21/n$; a = 18.160 (10), b = 11.051 (7), c = 9.956 (6) Å; β = 104.30 (4)^0; V = 1936 (2) Å^3; Z = 2; Mo radiation; 1588 reflections having $I > 3\sigma(I)$ and $2\theta \leq 45^0$. Refined anisotopically to $R_1 = 0.071$ and $R_2 = 0.088$.
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(11) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **97,** 5625 (1975).
(12) $Nb(OCH_2CMe_3)_5$ is monomeric in benzene, $Zr(OCH_2CMe_3)_4$ is dimeric in benzene. See ref 1 and references therein. We have recently prepared $Mo(OCH_2CMe_3)_4$ and find this to be dimeric in solution. M. H. Chisholm and W. W. Reichert, unpublished work.
(13) The reaction $Mo_2(NMe)_6 + 6ROH \rightarrow Mo_2(OR)_6$ was previously noted for R = t-Bu and $SiMe_3$ (ref 2c); for less bulky groups, e.g.; R = Et, Me, dinuclear compounds $Mo_2(OR)_6$ are not isolated. Results to be submitted for publication.
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(15) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, submitted for publication.

Malcolm H. Chisholm,* William W. Reichert
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

F. Albert Cotton,* Carlos A. Murillo
Department of Chemistry, Texas A&M University
College Station, Texas 77843

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Chirality Retention in Twist Rearrangements of Pseudooctahedral Molybdenum and Tungsten Complexes

Sir:

We wish to present new evidence for a type of stereochemically nonrigid behavior which is capable of maintaining chirality while allowing interconversion of certain isomers. The rearrangement appears to involve a trigonal twist about a specific axis of a pseudooctahedral complex. This mechanism and the unique structural features proposed for (η^3-C_3H_5)$Mo(CO)_2$(diphos)Cl and similar complexes are based on recent crystallographic and NMR results.

Low temperature ^{13}C NMR spectra of (η^3-C_3H_5)-$Mo(CO)_2$(diphos)Cl show that the two carbonyl ligands are nonequivalent. This contrasts with previous structural studies of analogous diamine and diether chelates,[1-6] which imply that the carbonyls should occupy equivalent positions in a pseudooctahedron. In the diamine and diether structures the bidentate ligand and the two carbonyls lie in a horizontal plane, whereas the allyl group and the remaining ligand lie in trans positions above and below the plane, respectively, as in configuration I. Either structure II or III would be consistent with most aspects of the low temperature NMR spectra, but the nature of the inequivalence was revealed straightforwardly by a three-dimensional x-ray crystallographic analysis. The molecular structure[7,8] is as shown in Figure 1. This establishes that the molecule can be appropriately described as pseudooctahedral.[9] An equatorial plane[10] can be defined to include the two carbonyls, the halogen, and one phosphorus atom of the chelate. The η^3-C_3H_5 ligand and the other phosphorus of the chelate ligand lie on opposite sides of this plane. Thus the complex has no plane of symmetry, which is consistent with the NMR results, and can be schematically represented by configuration III.

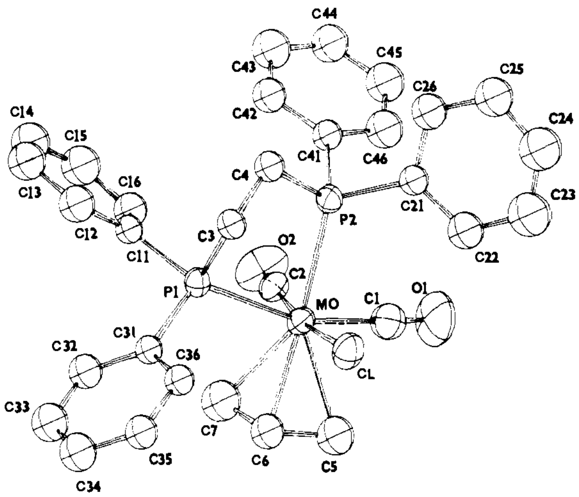
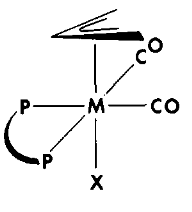
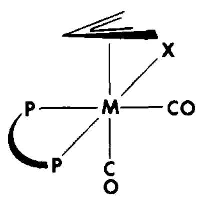


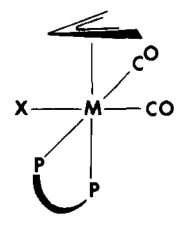
Figure 1. A perspective view of (η^3-C_3H_5)$Mo(CO)_2$(diphos)Cl. Hydrogen atoms are not shown.



I



II



III

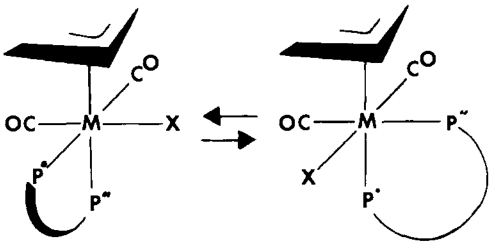
We have found that complexes of the general formula η^3-$C_3H_5M(CO)_2(L$-$L)X$ where M = Mo or W; L-L = the bidentate phosphines[1,11,12] diphos, dppm, dppe, or arphos; and X = Cl or I exhibit dynamic ^{1}H, ^{13}C, and ^{31}P NMR spectra indicative of intramolecular rearrangement barriers on the order of 12 kcal/mol.

The room temperature ^{31}P-decoupled proton NMR spectra of the iodide complexes containing diphos, dppe, or dppm exhibit three sets of resonances for the allyl moiety, typical of the AA′BB′X pattern of symmetrical η^3-allyls. At low temperatures, however, nonequivalence of the two ends of the allyl is indicated by an ABCDX pattern.[13] In the diphos complex, the diphos methylene protons appear as an ABCD pattern at −100 °C and an AA′BB′ pattern at 30 °C. The methylene protons of the dppm, however, remain nonequivalent and exhibit an AB pattern throughout the temperature range in which the allyl resonances average.[13]

Except in the arphos derivative, the ^{13}C spectra indicate equivalence of the terminal carbon nuclei of the allyl moiety and the carbonyls. The averaged spectra of the diphos complexes exhibit an apparent triplet for the methylene carbons. At low temperatures, the terminal carbons of the allyl, the carbonyl carbons, and the methylene carbons of the diphos ligand are nonequivalent.

The ^{31}P spectra of the complexes consist of a single resonance at room temperature and two (or four depending upon the resolution of ^{31}P–^{31}P coupling) lines of equal intensity at low temperature.

The infrared spectra are characteristic of cis-carbonyls; i.e., two carbonyl absorptions of approximately equal intensity are observed. Thus, the spectral data indicate that the solution structure is the same as that found in the crystal. A rearrangement that is fully consistent with the dynamic NMR spectra is shown below.



This mechanism can be described as a trigonal twist, in which the rotation of the triangular face formed by the halogen and the two phosphorus atoms relative to the face formed by the allyl and two carbonyl groups.[14] The chirality at the metal center may be designated (*S*) or (*R*) according to the octahedral sequence and chirality rules set forth by Cahn, Ingold, and Prelog.[15] Using this terminology, the inversion of chirality produced by the rearrangement can be described as an interconversion of (*S*)- and (*R*)-(η^3-C_3H_5)M(CO)$_2$(P-P)X. This process is consistent with the averaged spectra which show that the methylene protons of diphos remain nonequivalent, the methylene protons of dppm remain nonequivalent, the terminal allyl protons are not equally coupled to both phosphorus nuclei, but the vinylic protons of dppe are averaged. The carbonyl carbon nuclei show unequal coupling to the phosphorus nuclei as well, indicating that the relationship of the allyl to the carbonyls about that triangular face is retained. Therefore, even though enantiomerization occurs at the metal center in this case,[16] the spatial relationships within the X-P′-P″ unit are maintained. That is, even though the structure is nonrigid, the same side of the chelating phosphine remains oriented toward the halogen.

This implies that in the chiral structure formed with arphos, this twist process will interconvert certain pairs of isomers, but not invert the chirality of the X-As-P unit. A formal description of this process does not have an analogue in structures based on tetrahedra. In a tetrahedron on (*R*) or (*S*) designation can be assigned to each of the triangular faces; however, the specification of the chirality of one face is sufficient to completely describe the configuration about a tetrahedron. In sufficiently complex octahedral structures, the chirality rules break down;[16] nevertheless, the chirality associated with each of the triangular faces can still be specified. That is, if As replaces P′ in the diagram, an (*R*)-AsPX configuration should be retained during the rearrangement, whereas (*R*)-X(allyl)CO is inverted to (*S*)-X(allyl)CO. Thus the isomerization observed for the arphos derivative might be described as an epimerization.

The allyl-metal-dicarbonyl fragment is prochiral and since the As-P-X unit should retain its chirality, the carbonyls and the termini of the allyl should be diastereotopic. Thus, one observes that the terminal protons of the allyl are not equivalent in the averaged spectra of the arphos derivative.[17] The essential feature of this discussion is that, despite the nonrigidity of the molecule, certain elements of chirality are retained during the rearrangements; therefore, asymmetric induction can be anticipated in the reactions of the allyl moiety. A detailed discussion of the consequences of the chirality retention on the NMR spectra and the stereoselectivity of reactions of these complexes will be forthcoming.

Acknowledgments. This research was supported by a grant from the National Science Foundation (CHE76-10762). NMR spectra for ^1H and ^{13}C were obtained at 270 MHz and 67.9 MHz at the Southern New England High Field NMR Facility (NIH No. 1-P07-PR00798) and 36.5-MHz ^{31}P spectra through the courtesy of Dr. Ian Armitage.

Supplementary Material Available: Important bond distances (Table I) and bond angles (Table II) (3 pages). Ordering information is given on any current masthead page.

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(7) Space group = $P2_1/n$; unit cell: $a = 11.442$ (1), $b = 18.004$ (13), $c = 14.504$ (8) Å; $\beta = 106.54$ (3)°; $Z = 4$.
(8) Intensity data were collected on a Picker FACS-1 automatic diffractometer, operating in the θ–2θ scan mode with $K_\alpha = 0.7093$. The number of reflections with $F^2 > 3\sigma(F^2)$ used was 2006 and the reflections were collected in the scan range of 0–50. The structure was solved by heavy atom methods. Full-matrix least-squares refinement converged to the conventional discrepancy indices $R = 0.060$ and $R_w = 0.057$.
(9) These complexes can be viewed as octahedral if the η^3-allyl group is assumed to occupy only one coordination position.
(10) An unweighted least-squares plane including the atoms Cl, P1, C2, and C1 conforms to the equation $-7.611x + -13.037y + 5.123z + 1.8600 = 0$. The distances in Å of these atoms to the plane they describe are as follows: Cl = 0.079, P1 = −0.077, C1 = −0.108, and C2 = 0.105. The distance of the Mo atom from this plane is 0.237 Å.
(11) The abbreviations for the ligands are: bis(diphenylphosphino)ethane = diphos; *cis*-bis(diphenylphosphino)ethylene = dppe; bis(diphenylphosphino)methane = dppm, and 1-(diphenylphosphino)-2-(diphenylarsino)ethane = arphos.
(12) Similar infrared and limiting low-temperature ^1H, ^{13}C, and ^{31}P NMR spectra indicate that all compounds are isostructural.
(13) For example, the diphos-iodide complex shows an AA′BB′X pattern at 50 °C with chemical shifts of δ 1.82, 3.80, and 4.05 for the anti, syn, and central protons, respectively. At −100 °C resonances are observed at δ 1.33 and 1.99 for the anti, δ 3.25 and 4.46 for the syn, and δ 3.93 for the central protons. The diphos methylene protons resonate at δ 1.33, 1.99, 2.36, and 3.00 at −100 °C, and at δ 2.37 and 3.14 at 50 °C. The methylene protons of dppm resonate at δ 4.19 and 4.71 at 25 °C and do not vary significantly as the temperature is lowered in the ^{31}P decoupled spectra.
(14) These variations do not arise from conformations of the chelate rings. The similarity in the spectral properties of the diphos, dppm, and dppe demand that the dynamic NMR spectra result from processes other than conformational interconversion within the chelate rings. Effects from flexing of the five-membered ring in diphos begin to occur below −120 °C. It has been shown previously that the λ–δ interconversion in diphos rings occur rapidly on the NMR time scale (e.g., P. R. Hoffman, J. S. Miller, C. B. Ungermann, and K. G. Caulton, *J. Am. Chem. Soc.*, **95,** 7902 (1973)).
(15) The configuration assignments shown in the drawing refer to X = iodide. Priorities of polyhapto ligands follow the recommendations of K. Stanley, and M. C. Baird, *J. Am. Chem. Soc.*, **97,** 6598 (1975). The rules for octahedral complexes are given by R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5,** 385 (1966), and the IUPAC, *J. Org. Chem.*, **35,** 2849 (1970).
(16) Enantiomerization occurs at the metal center in twist rearrangements of tris chelates (e.g., M. Pickering, B. Jurado, and C. S. Springer, *J. Am. Chem. Soc.*, **98,** 4503 (1976)). In most tris chelates studied to date the chirality is associated with the helicity of the chelate rings and is thus termed "secondary" chirality.[15] Our complexes are chiral by virtue of having four different types of substituents; hence, the chirality is "primary" and descriptors of helicity are inappropriate. The octahedral sequence rules[15] assume that the ligands of highest priority can be placed in a fac arrangement. When X = chloride, the sequence P′ > P″ > (allyl) is in a mer arrangement and therefore the chirality cannot be specified by the existing rules.
(17) The arphos-iodide exhibits resonances for the terminal protons of the allyl at δ 1.71, 1.82, 3.68, and 3.88 at 20 °C.

J. W. Faller,* D. A. Haitko, R. D. Adams,* D. F. Chodosh
Department of Chemistry, Yale University
New Haven, Connecticut 06520

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An Azo Compound Route to Spiropentane Thermolysis Intermediates. Formation of Vibrationally Excited Organic Molecules in the Thermal Decomposition of Pyrazolines, and Evidence Concerning the Distribution of Excess Energy in Reaction Products

Sir:

Questions concerning the mechanism of thermal decomposition of spiropentane (**1**; Scheme I) have for some time centered around the relative energies of cleavage of the so-