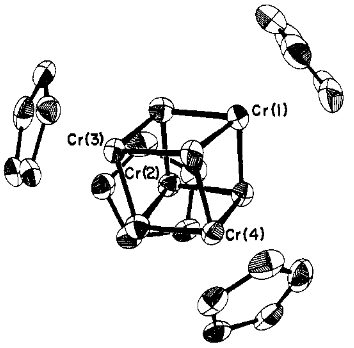

Figure 1. Molecular architecture of $(\eta^5\text{-}C_5H_5)_4Cr_4O_4$.

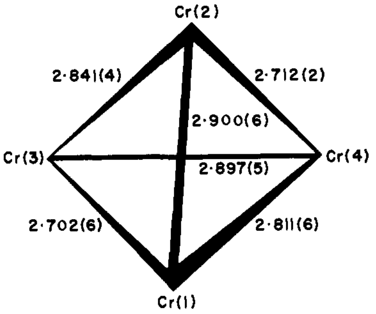

Figure 2. Arrangement of chromium atoms in $(\eta^5\text{-}C_5H_5)_4Cr_4O_4$.

V^{III}–O close to 2.00;[11] and Cr^{III}–O close to 1.96 Å[12] We therefore conclude that each oxygen atom is bonded to the triangle of metal atoms by three M–O single bonds, requiring a total of six electrons. Each M–Cp connection formally also requires six electrons. Therefore the M–O and M–Cp bonding requires in total 84 electrons for $Cp_6Ti_6O_8$, 66 for $Cp_5V_5O_6$, and 48 for $Cp_4Cr_4O_4$; $Cp_7Sc_7O_{10}$ would require 102 and $Cp_3Mn_3O_2$ 30 electrons. We see that $Cp_6Ti_6O_8$ has 2 electrons more than required, $Cp_5V_5O_6$ 8, and $Cp_4Cr_4O_4$ 12; $Cp_3Mn_3O_2$ would have 14 electrons in excess but $Cp_7Sc_7O_{10}$ would be electron deficient by 6 electrons.

The above electron count is important in understanding the magnetic properties of the three clusters $Cp_6Ti_6O_8$, $Cp_5V_5O_6$, and $Cp_4Cr_4O_4$. Caulton et al. reported $Cp_6Ti_6O_8$ to be diamagnetic, and this is to be expected by symmetry if the two excess electrons are to be equally shared by the six Ti atoms; preliminary molecular orbital calculations in fact indicate that this pair of electrons is localized in the center of the octahedron in an a_{1g} orbital.[13,14] For $Cp_5V_5O_6$ there are two unpaired electrons per cluster at room temperature.[1] The molecular orbital calculations support the simple view that the eight excess electrons can best be assigned among five vanadium atoms if two unpaired electrons are assigned to the axial and a pair of electrons to each of the equatorial V atoms. This makes the axial V atoms formally V(IV) and the equatorial V(III), which is in agreement with the shorter V(axial)–O distance compared to the V(equatorial)–O distance.

The 12 excess electrons in $Cp_4Cr_4O_4$ could simply be distributed 3 to each Cr atom, which atoms would then be formally 6-coordinated Cr(III) with 3 unpaired electrons. However, the Cr–Cr distances of 2.70–2.90 Å clearly allow antiferromagnetic interaction between the electrons on the individual Cr atoms. The magnetic moment of $Cp_4Cr_4O_4$ shows antiferromagnetism between 80 and 326 K, with no evidence of the Nêel temperature having been reached. At room temperature approximately two unpaired electrons are present. Fischer, Ulm, and Fritz also reported their material to be antiferromagnetic.[6] Molecular orbital calculations give inconclusive results because they depend on the number of unpaired electrons specified as input. However, in all calculations the HOMO and LUMO span the t_1 and a_1 representations of idealized T_d symmetry and are of very similar energies. Hence, one electron occupies the degenerate t_1 orbital, leading to a Jahn–Teller distortion. A similar distortion was observed in $Co_4(NO)_4[\mu_3\text{-}NC(CH_3)_3]_4$.[16]

Acknowledgment. We thank Professor E. O. Fischer, Munich, for unpublished observations on $[CpCrO]_4$; Professor K. Broderson, Erlangen, for discussions on $Cp_7Sc_7O_{10}$; and Professor A. B. P. Lever, York University, Ontario, for the magnetic measurements. Financial support from the Natural Sciences and Engineering Research Council of Canada and the University of New Brunswick Research Fund is greatfully acknowledged. D.E.P. thanks the Gran Mariscal de Ayacucho Foundation of Venezuela for the award of a scholarship.

Supplementary Material Available: Tables of fractional atomic coordinates, thermal parameters, bond distances and angles, and a key to the numbering scheme (7 pages). Ordering information is given on any current masthead page.

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Some Geometrical and Electronic Features of the Intermediate Stages of Olefin Metathesis

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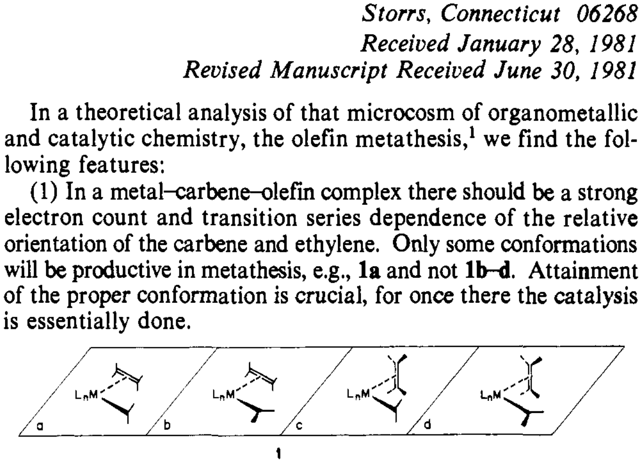
Received January 28, 1981
Revised Manuscript Received June 30, 1981

In a theoretical analysis of that microcosm of organometallic and catalytic chemistry, the olefin metathesis,[1] we find the following features:

(1) In a metal–carbene–olefin complex there should be a strong electron count and transition series dependence of the relative orientation of the carbene and ethylene. Only some conformations will be productive in metathesis, e.g., **1a** and not **1b–d**. Attainment of the proper conformation is crucial, for once there the catalysis is essentially done.



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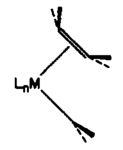
(2) For many electron counts neither the metal–carbene–olefin complex **1** nor a metallacyclobutane, **3**, may be the stable geometry, but instead an intermediate nonclassical structure, **2**, partway between the two.



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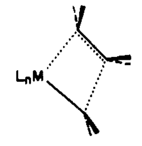

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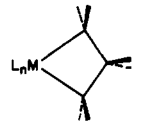

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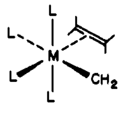
(3) The role of the metal is in some sense merely to hold the reactive partners, methylene and ethylene, in proximity, caught on the way to a cyclopropane, yet not allowed to consummate that reaction. Cyclopropane elimination from **2** or **3** is a forbidden process for some electron counts.

As models in our extended Hückel calculations we took a six-coordinate complex $L_4M(CH_2)(C_2H_4)$ (**4**), M = Fe, Mo, W; L = Cl, CO, H, and $Cp_2Ti(CH_2)(C_2H_4)$ (**5**), thus including two of the best studied homogeneous metathetic systems.[1]



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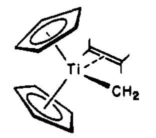

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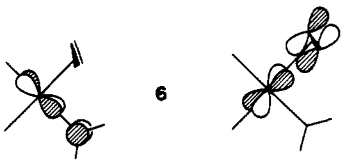
When two single-faced π-acceptor ligands are attached to a d^6 octahedral center, it is well understood that they will arrange themselves so as to maximize π bonding.[2] Thus each ligand acceptor orbital will single out a different member of the octahedral t_{2g} set (**6**, top view of **1d**) rather than both acceptor orbitals compete for the same metal d function (**7**). However, it is the "collinear" conformation **7** = **1a** which is required for metathesis.[3] From calculations, to be presented in detail elsewhere, we find that (a) the more positively charged the metal, the lower the activation energy required to reach the collinear geometry; (b) for second and third transition series metals there is a substantial barrier to attaining the collinear geometry for d^4 and d^6 electron counts, but the collinear arrangement is strongly favored for d^2 (counting the carbene and olefin as neutral ligands).



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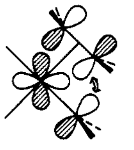

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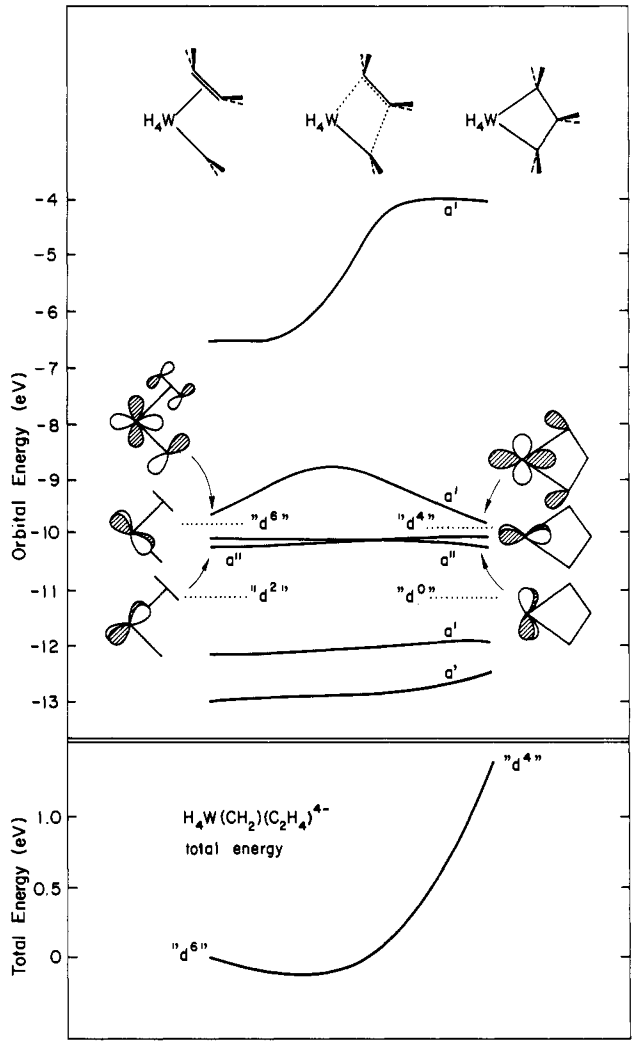
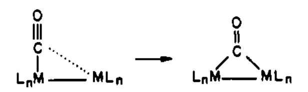


Figure 1. Frontier orbital energies (top) and total energy for a d^6 configuration (bottom) in $H_4W(CH_2)(C_2H_4)^{4-}$. The horizontal axis is a linear transit from a model carbene–olefin complex to a C_{2v} metallacyclobutane. The dotted lines show different orbital occupations. "d^n" is the configuration counting the $(CH_2)(C_2H_4)$ groups as neutral at left, the trimethylene $(CH_2)_3{}^{2-}$ as anionic at right (the hydrides are taken as H^-). Thus "d^6" on the carbene–olefin side corresponds to $H_4W(CH_2)(C_2H_4)^{4-}$ and is "d^4" on the metallacycle side.

Not necessarily relevant to the metathesis, but interesting nevertheless, is the fact that we find a reversal in preference for conformations such as **6** to **7** as one ascends from the second or third transition series to the first one, within a d^6 electron count. In **7** the two acceptor orbitals do compete for a single metal donor function. But in the process of doing so they generate a direct ligand–ligand bonding interaction. This is marked by an arrow in **7**, and it is substantial. As one goes from W(0) or Mo(0) to Fe(II), the metal–ligand back-bonding, which is known to be of major importance in the orientation of single-faced π-acceptor ligands, decreases. The π-competition effect is overcome by direct ligand–ligand interaction, and **7** comes out at lower energy.[4] There is an interesting analogy here to the propensity of carbonyls and other acceptors to enter into bridging in the first transition series, but not in the third—in a way bridging is also a ligand–ligand interaction (**8**).



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(3) In this paper we assume the essential features of the carbene–olefin mechanism for metathesis: Hérrison, J.-L.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161–176. We also assume that both the carbene and the olefin are bound to the metal. Model geometries were taken from structures of metal–carbene and -olefin complexes. For example: Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127–2134. Neugebauer, D.; Fischer, E. O.; Nguyen, Quy Dao; Schubert, U. *J. Organomet. Chem.* **1978**, *153*, C41–C44.

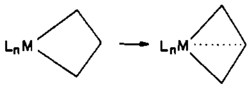
(4) This would imply that Fe(II) complexes should be good metathesis systems, since the collinear conformation is easily achieved. In fact they are not good catalysts[1] and we do not yet understand the reasons for this.

The methylene–ethylene interaction pointed to in **7** is large—the relevant CC overlap population is 0.12 in a model undeformed geometry for $H_4W(CH_2)(C_2H_4)^{4-}$. It is similar for L = Cl or CO. Yet when we study a hypothetical reaction coordinate, a linear transit, between the metal–carbene–olefin complex and a metallacyclobutane, the energy minimum comes at neither extreme but in the middle. Figure 1 shows the evolution of the frontier levels and the total energy along the transit. A similar total energy curve was obtained for **5**, as well as for the octahedral case with L = CO or Cl.

The nonclassical minimum should persist for all electron counts from d^2 to d^6 on the metal–carbene–olefin side. (Our electron counting convention takes the carbene as neutral, the trimethylene is dianionic. Thus d^n on the carbene–olefin side is d^{n-2} on the metallacycle side.) For two more electrons the low-lying empty orbital of Figure 1 is occupied. Filling it would wash out the nonclassical minimum and make for a stable metallacycle. Indeed such Pt(IV) metallacyclobutanes are well characterized.[5]

Extended Hückel calculations are not very reliable for surfaces where distances vary, as they do here. Nor did we carry out a complete search of the surface. However, our experience with similar deformations[6] gives us some confidence in these results. Supporting evidence comes from the observation of substituent effects on Cp_2Ti metallacyclobutene structures.[7] These effects are large enough that we choose to view them as also indicating distortion toward a nonclassical intermediate structure.[8] However, a recent crystal structure of $Cp_2Ti(CH_2CHPhCH_2)$ from the Grubbs group, as well as NMR studies on related titanacyclobutanes,[9] are in disagreement with our conclusions. They indicate a stable metallacycle, albeit with long CC bond lengths.

Some additional features of the crucial metathesis route **1** → **2** → **3** are the following: (a) In a d^6 (carbene, olefin side) complex there is a low-lying empty orbital. It is substantially localized on the carbene and available for attack by nucleophiles there. (b) The low-lying orbital on the metallacycle side could take up a seventh ligand. Coordination of a base on either side would hamper the metathesis traverse, for it is this empty orbital, through its bonding counterparts, which makes the transformation easy. Could the role of the Lewis acid cocatalyst in metathesis reaction be to tie up any stray base? (c) The metallacycle geometry is higher in energy than that of the nonclassical minimum, but not that high that interconversion from one minimum to type **2** to its partner would be that difficult. Nevertheless we are led to seek out deformations which stabilize a d^0–d^4 metallacyclobutane, for instance a change in bite angle[6a] (**9**) which could also be viewed as a rhomboid distortion. Puckering in the metallacycle appears to be unimportant.



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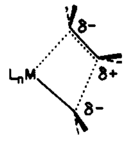
It remains to be seen if the nonclassical minima can be used as a basis for elucidating the stereoselectivity of metathesis.[1] Certainly they contain a highly polarized olefin component (**10**).



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We have already noted the strong methylene–ethylene interaction, even in the undistorted complex **1**. The CC overlap populations generated along the linear transit of Figure 1 parallel those of a free methylene attacking a free ethylene. So in a sense the metal seems to do little other than hold two reactive components together, in a geometry favorable[11] for their interaction. Yet it does more. It prevents, for some electron counts, the net addition. Cyclopropane elimination from the octahedral metallacycle turns out to be a forbidden reaction for d^0–d^4 (on the metallacycle side), allowed for d^6. It is also forbidden from Cp_2Ti(trimethylene). This is in accord with the general pattern of predominant metathesis for low d electron counts,[1] cyclopropane elimination or addition without metathesis for d^6 complexes.[12] There are exceptions to this pattern, i.e., both metathesis and cyclopropanation.[13,14]

Acknowledgment. We are grateful to R. J. McKinney, F. N. Tebbe, and D. L. Thorn for keeping us informed of their work in the area and C. N. Wilker for discussions. Our work was generously supported by the National Science Foundation through Research Grant CHE 7828048. The permanent affiliation of O.E. is with the Laboratoire de Chimie Theorique, Orsay, France, and her stay at Cornell was made possible by grants from CNRS and NATO. We thank J. Jorgensen for the drawings and E. Stolz for the typing.

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[5] Gillard, R. G.; Keeton, M.; Mason, R.; Pilbrow, M. F.; Russell, D. R. *J. Organomet. Chem.* **1971**, *33*, 247–258. McGinnety, J. A. *Ibid.* **1973**, *59*, 429–551. There are several other related d^8 Pt(II) four-coordinate structures.

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[7] McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T.; Tebbe, F. N. *J. Am. Chem. Soc.*, following paper in this issue.

[8] Several relevant molecules are in the literature. (a) $(C_5Me_5)Ta(PMe_3)(CHCMe_3)(C_2H_4)$ has the carbene and ethylene orthogonal and not collinear: Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R., *J. Am. Chem. Soc.* **1981**, *103*, 169–176. (b) $CpFe(CO)(C(OCH_3)(OC_6H_{11}))(C_2H_4)^+$ has an yet unknown structure: Priester, W.; Rosenblum, M. *J. Chem. Soc., Chem. Commun.* **1978**, 26–27. (c) An intermediate tungsten–carbene–alkene complex was detected by: Casey, C. P.; Shusterman, A. J. *J. Mol. Catal.* **1980** *8*, 1–13.

[9] Grubbs, R. H., private communication.

[10] In $Cp_2Ti(CH_2)(C_2H_4)$ this is the $1a_1$ orbital characteristic of Cp_2ML_2 complexes: Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.

[11] Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475–1485. Hoffmann, R.; Hayes, D. M.; Skell, P. S. *J. Phys. Chem.* **1972**, *76*, 664–669.

[12] Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149–194 and references therein.

[13] Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 7808–7809. Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *Ibid.* **1979**, *101*, 7282–7292.

[14] For a recent theoretical study of metathesis see: Rappé, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1980**, *102*, 5114–5115.

Substituent Effects in Metallacyclobutenes. Contributions from a Metal–Methylene–Acetylene Adduct Form

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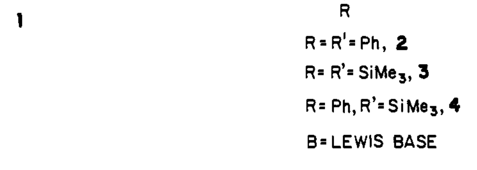
Received January 28, 1981
Revised Manuscript Received July 6, 1981

We have recently reported the syntheses of titanacyclobutenes **2** and **3** from the titanium–methylene reagent **1** and the appropriate acetylenes.[1-4] This transformation (eq 1)[5] is analogous



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