Structures of M(allyl)$_4$ (M = Mo, W, Zr)[†]

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The tetraallyl complexes of Mo, W, and Zr exhibit three intriguing spectroscopic properties:[1-6] (1) at temperatures from −80 to +90 °C the ^{1}H NMR spectra of the Mo and W complexes are consistent with four equivalent allyl groups but the terminal methylenes within the individual allyl fragments are inequivalent leading to two types of *syn* and *anti* protons,[1] (2) at temperatures above 70 °C, magnetization transfer experiments with W(allyl)$_4$ and Mo(allyl)$_4$ demonstrate *syn* → *anti* and *syn* → *syn′*, *anti* → *anti′* (hereafter referred to as *syn* → *syn′*) exchange with approximately equal rates,[1] and (3) at temperatures as low as −80 °C the analogous Zr complex exhibits higher symmetry with four equivalent allyl groups and eight equivalent terminal methylenes.[6] Previous speculations[1,2,4] regarding the structures of these complexes do not accommodate the entirety of these observations. In this note we suggest that fluxional S_4-symmetric ground state structures account for the observed properties of these tetraallyl complexes.

In their original report of various tetraallyl−transition metal systems, Wilke and co-workers[4,5] suggested overall tetrahedral metal coordination on the basis of steric considerations and the high symmetry demonstrated in the ^{1}H NMR spectra (e.g., Zr(allyl)$_4$ and Hf(allyl)$_4$ exhibit just three resonances in the ratio 1:2:2, indicating four equivalent allyls and equivalent terminal methylenes within each allyl). For W(allyl)$_4$ and Mo(allyl)$_4$ these authors noted the appearance of five resonances with a 1:1:1:1:1 intensity ratio in the ^{1}H NMR spectra and offered two possible interpretations: "^{1}H-NMR spectra indicate either that two of the allyl groups are bonded differently than the other two, or that the two terminal C atoms of each allyl group do not interact with the metal in the same way." Soon after, Ramey and co-workers[3] eliminated the former explanation via analysis of the scalar ^{1}H−^{1}H couplings which demonstrate that all five protons are interconnected via C−C and C−H bonds. That the four allyl groups are equivalent was supported further by the 1:1:1 ratio of ^{13}C NMR resonances reported in Jolly and Mynott's 1981 review,[2] which included many unpublished data originating from the Max-Planck-Institut in Mülheim. Also in 1981, Benn and co-workers[1] published a detailed analysis of the fluxional behavior of W(allyl)$_4$ and Mo(allyl)$_4$ as probed by magnetization transfer experiments. Whereas Benn and co-workers adopted the unsymmetrical structure also ("each allyl is unsymmetrically bonded to the metal"), Jolly and Mynott added a twist to the proposed structure by describing it as "a tetrahedral arrangement of the allyl groups about the central metal atom which...is distorted as a result of twist about the metal−allyl axis". The exact nature of the twist is not specified. The conceptual difficulty of a model that invokes unsymmetrically bonded allyl termini is that a very low energy barrier to bringing the termini into equivalence (i.e. *syn* → *syn′* exchange) is expected. To the contrary, Benn's magnetization transfer experiments indicate that the onset of measurable *syn* → *syn′* exchange requires warming to greater than 80 °C. Furthermore, it is not clear why the rate of exchange for the Zr complex should be so much faster than those of the Mo and W complexes.

If one assumes a tetrahedral arrangement of allyl centroids about the metal, models of tetraisopropylmethane in fully staggered conformations provide a simple method of generating possible structures for tetraallyl complexes with minimal steric clashing. Alternatively, one can arrange planar allyl groups on the faces of a tetrahedron such that the central carbon C−H vectors all point to a vertex of the tetrahedron. Using these approaches, we are able to generate seven unique conformations (Figure 1), only one of which is consistent with the observed data. That structure belongs to the achiral S_4 point group. The three S_4 operations (where $S_4^2 = C_2$) interchange each of the allyl groups but leave the two terminal methylenes of an allyl group distinct. Thus, the S_4 geometry satisfies the spectroscopic inequivalencies without resorting to unsymmetric metal−allyl bonding interactions. Rather, the inequivalencies of the terminal methylenes of any allyl arise from the different environments provided by the neighboring allyls. By releasing the constraint of using only staggered conformations, it is possible to generate other unique structures; however such structures are either unrealistically strained or lack the required symmetries. Square planar metal coordination geometries also are possible, but such structures suffer severe interligand nonbond repulsions at typical metal−carbon bond lengths.

Why should the tetraallyl complexes Mo, W, and Zr have the S_4 geometry? The simplest explanation invokes steric arguments. To assess these arguments quantitatively (although not necessarily accurately), we have performed molecular mechanics computations using the SHAPES/CHARMM force field.[7-9] We were encouraged to find that, of the 14 nonredundant local minima located using random searches of metal−allyl torsion angles, the S_4 geometry has the lowest energy. A detailed examination of the number of nearest neighbors for each of the methylene H's reveals that the two *anti* protons are "more" inequivalent (11 vs 7 neighbors within 3.5 Å) than the two *syn* protons (7 vs 7 neighbors). Such a geometry is consistent with Benn's resonance assignments for which the chemical shift differences between the *anti* protons (3.09 ppm) are much greater than those for the *syn* protons (1.16 ppm).

[†] Dedicated to Professor Lawrence F. Dahl, University of Wisconsin, Madison, on the occasion of his 65th birthday.

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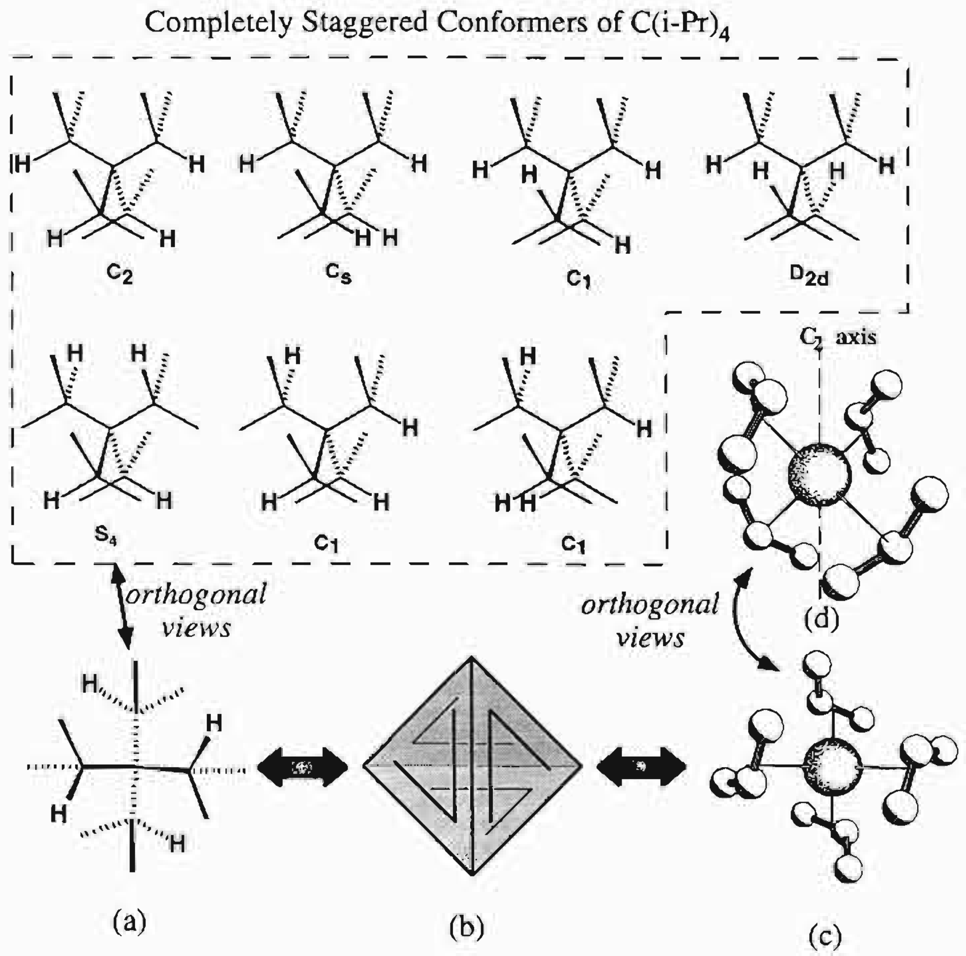

Figure 1. Conformations of M(allyl)$_4$ as derived from fully staggered tetraisopropylmethane. The sequence of structures **a**–**c** demonstrates the isostructural relationships of C(*i*-Pr)$_4$, a structure derived from placement of allyls on the surface of a tetrahedron with each allyl pointing to a unique vertex, and the lowest energy conformation of W(allyl)$_4$ as determined by molecular mechanics, respectively.

Molecular mechanics computations can be used to probe the structure and energetics of the transition state of a fluxional process, provided that the process does not involve bond rupture or formation. For example, simple rotation of the allyl groups about the metal to allyl centroid axis provides a mechanism for *syn* → *syn′* exchange (the allyls remain η^3 throughout). By molecular mechanics, the corresponding transition state is found to have C_s symmetry and lies just 3.8 kcal/mol above the ground state. Thus, although molecular mechanics computations support our proposed ground state geometry, they also suggest a lower than observed barrier to *syn* → *syn′* exchange. More importantly, simple rotation of the allyl groups does not provide a mechanism for *syn* → *anti* exchange. Furthermore, steric arguments alone do not provide a means of understanding the apparently higher symmetry of the Zr tetraallyl.

Ab initio electronic structure calculations compute the structures and energies of metal complexes with fewer assumptions than the molecular mechanics method.[10] Although computer time restrictions preclude a thorough search of the conformational space of the tetraallyl complexes, our Hartree–Fock level computations are consistent with a preferred S_4 geometry for Mo(allyl)$_4$, W(allyl)$_4$, and Zr(allyl)$_4$. Compared to molecular mechanics computations, ab initio computations yield much higher transition state energies for rotation of the allyls to the C_s transition state (ΔE = 32, 43, and 35 kcal/mol for Mo, W, and Zr, respectively). These results suggest that (1) allyl rotation should be slow at the temperatures of the magnetization transfer experiments and (2) may involve substantial electronic structure rearrangement. Ab initio computations were used to test the feasibility of square planar arrangements of the allyl centroids as well. As expected, the D_{2d} geometries were substantially destabilized (by >100 kcal/mol on average) relative to tetrahedrally derived geometries. A difference of all Zr tetraallyl geometries vis-à-vis those of the Mo and W complexes is the consistently longer optimized bond lengths for the Zr–allyl centroid distances (by 0.18 Å on average), suggestive of a weaker Zr–allyl interaction.

A likely pathway for *syn* → *anti* and *syn* → *syn′* exchange involves shift of an allyl from η^3 to η^1 coordination followed by rotation about the C–C bond and a shift back to η^3 coordination.[6] We have found two particularly attractive pathways (see the following diagrams). For the first pathway, the combined motions of $\eta^3 \rightarrow \eta^1$ interconversion, rotation about the C–C bond, and rotation about the metal–allyl centroid axis lead to a C_s-symmetric intermediate. Each time this intermediate is accessed, there is a 50% probability of one of the methylenes undergoing *syn* → *anti* exchange and 50% probability of exchange of terminal carbons. Alternatively, one can imagine $\eta^3 \rightarrow \eta^1$ interconversion and C–C bond rotation while

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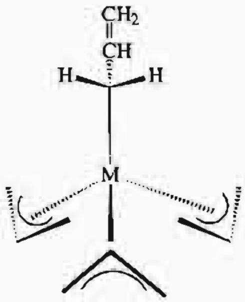
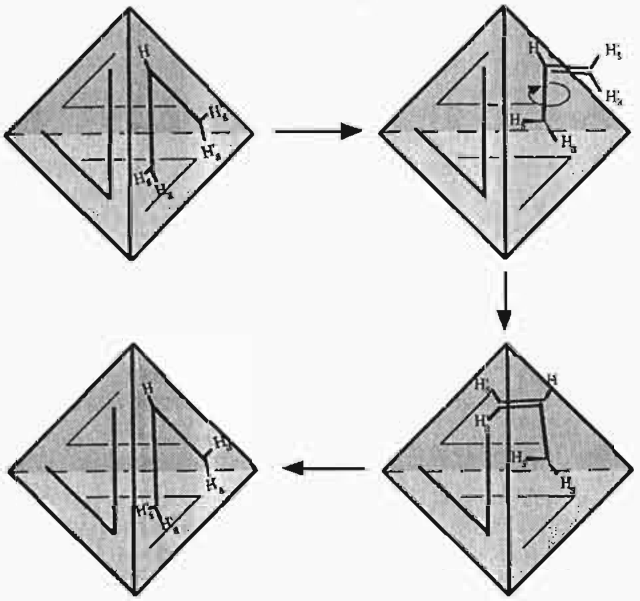
[10] Previously the electronic structures of tetraethylene metal complexes have been explored by extended Hückel calculations and used to predict the geometries of tetraallyl metal complexes: Rösch, N.; Hoffmann, R. *Inorg. Chem.* **1974**, *13*, 2656.

Pathway 1



Pathway 2



maintaining the S_4-like orientations of the other allyl groups. This pathway leads to *syn* → *anti′* and *anti* → *syn′* exchange at one methylene (i.e., a *syn* proton on the first type of methylene becomes an *anti* proton on the second methylene type) whereas the other methylene undergoes *anti′* → *anti* and *syn′* → *syn* exchange. Thus, for each interchange of terminal carbons, one of the methylene carbons undergoes *syn* → *anti′* interchange. We attribute the dramatically faster rates of fluxionality for the Zr complex to a weaker metal−allyl interaction, leading to a lower barrier for $\eta^3 \rightarrow \eta^1$ change in the allyl coordination. In order to better understand the factors that give rise to these proposed bond strength patterns, we currently are examining the electronic structures of the group 4 and 6 complexes using computations.

In principle, information about the exchange pathway is contained within dynamic ^{1}H NMR data. However, these fine mechanistic distinctions require quantitative analysis of all exchange pathways. At the time of Benn's original experiments, the instrumentation necessary to fully characterize the exchange pathways was not available.

In summary, the unusual spectroscopic properties of the group 4 and 6 tetraallyl complexes are consistent with a ground state structure of S_4 symmetry. This structure can be viewed as tetrahedral coordination of the allyls about the metal with rotation about the metal−allyl centroid axis so as to minimize steric effects. However, electronic effects are important also and result in a barrier to metal−allyl rotation that is substantially higher than that predicted by molecular mechanics computations. It is likely that the observed dynamic spectroscopic properties result from an $\eta^3 \rightarrow \eta^1$ shift of allyl coordination, but further quantitation of the dynamic behavior is required to substantiate the pathways of fluxionality. We attribute the much faster fluxional processes for the group 4 complexes relative to those of group 6 to weaker metal−allyl bonding and a corresponding lower barrier to an $\eta^3 \rightarrow \eta^1$ shift.

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Supplementary Material Available: Listings of molecular mechanics parameters and a template for creating cutout models of the S_4-symmetric tetraallyl coordination geometry (3 pages). Ordering information is given on any current masthead page.

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