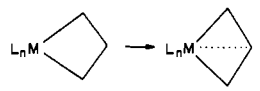
The methylene–ethylene interaction pointed to in **7** is large—the relevant CC overlap population is 0.12 in a model undeformed geometry for $H_4W(CH_2)(C_2H_4)^{4-}$. It is similar for L = Cl or CO. Yet when we study a hypothetical reaction coordinate, a linear transit, between the metal–carbene–olefin 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]

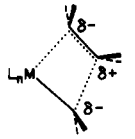
Extended Hückel calculations are not very reliable for surfaces where distances vary, as they do here. Nor did we carry out a complete search of the surface. However, our experience with similar deformations[6] gives us some confidence in these results. Supporting evidence comes from the observation 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.



9

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**).



10

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]

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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.

(6) (a) Kubáček, P.; Hoffmann, R. *J. Am. Chem. Soc.*, to be published. (b) Thorn, D. L.; Hoffmann, R. *Ibid.* **1978**, *100*, 2079–2090. (c) Berke, H.; Hoffmann, R. *Ibid.* **1978**, *100*, 7224–7236.

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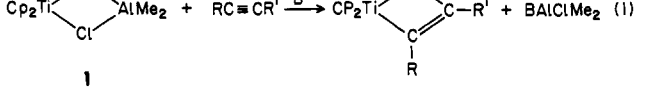
We have recently reported the syntheses of titanacyclobutenes **2** and **3** from the titanium–methylene reagent **1** and the appropriate acetylenes.[1-4] This transformation (eq 1)[5] is analogous



1

R = R' = Ph, **2**
R = R' = $SiMe_3$, **3**
R = Ph, R' = $SiMe_3$, **4**
B = LEWIS BASE

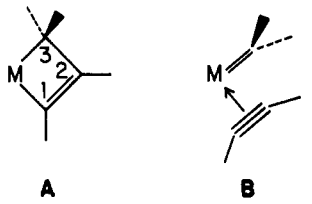
0002-7863/81/1503-5584$01.25/0

Table I. Structural Parameters for Complexes 2–4[a]

	2	3[b]	4
	Bond Length, Å		
Ti–C(1)	2.104 (4)	2.099 (3)	2.050 (4)
Ti–C(3)	2.122 (5)	2.064 (4)	2.083 (5)
Ti–C(2)	2.533 (5)	2.355 (3)	2.348 (4)
C(1)–C(2)	1.344 (6)	1.335 (5)	1.340 (5)
C(2)–C(3)	1.537 (6)	1.598 (5)	1.556 (5)
C(1)–C(3)	2.403 (7)	2.573 (5)	2.521 (5)
	Bond Angle, deg		
C(1)–Ti–C(3)	69.3 (2)	76.0 (2)	75.2 (2)
Ti–C(1)–C(2)	91.8 (3)	83.4 (2)	85.0 (2)
Ti–C(3)–C(2)	86.0 (3)	78.9 (2)	78.9 (2)
C(1)–C(2)–C(3)	112.8 (6)	121.6 (3)	120.9 (3)

[a] Refer to Figures 1 and 3 for atom labels. [b] Average of two independent data; esd shown is higher of two calculated values.

to the metallacyclobutane-forming step pivotal in the currently favored mechanism for the olefin metathesis reaction.[6-8] Solid-state structural data for complex **2**[1] are consistent with the metallacyclobutene formalism A. We observed that the $C_2(SiMe_3)_2$ unit in **3** is labile and may be substituted by acetylene, olefin, or chloroaluminum reagents.[1] We now find that the C_2Ph_2 unit of **2** is quite inert to such substitution reactions. This difference in reactivity prompted us to determine the solid-state structure of complex **3**. One important feature of this structure is a long [1.598 (5) Å] distance between the methylene and adjacent acetylenic carbon atoms, C(3) and C(2), respectively. This and other structural results indicate a substantial contribution from another valence isomer, a titanium–methylene–acetylene adduct B. We have successfully utilized a molecular orbital



A B

treatment to explain these structural and reactivity differences. To examine the possible effects of unsymmetrical substitution in the acetylene moiety, we have prepared and structurally characterized the complex $Cp_2TiCH_2(Me_3SiCCPh)$ (**4**). We herein report the initial results of these studies.

An X-ray structural determination of complex **3**[9] reveals a structure (Figure 1) in which the basic features are analogous to those of complex **2**, e.g., both complexes contain a planar metallacyclic fragment which bisects the Cp–Cp′ dihedral angle.

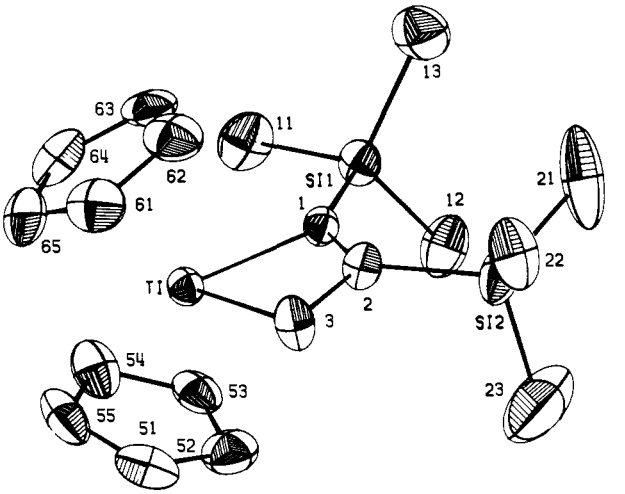


Figure 1. A perspective view of $Cp_2\overline{TiCH_2C(SiMe_3)}CSiMe_3$ (**3**). Hydrogen atoms have been omitted. The vibrational ellipsoids here and in Figure 3 are drawn at the 50% level. The numbered ellipsoids represent carbon atoms.

Close inspection, however, indicates substantial differences between the metallacyclic parameters of the two complexes. A compilation of these parameters is presented in Table I. Note that in complex **3**, the C(2)–C(3) distance is longer but Ti–C(2) and Ti–C(3) distances are shorter than the corresponding distances in complex **2**. These differences suggest a partial fragmentation of the metallacyclobutene ring and incipient formation of separate titanium–methylene and titanium–acetylene bonds. This trend in complex **3** toward the extreme form B is consistent with the greater chemical lability of the acetylene unit as compared with that of complex **2**. While marked structural and reactivity differences exist between the diphenyl and bis(trimethylsilyl) complexes, the electronic causes of these differences are not obvious. Our MO calculations[10] explore the relationship between the metallacyclobutene and methylene–acetylene complex structures and examine substituent effects thereon.[11]

We have constructed a Walsh diagram (Figure 2) using the conceptual device of sliding an acetylene approximately parallel to the titanium–methylene fragment.[12,13] The metallacyclobutene structure A is in the center, and geometries resulting from translating along the acetylene C–C axis are on the left and right. Note that while the structure on the right is an acetylene complex (B), the structure on the left (C) resembles a hypothetical edge-bound cyclopropene complex.

From the Walsh diagram, its is apparent that structure C is strongly disfavored. However, it is not clear whether the lowest energy geometry will resemble A or will be shifted toward B. In fact, the calculated optimum geometry (R = R′ = H) is slightly to the right of A and resembles the structure of complex **3**; compare the calculated distances Ti–C(1) = 2.11, Ti–C(2) = 2.38, and C(2)–C(3) = 1.65 Å with the corresponding values for complex **3** in Table I. Complex **3**, with its unpolarized, symmetrically substituted acetylene moiety, is reminiscent of the "nonclassical" structure predicted by Eisenstein et al. for metallacyclobutane complexes.[11] The structural differences between

(1) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149–6151.
(2) Klabunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Catal.* **1980**, *8*, 37–51.
(3) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074–5075.
(4) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613.
(5) Abbreviations: Cp, η^5-C_5H_5; Me, CH_3; Ph, C_6H_5; THF, tetrahydrofuran.
(6) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1–50.
(7) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449.
(8) Katz, T. J.; Lee, S. J.; Nair, M.; Savage, E. B. *J. Am. Chem. Soc.* **1980**, *102*, 7940–7942. Katz, T. J.; Savage, E. B.; Lee, S. J.; Nair, M. *Ibid.* **1980**, *102*, 7942–7944.
(9) Complex **3**: $C_{19}H_{30}Si_2Ti$; M_r 362.52; crystal grown from toluene solution. Crystal data: monoclinic; C_{2h}^5-$P2_1/c$ (No. 14); a = 17.800 (8), b = 8.704 (4), c = 26.859 (8) Å; β = 102.26 (3)°; V = 4066 (1) Å^3; Z = 8 (2 molecules per asymmetric unit), ρ(calcd) = 1.18 g cm^{-3}3. Intensity data: Syntex P3 diffractometer, Mo Kα (λ = 0.71069 Å) radiation, graphite monochromator; −100 °C; Ω scans of 1.0°; $4 < 2\theta < 48°$; 6996 reflections; absorption correction applied, μ = 5.46 cm^{-1}; transmission factors 0.86–1.00. Solution and refinement: direct methods, QTAN series, H atom positions calculated and included as fixed contribution, full matrix least-squares refinement, 44 anisotropic atoms, 397 variables, 4141 observations [$F_o^2 > 2\sigma(F_o^2)$], R = 0.053, R_w = 0.044; all Fourier residuals < 0.2 e Å^{-3}. The parameters of the two independent molecules do not differ significantly; average values are cited.
(10) The semiempirical technique used is similar to the extended Hückel technique (Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *Ibid* **1962**, *36*, 2179, 3489; **1962**, *37*, 2872) but includes a correction for two-body repulsion (Anderson, A. B. *Ibid.* **1975**, *62*, 1187). The parameter set is that described previously (Pensak, D. A.; McKinney, R. J. *Inorg. Chem.* **1979**, *18*, 3407) except that the titanium orbital energies were 4s, −8.82; 4p, −5.50; 3d, −10.5 eV.
(11) Also see accompanying paper: Eisenstein, O.; Hoffmann, R.; Rossi, A. R. *J. Am. Chem. Soc.*, preceding paper in this issue.
(12) The starting geometry used for the Walsh diagram was that of the diphenyl complex **2** with the phenyl rings replaced by H. The acetylene was then translated in either direction along its C–C axis.
(13) Note the resemblance of the metallacyclobutene MOs to those of cyclobutane: Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973; pp 222–223.

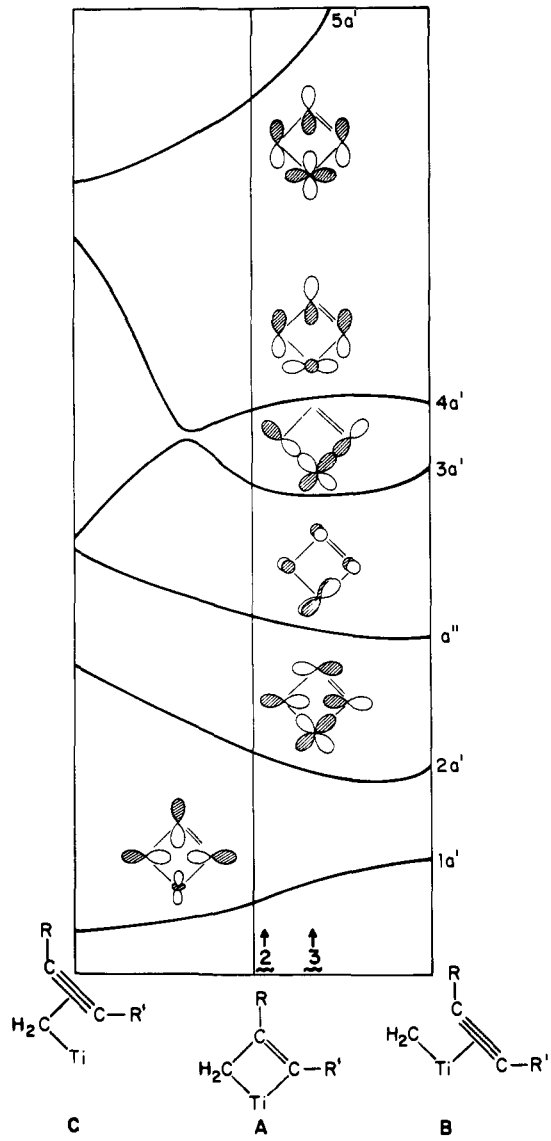
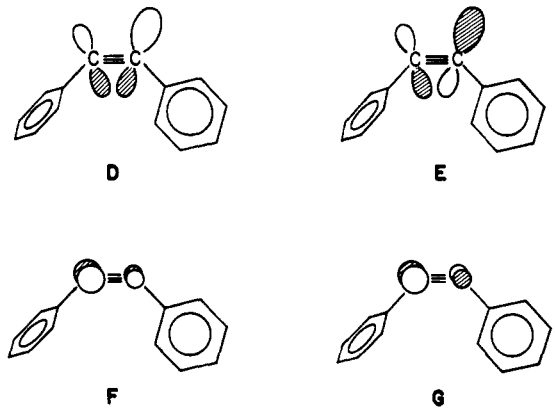


Figure 2. Walsh diagram of selected orbitals generated by translating the acetylene along its C–C axis parallel to the titanium–methylene fragment. The highest occupied MO is 4a′. Top to bottom of the figure is an energy difference of 5 eV.

complexes **2** and **3** can be traced primarily to the polarization of the acetylene moiety by the two mutually orthogonal phenyl rings. The directions of polarization of the two π systems are opposite (in plane, D and E; out of plane, F and G).



The effect of polarizing the in-plane acetylenic π system by a perpendicular phenyl ring on C(1) is most significant in MO 4a′: The p orbital component on C(2) is emphasized at the expense of that on C(1) and enhances overlap between C(2) and C(3), thereby favoring structure A. In a complementary trend in MO a″, the coplanar phenyl ring on C(2) polarizes the out-of-plane π orbital to emphasize the C(1) component. This enhances bonding overlap between C(1) and Ti, diminishes repulsion between C(2) and C(3), and reduces the preference of MO a″ for structure B. Note that interchanging the positions of the coplanar and perpendicular phenyl rings causes a shift toward structure B.

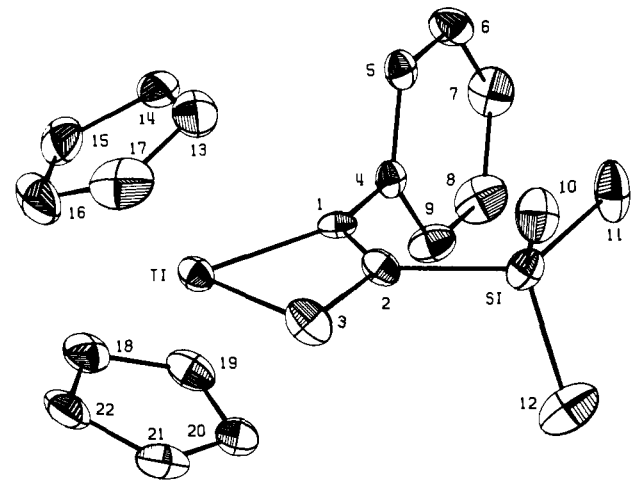


Figure 3. A perspective view of $Cp_2TiCH_2C(SiMe_3)CPh$ (**4**). Hydrogen atoms have been omitted.

The observation that the diphenyl complex **2** adopts the metallacyclobutene structure A, whereas the disilyl complex **3** distorts toward the methylene–acetylene complex B, has led us to investigate the phenyl, trimethylsilyl derivative **4**.[14] The molecular structure is shown in Figure 3.[15] The trimethylsilyl group is bound at C(2) and the C(1)-bound phenyl ring is oriented perpendicular to the metallacyclic plane as in complex **2**. Selected parameters are included in Table I. Complex **4** is in many respects structurally intermediate between complexes **2** and **3**. The Ti–C(1) distance is noteworthy, being ca. 0.05 Å shorter than that of complexes **2** and **3**. The orientation of the phenyl group suggests that the substituent effect on MO 4a′ is more important than that on MO a″, since by symmetry the phenyl group ring has no effect on the latter orbital. The MO analysis is, however, complicated by the noncomplementary polarization induced by σ and π effects. A detailed discussion will be the subject of future publication, which will also contain complete details of synthetic, structural, and reactivity aspects of these and related metallacycles.

Acknowledgment. We thank Dr. J. F. Whitney for crystallographic support, L. F. Lardear for skilled technical assistance, Dr. U. Klabunde for useful discussions, and Professor R. Hoffmann for generous communication of results prior to publication.

Supplementary Material Available: Positional and thermal parameters and listings of structure factor amplitudes (46 pages). Ordering information is given on any current masthead page.

(14) Caution: Titanacyclobutenes and their precursor **1** are prepared and handled in a high quality dinitrogen atmosphere. The byproduct of the synthesis of **1**–**4** is $ClAlMe_2$ or its THF adduct and should be treated with precautions appropriate for aluminum alkyls. The synthesis of **4** is as follows: A solution of **1** (5.0 g, 18 mmol) and $PhC{\equiv}CSiMe_3$ (3.25 g, 19 mmol) in toluene (12 mL) was treated with THF (1.7 mL, 21 mmol). After 2.5 h at room temperature, volatiles were evaporated and the resulting oil dissolved in hot *n*-hexane (80 mL). Chilling the solution to −25 °C yielded reddish crystals. Recrystallization produced spectrally pure **4** (3.6 g, 56% yield). Further recrystallization yielded the analytical sample. Anal. Calcd for $C_{22}H_{26}SiTi$: C, 72.1; H, 7.1. Found: C, 72.0; H, 7.2.

(15) Complex **4**: $C_{22}H_{26}SiTi$; M, 366.44; crystal grown from *n*-hexane solution. Except as noted, details are as for complex **3**.[9] Crystal data: orthorhombic, C_{2v}^{19}-$Fdd2$ (No. 43), a = 30.233 (5), b = 32.533 (4), c = 7.935 (1) Å; V = 7805 (3) Å^3; Z = 16; ρ (calcd) = 1.25 g cm^{-3}. Intensity data: 1927 reflections, no absorption correction required, μ = 5.15 cm^{-1}. Solution and refinement: 24 anisotropic atoms, 244 variables, 1469 observations [$F_o^2 > 3\sigma(F_o^2)$], R = 0.032, R_w = 0.029; all Fourier residuals <0.15 e Å^{-3}.