boron clusters is quite illuminating. If the motions required for interconversion of idealized forms in $B_8H_8^{2-}$ are compared with those in $B_9H_9^{2-}$ for $D_{3h}$ (symmetrical tricapped trigonal prism) $\rightleftharpoons$ $C_{4v}$ (capped square antiprism), there is little substantive difference; if anything, the requisite motions are smaller in the latter case. Yet the barrier to rearrangement in $B_9H_9^{2-}$ must be substantially larger than in $B_8H_8^{2-}$ since the characteristic $^{11}B$ resonance for $D_{3h}$ $B_9H_9^{2-}$ is observed up to temperatures of 200°.[19] We conclude that in the $B_9$ case that there is an electronic factor operative in raising the rearrangement barrier; the $C_{4v}$ (capped square antiprism) form, which is the most logical reaction intermediate or transition state, is degenerate[20] for $B_9H_9^{2-}$ making the $D_{3h} \rightleftharpoons C_{4v}$ cycle spin disallowed. (We have no way in which to assess how high in energy the corresponding spin singlet state in $C_{4v}$ symmetry may be but this state need be only ~8 kcal/mol higher to account for the different nmr behavior for $B_8H_8^{2-}$ and $B_9H_9^{2-}$.) This feature *may* largely account for the substantially higher rearrangement barrier in $B_9H_9^{2-}$ than in $B_8H_8^{2-}$ where all plausible intermediates are nondegenerate.[2]

We restate our convictions[6-9] that these data on polytopal form and isomerism in boron clusters relate in a reasonable fashion to the analogous *x*-atom coordination complexes. Rearrangement barriers in eight-coordinate complexes (all ligands identical) should generally be *very* low,[8,21] and if such aggregates are charged, the ground-state form may be very sensitive to environment. The relatively unchartered area of rearrangements in $ML_7$ and $ML_9$ complexes should prove rich in stereochemically nonrigid structures. We anticipate that rearrangement barriers in $D_{5h}$ $ML_7$ complexes will generally be comparable to or slightly higher than for $ML_8$ species whereas $ML_9$ barriers should be less than or comparable to those for $ML_8$ unless, as in $B_9H_9^{2-}$, electronic features proscribe a low-energy rearrangement itinerary.

The polyhedral borane anions, $B_nH_n^{2-}$, are ideal probes for delineation of cluster rearrangement barriers in the comparison with coordination compounds or metal clusters of the form $ML_n$ or $M_nL_m$. This is especially true where the preferred coordination polyhedron is not a regular polyhedron. Rearrangement barriers for carboranes or any heteroborane cannot be used for normalization procedures since electronic features may obscure intrinsic *x*-atom cluster rearrangement features; the heteroatom residing in a unique position of an irregular polyhedron may substantially raise or lower the rearrangement barrier. In this context, we note that our nmr studies of the $B_6C_2H_8$ carborane system reveal none of the striking fluxional features of the parent $B_8H_8^{2-}$ ion. The carborane $B_6H_6(CCH_3)_2$, like $B_8H_8^{2-}$ in the $Zn(NH_3)_4^{2+}$ salt, is dodecahedral in the solid state.[4] However, $^{11}B$ nmr studies of this carborane show only two of three required boron atom environments for the dodecahedral form.[22] New and extensive $^{11}B$ nmr experiments of $B_6C_2H_8$ in various solvents, including $CS_2$, acetone, and $CHCl_2F$, to temperatures as low as −140° and of *C,C'*-$B_6H_6(CCH_3)_2$ to −140° have shown no indication of the requisite three environmental sets of boron atoms (only two are discerned). These data are consistent with a relatively nonfluxional molecule with accidental equivalence of two sets[22] or a rapid Hoard–Silverton[8,23] rearrangement which equilibrates square-antiprismatic and dodecahedral forms and on the average[8] yields two boron atom environments. The experimental data do not provide a basis for selection of alternatives.[24]

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**Registry No.** $B_8H_8^{2-}$, 12430-13-6; $B_{11}H_{11}^{2-}$, 12430-44-3; $B_7H_7^{2-}$, 12430-07-8.

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## Mechanism for the Olefin Metathesis Reaction

AIC40767E

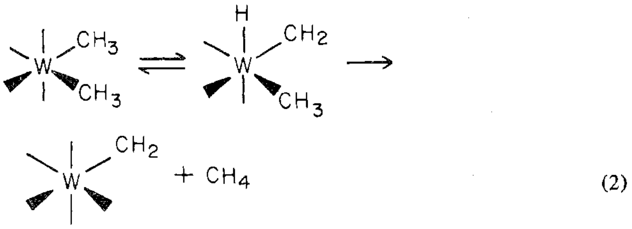
*Sir:*

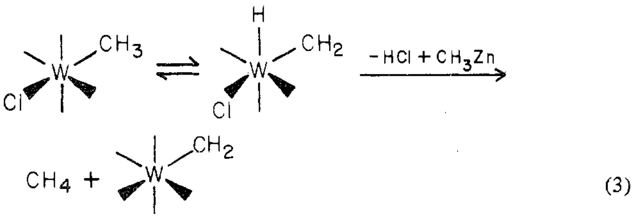
One of the more remarkable catalytic reactions is olefin metathesis[1] (1) in which the net transformation comprises

$$RHC{=}CHR' \rightleftharpoons RHC{=}CHR + R'HC{=}CHR' \qquad (1)$$

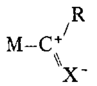
scission of a carbon–carbon double bond. With appropriate catalysts, this reaction is very fast at 25° with equilibrium attained in 1–3 min. The reaction mechanism is as yet unestablished, and an understanding of this profound C=C bond breaking-making reaction remains a major scientific challenge. I wish to present here a simple metathesis reaction scheme based on metal–carbene intermediates. This scheme applies principally to the metathesis[2,3] catalyzed by the products from the interaction of tungsten(VI) chloride and alkylating (or reducing) reagents.

We have found that tungsten(VI) chloride, dissolved in benzene, reacts with metal alkyls at 25° with evolution of alkanes and small amounts of alkenes.[5,6] Especially instructive is the reaction course of dimethylzinc with tungsten(VI) chloride in benzene (presence or absence of olefin). Methane is produced. This methane contains no deuterium when the reaction is allowed to proceed in a deuterated-solvent medium.[5] Clearly, α-hydrogen elimination from the tungsten methyl group must be taking place (eq 2 or 3).

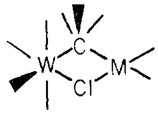

(2)


(3)

The resulting tungsten complex from (2) or (3) would have a carbene ligand at least initially. Stable carbene complexes of transition metals are known but with one exception, W(CO)$_5$C(C$_6$H$_5$)$_2$,[7] these are of the type M–CRX, with X an electronegative group, in which canonical forms like contribute to stability.

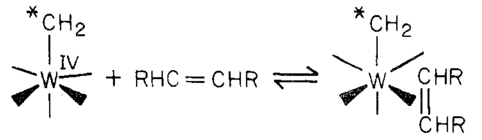

$\mathrm{M{-}C^{+}(R)X^{-}}$

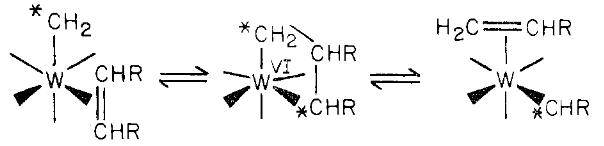
Simple CH$_2$ carbene–metal complexes are unknown; these are expected to be relatively unstable or at the very least highly reactive. However, high reactivity is evident in the metathesis catalyst which provides a pathway to equilibrium in minutes at 25°. Furthermore, we find the catalyst life in the most active WCl$_6$–C$_2$H$_5$AlCl$_2$–C$_2$H$_5$OH system to be in the range of 10–25 min at 25° which would not be inconsistent with an initially high concentration of a relatively short-lived carbene complex.[5,6] Nevertheless a simple WCl$_x$CH$_2$ carbene complex is probably an unlikely form of the metathesis catalyst. I propose that the alkylating reagents play a role (in the absence of coordinating solvents) beyond that of an alkyl group source. The alkylating reagents are converted to metal halides which are, in varying degrees, Lewis acids. I suggest that these interact with the tungsten complex intermediates through halogen, alkyl, and carbene bridges. For the latter situations, three-center two-electron bonds between W, C, and the second metal atom would be formed; these are established bonding modes in lithium and aluminum compounds. In fact, the initial interaction of the metal alkyl with tungsten hexachloride (absence of coordinating or basic solvents) probably is of the form I wherein α-hydrogen elimination may become a more facile process.

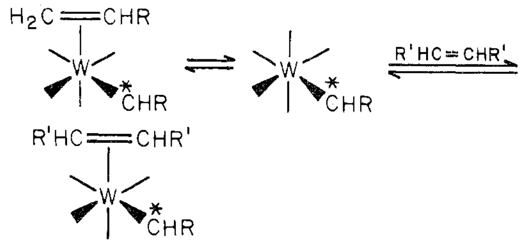

I

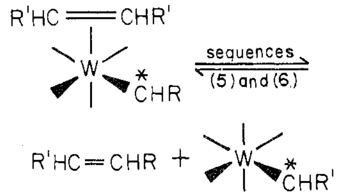
In any case the second metal must be intimately involved in the bonding since the reactivities of the various WCl$_6$–MR recipes vary drastically with the nature of M.[1,5] In addition, Tebbe[8] has convincingly demonstrated many modes of aluminum interactions with organo(transition metal) complexes. Other reactions and speculative models also germane to such modes of interaction have been suggested.[9]

A simple reaction sequence that can then account for the metathesis reaction is delineated in reaction sequences (4) through (7) where possible sites for interaction of metal atom in the halide derived from the alkylating reagent are starred (M–Cl–W bridge bonding is probably also operative).

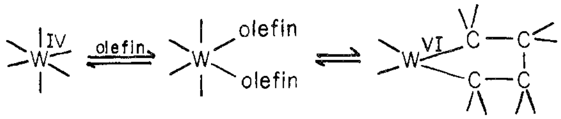

(4)


(5)


(6)


(7)

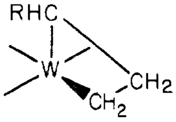
This sequence, which is formally analogous to a sequence presented by Chauvin, *et al.*,[10] comprises simple, plausible reaction steps in which the formal oxidation state of tungsten is either IV or VI. Certainly this is more reasonable than such reaction mechanism postulates as a tungsten–cyclobutane complex in a reaction intermediate or transition state or the formulation of multiple carbene ligand sites at a single metal center.[1,3] Another excellent alternative first set forth by Grubbs and Brunck[11] involves a metallocycle intermediate (eq 8).


(8)

This attractive proposal does have a questionable feature notably that π coordination of two olefins in a simple d$^2$ complex would seem somewhat improbable, and relatively complex rearrangement schemes must be set forth to achieve permutation of carbon atom positions in the metallocycle. On the other hand this proposal is supported by experimental findings. For example, Grubbs and Brunck[11] demonstrated that a putative 5-atom metallocycle ring derived from WCl$_6$ and Li(CH$_2$)$_4$Li can give rise to olefins with scrambling (metathesis) of the ethylenic carbon atoms, a feature that has not as yet been shown for the 4-atom metallocycle postulated in this article; and McDermott and Whitesides[12] elucidated considerable chemistry for this type of metallocycle with titanium as the metal center.

Recently, Casey[13] has found evidence in support of a carbene type of mechanism for olefin metathesis-like reactions using a low-valent tungsten complex. Mechanistic featurues in his system may relate in a formal fashion to the WCl$_6$ system discussed above.

Most of the catalysts derived from tungsten(VI) chloride are inactive for metathesis of terminal olefins; in fact we have found that terminal olefins inhibit the metathesis of internal olefins with these catalysts.[5,6] It is eminently reasonable to presume that terminal olefins will compete more effectively 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 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.



II

$$RHC{=}^{13}CH_2 + RH^{13}C{=}CH_2 \rightleftharpoons RH^{13}C{=}^{13}CH_2 + RHC{=}CH_2 \tag{9}$$

$$RHC{=}^{13}CH_2 + R'HC{=}CH_2 \rightleftharpoons RHC{=}CH_2 + R'HC{=}^{13}CH_2 \tag{10}$$

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.

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## 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.

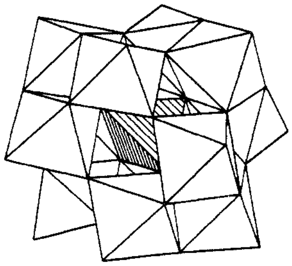

**Figure 1.** The Keggin structure for $MZ_{12}O_{40}{}^{n-}$ heteropoly anions showing the arrangement of $ZO_6$ octahedra around the central $MO_4$ tetrahedron.