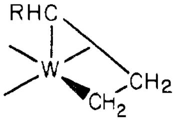
than internal olefins for the coordination site on tungsten. If it is assumed that an RCH carbene is preferred over a CH_2 carbene complex, then terminal olefins would metathesize, reaction sequences (4)–(7), preferentially to the original terminal olefin through the aegis of intermediate II. However



II

there should in fact be scrambling of the ethylenic carbon atoms; *i.e.*, labeled experiment (9) or more simply the labeled experiment (10) should establish this facet of the metathesis reaction.

$$RHC{=}^{13}CH_2 + RH^{13}C{=}CH_2 \rightleftharpoons RH^{13}C{=}^{13}CH_2 + RHC{=}CH_2 \qquad (9)$$

$$RHC{=}^{13}CH_2 + R'HC{=}CH_2 \rightleftharpoons RHC{=}CH_2 + R'HC{=}^{13}CH_2 \qquad (10)$$

The major difficulty in an experimental definition of reaction mechanism in the metathesis reaction is the low solubility of WCl_6 in nonreactive solvents and the insolubility of the reaction products from the interaction of WCl_6 and alkylating reagents in nonpolar solvents.[6] Nevertheless, there seems to be an excellent opportunity to assess this proposal by a study of the interaction of $RWCl_5$ or R_2WCl_4 (prepared in ethereal media and then isolated in pure form) and a Lewis acid in the presence or absence of an olefin. It is also possible that single crystals of postulated intermediates may be obtained from low-temperature investigations of such interactions. These possibilities are being pursued.

Acknowledgment. Acknowledgment for research support is made to the donors of the Petroleum Research Fund, administered by American Chemial Society, and to the National Science Foundation (Grant No. GP-39306X).

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(2) The number of catalyst compositions or "recipes" active in olefin metathesis is very large.[1] One nearly pervasive feature of the catalysts is the presence of tungsten or molybdenum in an intermediate oxidation state. Some catalysts are solid-state compositions. The majority of catalysts derived from discrete coordination compounds are prepared from WCl_6 and a metal alkyl (or metal hydride). A few are obtained from molybdenum or tungsten(0) complexes, *e.g.*, reaction of $W(CO)_5PR_3$ with alkylaluminum compounds and oxygen. Activity (very low) has been reported also for (arene)$W(CO)_3$ complexes.[3] Mechanistically,[4] the last system would appear to be distinct from the rest. It is not a valid presumption that the "coordination" catalysts are discrete and are soluble in the reaction medium.[6]

(3) G. S. Lewandos and R. Pettit, *J. Amer. Chem. Soc.*, **93**, 7088 (1971).

(4) There is probably a family of metathesis reactions most of which are relatively closely related in a mechanistic sense. Stereochemical features do in fact vary. For example, some catalysts are active for metathesis of internal and terminal olefins whereas the majority are active only with internal olefins.[1,5]

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Received November 5, 1974

Geometrical Isomerism Arising from Partial Substitution of Metal Atoms in Isopoly and Heteropoly Complexes. Possibilities for the Keggin Structure

AIC40749X

Sir:

The existence of so-called mixed heteropoly anions of tungsten, molybdenum, and vanadium is well established, particularly for those complexes with the Keggin structure (Figure 1). Individual members of the series $PV_xW_{12-x}O_{40}{}^{(3+x)-}$, $PV_xMo_{12-x}O_{40}{}^{(3+x)-}$, and $PMo_xW_{12-x}O_{40}{}^{3-}$, for example, can be separated and are identifiable by voltammetry.[1] It has been clear for some time that there are many possibilities for isomerism[2] in such complexes, but until now there has been little reason to discuss these in any detail since there appeared to be no experimental way of distinguishing one isomer from another. Recently, however, we have been able to verify the existence of isomers of P–V–W and P–V–Mo anions by means of nmr and esr spectroscopy,[3] and it appears likely that in favorable cases individual isomers of reduced species could be separated. Such complexes would afford novel opportunities for examining isolated magnetic interactions in oxide-like environments. In order to provide the necessary background for further work in this area we have computed the numbers and degeneracies of all isomers of the "binary" mixed anions $MZ_xZ'_{12-x}O_{40}{}^{n-}$ and list them here together with a convenient way of representing individual species.

Table I. Isomer Count for $MZ_xZ'_{12-x}O_{40}{}^{n-}$ Anions

x	Numbers of isomers[a] (degeneracies)	Total isomers
1	$\underline{1}$ (12)	1
2	$\underline{1}$ (6), $\underline{2}$ (12), 1 (12), 1 (24)	5
3	$\underline{2}$ (4), 1 (8), $\underline{3}$ (12), 7 (24)	13
4	$\underline{1}$ (3), $\underline{2}$ (6), $\underline{6}$ (12), 2 (12), 16 (24)	27
5	$\underline{9}$ (12), 1 (12), 28 (24)	38
6	$\underline{2}$ (4), $\underline{2}$ (6), 2 (8), $\underline{6}$ (12), 4 (12), 32 (24)	48

[a] All isomers are dissymmetric except those underlined.

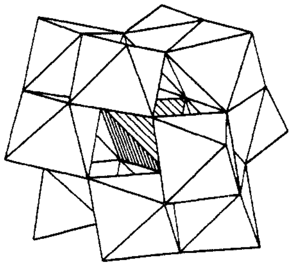

Figure 1. The Keggin structure for $MZ_{12}O_{40}{}^{n-}$ heteropoly anions showing the arrangement of ZO_6 octahedra around the central MO_4 tetrahedron.

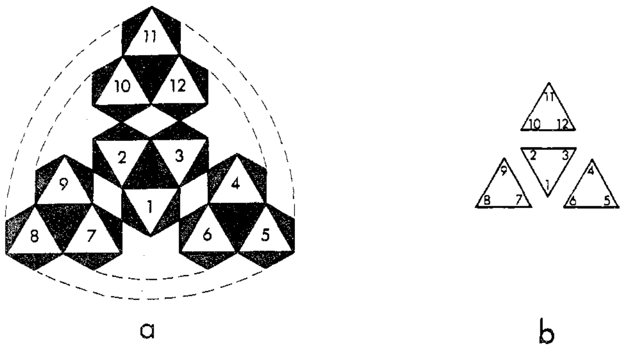

Figure 2. (a) Unfolded Keggin structure showing the numbering of Z atoms. (b) Simplified version of (a) in which only edge-shared octahedra are shown linked.

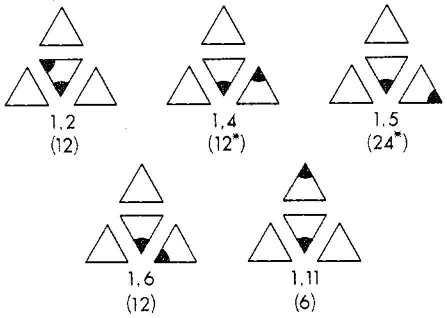

Figure 3. The five isomers of $MZ_2Z'_{10}O_{40}{}^{n-}$ with their respective degeneracies (in parentheses). Dissymmetric species are labeled with an asterisk.

The Keggin structure (minus the central tetrahedron) is shown in an unfolded form in Figure 2a, with the numbering scheme that we have adopted. Figure 2b shows a simpler graphical representation, and its use is illustrated in Figure 3 with the five isomers of $MZ_2Z'_{10}O_{40}{}^{n-}$. For larger values of x in $MZ_xZ'_{12-x}O_{40}{}^{n-}$ the isomers were retrieved by determining which of the $12!/x!(12-x)!$ arrangements of Z and Z' atoms were equivalent under the operations of the molecular point group (T_d).[4] A summary of the results[5] is given in Table I and a complete listing of isomers in Table II (supplementary material). Most of the isomers, except those underlined in the tables, are dissymmetric and the degeneracies listed include both enantiomorphs.

Acknowledgment. Support of this research through Grant GP 10538 from the National Science Foundation is gratefully acknowledged. High-speed computations were carried out at the Georgetown University Computation Center.

Supplementary Material Available. Table II, listing all possible isomers, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number AIC40749X.

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(4) The process was programmed for a digital computer. It is of course not necessary to consider more than $11!/x!(11-x)!$ arrangements since a Z atom is always placed in position 1. In practice all isomers were retrieved before half of the possible arrangements had been read.

(5) Weakley[2] has recently presented a correct solution for $x = 2$ and an incomplete solution (11 isomers) for $x = 3$.

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Received October 29, 1974