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THE STRUCTURE OF TRIMETHYLENEMETHANE-ML_2 COMPLEXES AND THEIR RELATIONSHIP TO CYCLOADDITION REACTIONS

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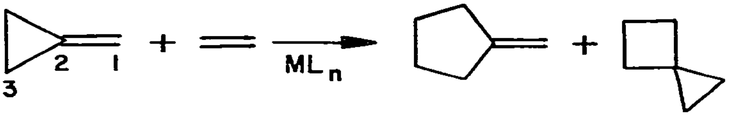
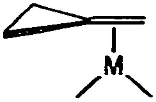
Summary

An electronic reason is offered why d^{10} and d^8 trimethylenemethane-ML_2 complexes should be η^3 rather than η^4. This was checked by molecular orbital calculations of the extended Hückel type. Both sets of complexes can be regarded as zwitterionic with the uncomplexed methylene group for the d^{10} compounds anionic and cationic for the d^8 analogs. In both cases, interconversion between the three equivalent η^3 geometries does not proceed via an η^4 structure. We find that η^2 geometries serve as way-points in this fluxional rearrangement. Implications are also drawn to the mode of cycloaddition of methylenecyclopropanes to electron deficient olefins by d^{10} ML_n catalysis and ring-opening of the methylenecyclopropanes.

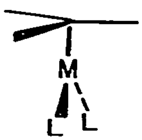
Methylenecyclopropanes add to olefins in the presence of several d^{10} metal(0) catalysts to form methylenecyclopentanes [1—3] * as is shown in (1). In some cases spirohexanes are also formed. It is reasonable to assume that a methylenecyclopropane-ML_2 complex (I) is initially formed in the catalytic cycle. Indeed, there are several examples of stable methylenecyclopropane platinum bisphosphines known [4]. The subsequent fate of I seems to involve three



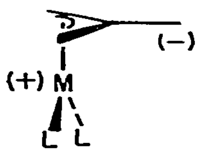
(1)



I



II



III

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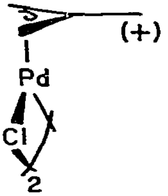
* Carbon dioxide also adds to methylenecyclopropanes in this manner [3].

distinct pathways. The olefin can add in a formal sense across the C(1)—C(3) double bond (see eq. 1 for the numbering scheme employed) to form the spirohexane product. Alternatively, the olefin could add across the C(2)—C(3), C(1)—C(3) or C(3)—C(3′) units which yields the methylenecyclopentane. Recent evidence for a third path has been given [1a] which necessitates the intermediacy of a novel trimethylenemethane-ML_2 species. This complex then undergoes the cycloaddition reaction to give methylenecyclopentanes wherein the addition proceeds in a statistical fashion across C(1)—C(3) and (C(3)—C(3′). An analogous trimethylenemethanepalladium complex generated by a different route also undergoes cycloadditions with olefins [5]. The structure of these trimethylenemethane complexes remains uncertain. Either a symmetrical η^4 complex, as in II with a small barrier of rotation about the metal—polyene axis, or an unsymmetrical complex undergoing a rapid fluxional motion are viable candidates. It has been suggested [5b] that III might be a possibility since the reaction proceeds only in the presence of electron deficient olefins. Furthermore the palladium intermediate was shown [5b] to be capable of abstracting acidic protons from hydrocarbons. We shall show that there are definite electronic reasons for favoring III over II. A complex with two electrons less also should favor to a lesser extent an unsymmetrical structure. This is in agreement with the dynamic behavior exhibited by the isoelectronic trimethylenemethanepalladium chloride dimer (IV) [6].



IV

Electron counting does not help us to understand why the trimethylenemethane (TMM) ligand is coordinated in an unsymmetrical manner since structure II for a formally d^{10} metal (TMM can be regarded as a neutral four electron donor) has 18 electrons. Slipping the ML_2 unit to III gives a 16 electron complex, both are reasonable alternatives. A system with two electrons less could be counted as having 16 electrons for both the η^3 and η^4 geometries.

d^{10}-TMM-ML_2 complexes

The energetic evolution of the orbitals for going from a symmetrical TMM-ML_2 complex (II) to III can be constructed by interacting the important valence orbitals of an ML_2 fragment [7] with the π orbitals of TMM. This is done in Fig. 1 at the symmetrical, II, geometry. At the right of this figure are shown the valence orbitals of a d^{10}-ML_2 fragment. For convenience the symmetry labels appropriate for C_{2v} are given. At low energy is a nest of four orbitals $1a_1 + a_2 + b_1 + 2a_1$, readily identifiable with the $e_g + b_{2g} + a_{1g}$ levels of a D_{4h}, square-planar complex. At somewhat higher energy is b_2. This orbital is beautifully hybridized towards the TMM fragment. Finally, at very high energy is $3a_1$. These latter two orbitals can be viewed as being derived from the symmetry adapted combination of two hybrid orbitals which point towards the missing

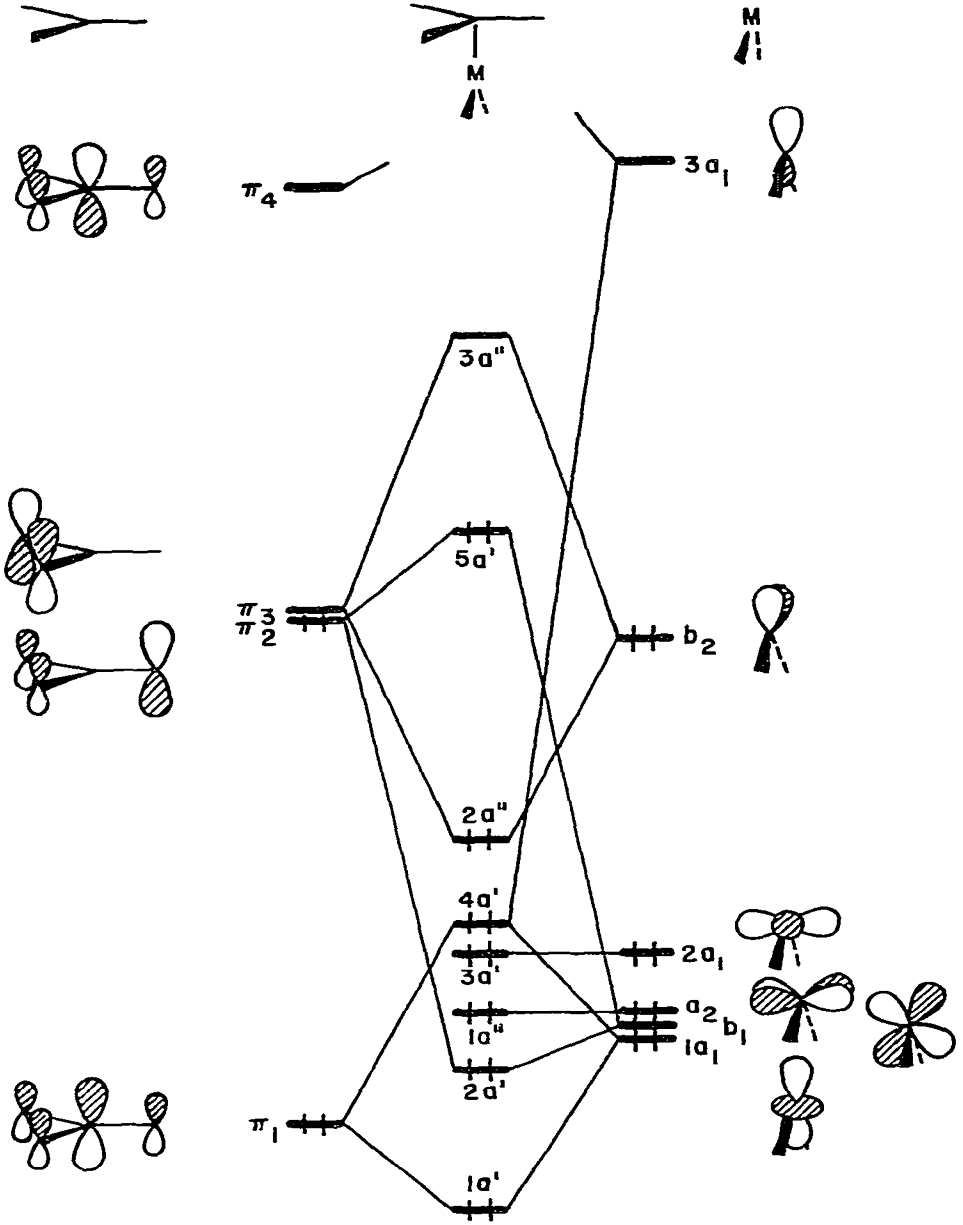
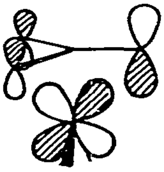
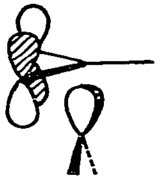


Fig. 1. Orbital interaction diagram for a symmetrical, d^{10} TMM-ML_2 complex.

ligands in a square-planar complex. Notice that b_1 and b_2 are orthogonal complements. There are important differences between the two; b_2 is beautifully hybridized towards the TMM fragment, b_1 is not while b_2 is also at much higher energy and closer to the π orbitals of TMM than b_1. Both comparisons make b_2 a stronger π donor than b_1 for a d^{10}-ML_2 fragment. The four π orbitals of TMM on the left of Fig. 1 are labeled π_1—π_4 in the C_s symmetry of the molecule $1a_1$ $2a_1$ and π_1 combine to produce three molecular orbitals. The two at lower energy, $1a'$ and $4a'$, are filled. The a_2 and $2a_1$ orbitals are essentially nonbonding. This leaves us with b_1 and π_2 along with b_2 and π_3. Both sets form the bonding combinations $2a'$ and $2a''$, redrawn in V and VI, respectively. Of the antibonding combinations $5a'$ and $3a''$ the former lies at lower energy and is

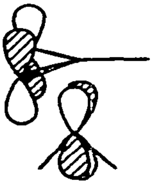


V

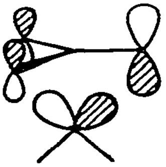


VI

filled. The reason why the highest occupied molecular orbital is $5a'$ rather than $3a''$ is again an outgrowth of the overlap and energy differnce between b_2 and b_1. The rotational barrier about the polyene—ML_2 axis will be essentially zero. Rotation by 90° (really only 30°) allows b_2 to interact with π_2 and b_1 with π_3. The counterpart of V and VI, now $4a'$ and $1a''$, respectively, are shown by VII and VIII. The antibonding analog of VII, $3a''$, will once again be filled. Since π_2 and π_3 are degenerate, b_2 interacts to exactly the same extent with each, and so on, which leads to the negligible rotational barrier. A Walsh diagram for slipping from II to III is presented on the bottom left side of Fig. 2. This figure refers to extended Hückel calculation on TMM-Pt(PH_3)$_2$ [8] *. $2a''$, VI,



VII



VIII

decreases in energy along this distortion path since the overlap between b_2 and π_3 increases. Conversely, the overlap between b_1 and π_2 decreases. This causes $2a'$, V, to rise in energy and the antibonding $5a'$ to decrease. This is a stabilizing factor since $5a'$ is destabilized more than $2a'$ is stabilized. Both reasons greatly favor III over II. The total energy calculated for TMM-Pt(PH_3)$_2$ as a function of the slipping distance, r, is presented by the solid line in the top left of Fig. 2. Here r is defined as the distance between the central carbon of TMM and the projection of the Pt on the plane of TMM. The optimum structure for the d^{10} complex is predicted to be one where the ML_2 unit is approximately below the two methylene carbons (r 0.77 Å). The energy difference between it and II is 9.4 kcal/mol. The shape of the HOMO ($5a'$) at the optimized structure, IX, is quite similar to π_2 itself, with a large coefficient on the uncoordinated methylene carbon and little density on the metal, which leads to the zwitterionic formulation in III. The charge calculated for this carbon was -0.792. One possible mode of cycloaddition of the olefin to III is shown in X. Notice that the

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* The C—C and Pt—polyene distances were set at 1.41 and 2.25 Å. The other geometrical details and parameters were taken from previous work [7a]. The calculational method is described in ref. 8.

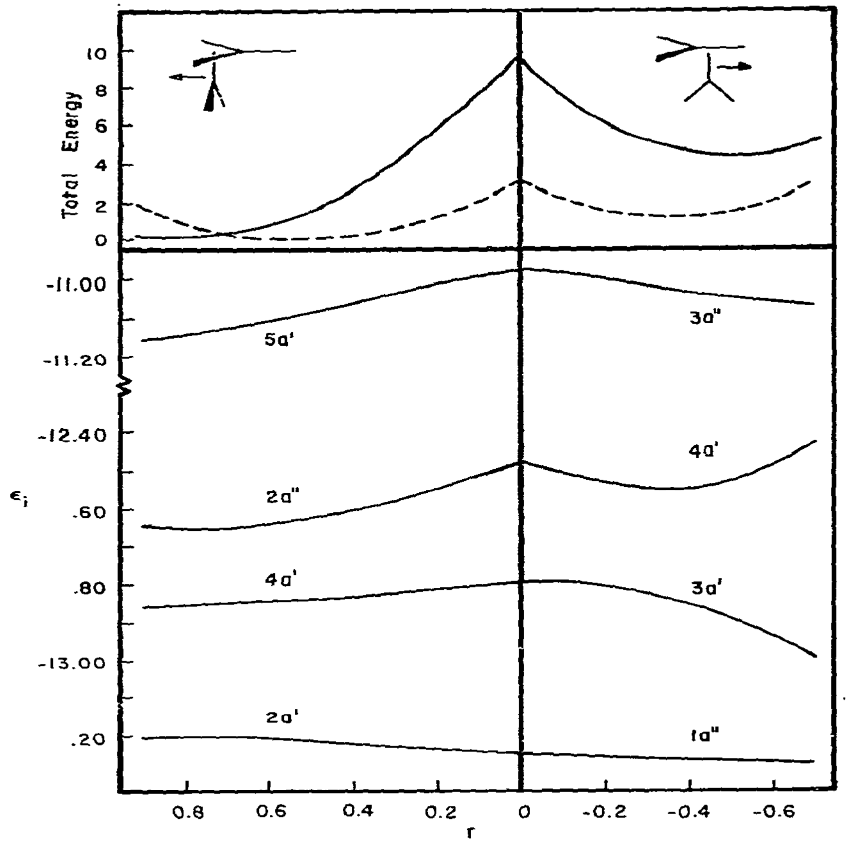
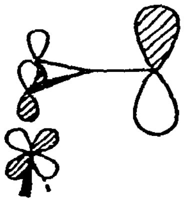
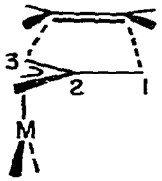


Fig. 2. Extend Hückel calculations for slipping in TMM-Pt(PH_3)$_2$. Here r is the distance between the projection of the Pt on the plane of the TMM ligand and the central carbon of TMM. The top of this Figure shows the variation in total energy (kcal/mol) with respect to r for a d^{10} case (solid line) and d^8 case (dashed line). The bottom portion of the Figure plots the variation in energy of the important orbitals (eV).

symmetry of $5a'$, IX, matches that of ethylene π^* in X. The lowest unoccupied orbital $3a''$ together with π_4 have the same local symmetry as the ethylene π orbital. There is some indication that the cycloaddition occurs in a stepwise fashion [5b], although we see nothing electronically wrong with a concerted, one-step mechanism. Note that the bond to C(1) in X would be predicted to form at a faster rate than to C(3) because of the unequal coefficients in IX.

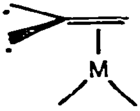

IX



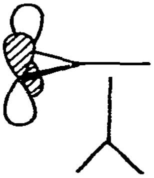
X

The alternative conformation of III, where the ML_2 unit lies in the mirror plane of the TMM ligand is greatly destabilized. Such a structure lies 18.7 kcal/mol higher in energy at the same value of r for TMM-Pt(PH_3)$_2$. The rationale behind this is precisely the same as why 16 electron π-allyl-ML_2 complexes have the conformation analogous to III [9]. Rotation of the ML_2 unit at III destroys the principal bonding interaction, b_2 with π_3. Futhermore, the overlap of b_2 with π_2 is very poor at the endpoint of rotation.

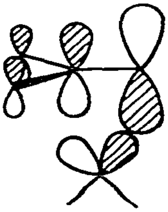
An alternative motion in the d^{10} TMM-ML_2 complex to be discussed is slipping in the opposite sense. This motion ultimately goes to an η^2 diradical structure, XI, which should be linked to that portion of a potential surface for the ring opening of the d^{10} methylenecyclopropane-ML_2 precursor, I. As was indicated previously the rotational barrier in III is essentially zero. The antibonding combination of b_1 with π_3, $3a''$, is now the HOMO. The Walsh diagram for this distortion is presented on the lower right of Fig. 2. Once again the dominant driving force for the distortion is relief of the antibonding between π_3 and b_1. The bonding combination between b_2 and π_2, $4a'$, at the η^4 geometry does not diminish in energy as much as before in $2a''$ of III. The reason is that the overlap of π_2 with b_2 drops and is replaced with π_4. The shapes of $3a''$ and $4a'$ at the calculated minimum (r —0.52 Å) for TMM-Pt(PH_3)$_2$ are given by XII and XIII, respectively. π_4 lies higher in energy and consequently is a poorer π-acceptor towards b_2. Therefore, the η^2 geometry, XI, is not as stable as the η^3 geometry, III. We calculate the difference to be 4.3 kcal/mol. Both are more stable than the η^4 structure, II. There are three equivalent η^3 and η^2 structures. The interconversion between any two η^3 structures does not take place via a transition state, III. This violates the McIver—Stanton rules [10] governing the symmetry of potential surfaces. Instead the interconversion proceeds directly via the η^2 geometries as shown in Scheme 1. The full surface is one with threefold symmetry: a peak at the middle representing II; three minima, IIIa—IIIc; and three transition states, XIa—XIc. This is typical of many cases where a Jahn—Teller instability is found [11], although this is not the reason for the instability in II.



XI



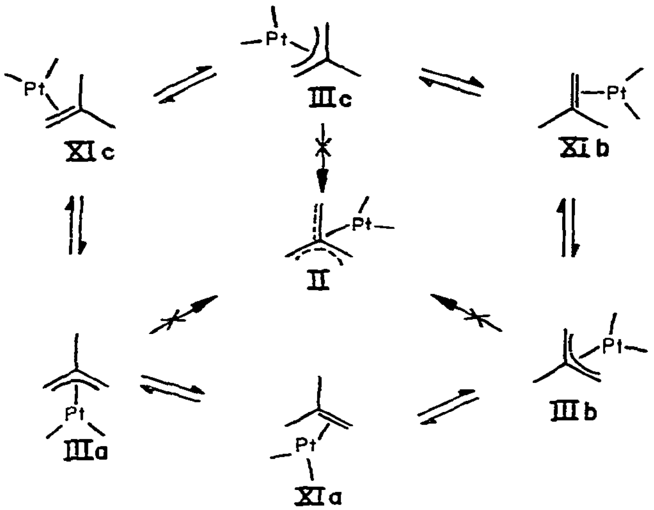
XII



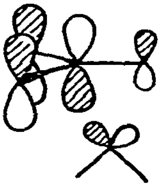
XIII

The HOMO in the η^2 transition state, XII, has the appropriate symmetry for the interaction of ethylene π^*. The shape of the LUMO is given by XIV; its symmetry matches ethylene π. Thus, the cycloaddition of ethylene could also

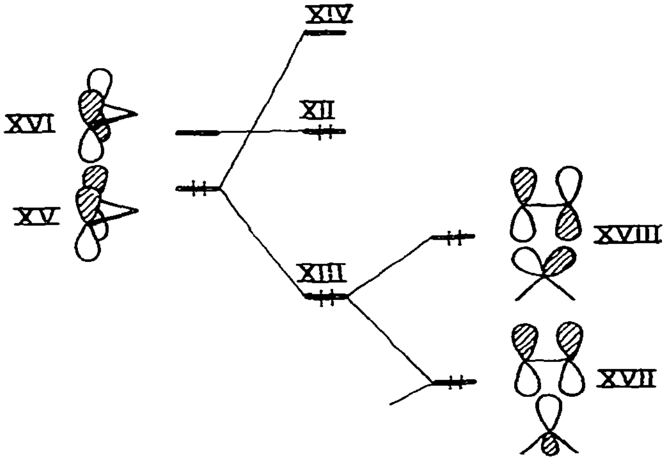
SCHEME 1



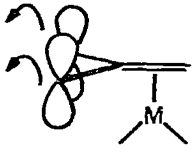
take place via geometry XI. This, however, is not consistent with the dependence of the cycloaddition reaction upon electron-withdrawing groups on the ethylene. Therefore, either a concerted or stepwise path from III is the most likely. There is one exception to this kind of mechanism. α,β-cyclohexenones add to methylenecyclopropanes in the presence of d^{10} palladium catalysts to give a product where the β carbon on the cyclohexenones rather than the expected γ one has been attacked [12].



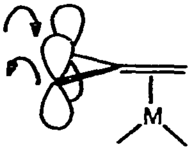
XIV



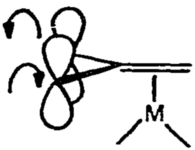
Before leaving the d^{10}-TMM-$\mathrm{ML_2}$ complexes, let us take a little closer look at the η^2 structure, XI, from another perspective. XI can be represented as a diradical. The two p orbitals on the uncoordinated methylenes will split each other into symmetric, XV, and antisymmetric, XVI, combinations with the latter at slightly higher energy (Fig. 3). Therefore, one expects the two electrons from the diradicaloid configuration to be located in XV. There is, however, through-bond conjugation [13] at work here. We could regard the remaining portion of the molecule as a 16 electron ethylene-$\mathrm{ML_2}$ unit. The two dominant interactions are given by XVII and XVIII [7a]. Both are filled and push XV to higher energy giving the LUMO the shape indicated by XIV. The highest occupied level is then the antisymmetric combination of the two p orbitals, XII. Finally the shape of XIII is given by the in-phase interaction of XVIII and XV, moderated by some antibonding from XVII. The shape of the HOMO, whether it is the symmetric-XIV or antisymmetric-XII combination of the two p orbitals, is crucial. There are three stereochemically distinct ways to close the ring to a methylenecyclopropane complex, XIX—XXI. Both modes of disrotatory ring closure, XX and XXI, are symmetry forbidden [14]. A full correlation diagram shows that XII correlates with an unfilled orbital of a'' symmetry and the empty XIV with one which is filled. From a frontier orbital perspective [14b], XII correlates with the σ^* orbital of the C(3)—C(3′) bond in I and XIV becomes the σ orbital. In the conrotatory path no symmetry element is present so that a level crossing is avoided. Furthermore, in a frontier orbital sense XII now correlates with σ and XIV becomes σ^*. Further experimental and theoretical effort must be devoted to this point. An analysis of the ring opening of methylenecyclopropane-$\mathrm{Fe(CO)_3}$ complex shows the same features, namely the conrotatory rather than either disrotatory paths should be favored. However, a disrotatory path, presumably XX, has been found [15]. This has been also established for a $\mathrm{CpMo(CO)_3}^+$ complex of methylenecyclopropane [16]. There are important differences in these complexes. The $\mathrm{Fe(CO)_3}$ complexes move to an η^4 TMM species. In the present case either the $\mathrm{ML_2}$ stays at approximately the same position or it moves from something like XI to III avoiding II, along the ring-opening path. Apparently one carbonyl in methylenecyclopropane-$\mathrm{CpMo(CO)_3}^+$ is lost in concert with ring opening [16]. Our preliminary calculations place the activation energies of XIX < XX < XXI for the $\mathrm{Pt(PH_3)_2}$ complex.



XIX



XX



XXI

d^8-TMM-$\mathrm{ML_2}$ complexes

With two electrons less, isoelectronic to IV, a major driving force to η^3 (or η^2) is lost since $5a'$ ($3a''$) is now empty. The dashed line at the top of Fig. 2 shows the variation of the total energy for slipping in either direction in TMM-

$Pt(PH_3)_2^{2+}$. On the η^3 side $2a''$, of course, is still stabilized and this is calculated to be greater than the amount that $2a'$ is destabilized. The optimum structure (r 0.55 Å) is now only 3.1 kcal/mol more stable than the η^4 geometry. Another factor stabilizing the η^3 geometry is $4a'$. At η^4, referring back to Fig. 1, molecular $4a'$ is the antibonding combination of π_1 with $1a_1$. Some $3a_1$ is mixed in a bonding fashion. Moving towards η^3 allows π_1 to be in the nodal plane of $1a_1$. In other words, there is a loss of overlap between π_1 and $1a_1$ and at the same time not much is lost between π_1 and $3a_1$. Similar arguments can be constructed for the η^2 side. Complicating the issue is an avoided crossing between $4a'$ and $3a'$. The minimum calculated for the η^2 geometry (r 0.34 Å) is 1.0 kcal/mol less stable than the optimum η^3 structure. A very small barrier then interconnects the three η^3 structures. Either the bridging chlorides in IV substantially raise this difference between η^2 and η^3 geometries or inhomogeneity effects cause the line broading upon cooling in IV [6]. We suspect the latter. d^8-ML_n, usually palladium chlorides, cause the ring opening of methylenecyclopropanes [17] *. Either an η^3 or η^2 intermediate (see [17a] for the suggestion of a species analogous to our η^2 structure) is likely to be formed.

In conclusion, it is the difference between b_1 and b_2 in the d^8 or d^{10} ML_2 fragment which sets up a driving force to move towards an unsymmetrical coordination of the TMM ligand. In an ML_3 complex, e.g. $Fe(CO)_3$, the difference is lost and an η^4 structure is formed [18]. Whenever a polyene-ML_2 complex is suggested we always should look for slipping distortions, e.g. the case of d^{10}-cyclopropenyl and cyclobutadiene-ML_2 [9,19], substituted cyclopentadienyl and carborane-ML_2 [20,21]. Alternatively, the polyene ligand itself will distort. 18-electron cyclopentadienyl and benzene-ML_2 [9,22,23] are examples.

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