Metallacyclobutane Rearrangements

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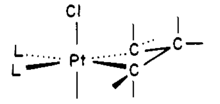
Abstract: Platinacyclobutanes undergo a highly stereospecific skeletal rearrangement. The isolobal analogy suggests a mechanism for the isomerization. In $L_2Cl_2Pt(C_3H_6)$ after initial loss of a ligand, the LCl_2Pt fragment rearranges to a pyramidal geometry in which it is isolobal to CH^+. Thus $LCl_2Pt(C_3H_6)$ is like $C_4H_7^+$, a nonclassical carbonium ion. The topographies of the potential surfaces of the organic and organometallic species are similar. They include a Jahn–Teller hill for a C_{3v} geometry and stabler T- and Y-shaped intermediates or waypoints. Detailed examination of the mechanism of the rearrangement leads to the suggestion of a new mechanism for metathesis and an understanding of how electron count and ligand electronegativity affect the stability of various intermediates in the $L_3M(C_3H_6)$ system.

Ziese's dimer ($(Cl)_2Pt(C_2H_4)_2$) reacts with a variety of substituted cyclopropanes to yield polymeric metallacyclobutane products. When these polymeric compounds are treated with an excess of hard ligands, L (L = pyridine, THF, Cl^-, etc.), a monomeric metallacyclobutane precipitates, **1**.[1] These are stable complexes and many crystal structures have been reported.[2]



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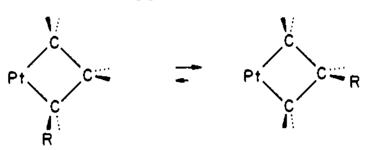
The formation of metallacyclobutane occurs with retention of stereochemistry in the cyclopropane. Thus a trans-disubstituted cyclopropane yields a trans-disubstituted metallacyclobutane.[3-7]

Puddephatt, Tipper, and their co-workers in the course of their extensive studies of the chemistry of these platinacyclobutanes uncovered a most remarkable rearrangement.[8] A substituent at the carbon α to the metal appears to migrate to a β position, **2**.



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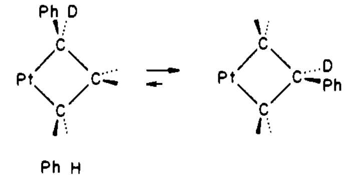
In fact the rearrangement is not a substituent migration, but a skeletal rearrangement, as the experiment, **3**, of Puddephatt and Tipper demonstrates.[9] The rearrangement in fact is stereospecific, retaining stereochemistry in the metallacycle. This was shown most clearly by experiment **4** of Casey and co-workers.[6] Both the phenyl and deuterium are on the same side of the metallocyclobutane complexes. In addition, when a metallacyclobutane is treated with soft ligands a reductive elimination of cyclopropane



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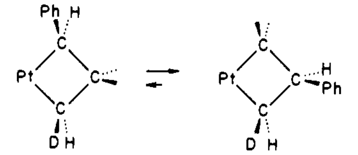

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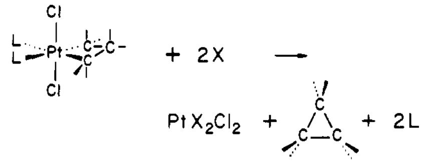
occurs, **5**. The recovered cyclopropane has the same stereo-



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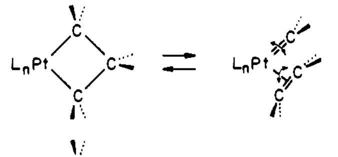
chemistry as the original cyclopropane used to make the metallacyclobutane.[3,4] However, the crossover experiments of Casey and co-workers show that the isomerization does not involve the reductive elimination of a cyclopropane.[6]

Several mechanisms have been proposed at various times to explain the available data, and these are summarized in **6**–**8**. Platinacyclobutanes were originally thought to be models for a metathesis intermediate,[10,11] and the first mechanism, **6**, invokes the metathesis pathway, in particular a carbene–olefin complex.[12]



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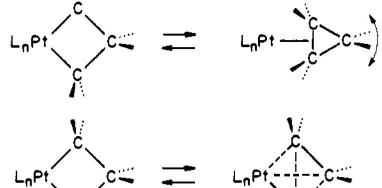

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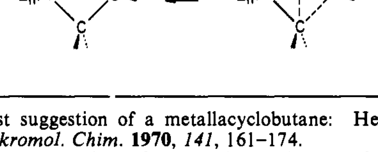

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[1] (a) Tipper, C. F. H. *J. Chem. Soc.* **1955**, 2045–2048. (b) Adams, D. M.; Chatt, J.; Guy, R. G. *Proc. Chem. Soc.* **1960**, 179–180. (c) Adams, D. M.; Chatt, J.; Guy, R. G.; Sheppard, N. *J. Chem. Soc.* **1961**, 738–742.

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[3] (a) Irwin, W. J.; McQuillin, F. J. *Tetrahedron Lett.* **1968**, 1937–1940. (b) Powell, K. G.; McQuillin, F. J. *Ibid.* **1971**, 3313–3316. (c) McQuillin, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123–2129.

[4] (a) Al-Essa, R. J.; Puddephatt, R. J.; Tipper, C. F. H.; Thompson, P. J. *J. Organomet. Chem.* **1978**, *157*, C40–C42. (b) Al-Essa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *Inorg. Chim. Acta* **1979**, *34*, L187–L188.

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[7] Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Chem. Soc., Chem. Commun.* **1976**, 626–627.

[8] See: Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149–194.

[9] Al-Essa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Am. Chem. Soc.* **1979**, *101*, 364–370.

[10] The first suggestion of a metallacyclobutane: Herrisson, J. L.; Chauvin, J. *Makromol. Chim.* **1970**, *141*, 161–174.

[11] There are many reviews of metathesis chemistry, see for example: (a) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449–492. (b) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1–50.

[12] For an explanation of why $(py)_2(Cl)_2Pt(C_3H_6)$ is not a metathesis catalyst, see: Eisenstein, O.; Hoffmann, R.; Rossi, A. R. *J. Am. Chem. Soc.* **1981**, *103*, 5582–5584.

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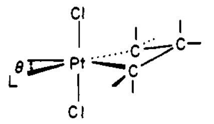
Kinetic studies have shown that the loss of one ligand, L, occurs before the skeletal rearrangement takes place.[7] The five-coordinated metallacyclobutane is now a 16-electron complex, and the carbene–olefin intermediate is an 18-electron complex. If the olefin rotates and then recombines with the carbene, the complex has isomerized. If, however, the carbene also rotates (and it will), then the stereochemistry of the cyclopropane is lost. To be specific the observed stereochemical result is consistent with the number of olefin rotations differing from the number of carbene rotations by an odd number.

The second mechanism involves an edge complex of Pt and a cyclopropane, **7**. A reductive elimination of a trimethylene produces a complex which consists of a cyclopropane bound to the metal. The cyclopropane is then envisaged to rotate and exchange the edge which is coordinated to the platinum.

Upon oxidative readdition a different metallacyclobutane is formed, maintaining stereochemistry. The problem with this mechanism is the energy of the postulated intermediate, a metal-bound yet ring-closed cyclopropane. Since trimethylene is not exchanged with any cyclopropane from solution,[6] the ring in the intermediate must bind strongly to the metal. There is no precedent for that. Our calculations indicate that the binding of cyclopropane to a Pt(py)Cl_2 is worth less than 12 kcal/mol.

A third mechanism has been proposed by Puddephatt and Tipper, **8**. The C–C and Pt–C bond breakage and reformation occur concertedly. In this way the carbon atoms are always bound to the metal and so are not free to rotate. This mechanism explains the available data.

We now propose a fourth mechanism based on their activity and capabilities for polytopal rearrangement of the five-coordinate (L)(Cl)$_2$Pt(C_3H_6) complex, **9**. When an L ligand is removed,



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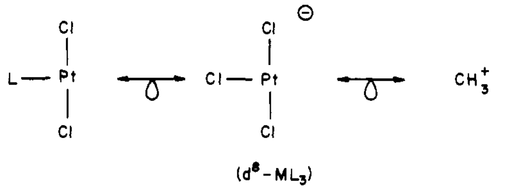
we would expect the d^6 ML_5 fragment to retain a square-pyramidal geometry.[13] In fact our calculations indicate that the remaining L ligand relaxes partway toward a trigonal-bipyramidal geometry ($\theta = 0°$). Our calculations show a minimum at $\theta = 26.7°$, but the motion of the ligand is very soft. The energy of the $\theta = 0°$ complex is only 0.05 eV higher with no barrier.

The mechanism we would like to propose begins from the established $LCl_2Pt(C_3H_6)$ intermediate and is motivated by application of the isolobal analogy[14] to the LCl_2Pt fragment in the metallacyclobutane. In the T-shaped geometry of the fragment LCl_2Pt, similar to Cl_3Pt^-, is isolobal to a methyl cation, **10**. The



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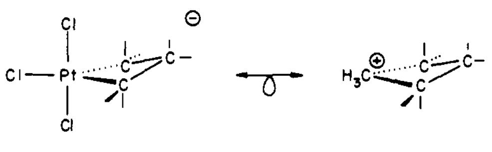

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metallacyclobutane is therefore isolobal to a protonated cyclobutane, $C_4H_9^+$, **11**. The organic species would be expected to lose a proton and become just cyclobutane. The analogous reaction for the inorganic complex would be the loss of a chlorine cation Cl^+ or a L^{2+}, leaving behind a square-planar d^8 Pt(II) complex. Neither course is likely in normal solvents. In fact a neutral ligand is lost in solution leaving $Cl_2Pt(C_3H_6)$, a Pt(IV) d^6 square-planar complex with an empty d_{z^2} orbital. This species should and does polymerize.[1]

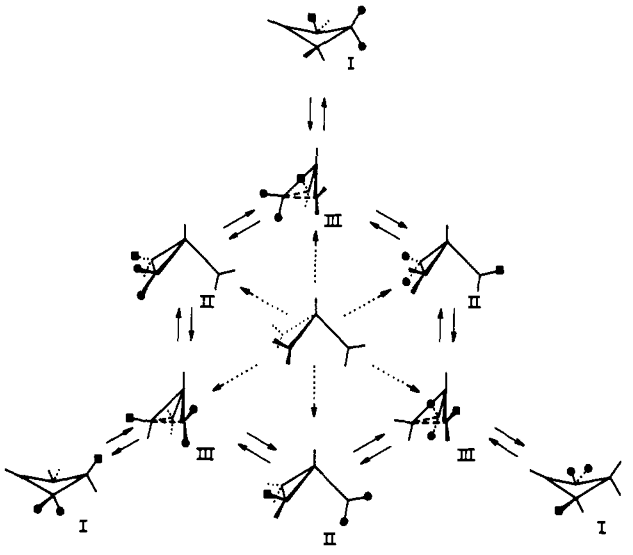
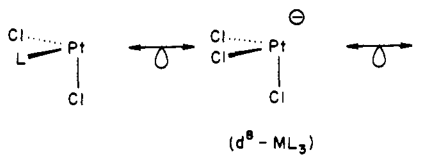


Figure 1. The interconversions of the $C_4H_7^+$ isomers I, II, III, and IV. ● and ■ are labels to demonstrate the stereochemistry of the various isomerizations. The C_{3v} isomer sits atop a Jahn–Teller hill.

A simple reorganization of the ligand sphere about the platinum leads to a more productive result. If instead of a T-shaped arrangement the ligands adopt a pyramidal near C_{3v} geometry, the Pt fragment is now isolobal to methylidyne or carbyne cation, CH^+, **12**. The metallacyclobutane is then isolobal to $C_4H_7^+$, a stable nonclassical carbonium ion, **13**.



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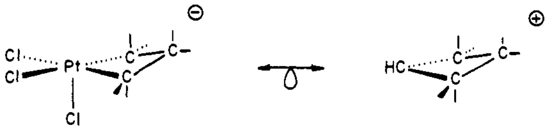

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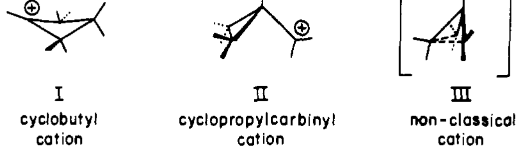
Much attention has been paid to the cyclobutyl–cyclopropylcarbinyl cation system. Three locally stable intermediates have been suggested, **14**. An STO-3G calculation found these three species to lie within 0.4 eV of one another, with II as a global minimum.[15] The interconversions of the various extreme structures are best summarized in Figure 1.



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A beautiful deuterium perturbation NMR study by Saunders and co-workers,[16] concluded that III is the major isomer present. A rapid equilibrium of the III isomers (a barrier of ~3 kcal) would make the CH_2 groups equivalent. The result appears symmetrical, IV, but this tricyclobutonium species is most likely not present. In it there are three orbitals (the p orbitals perpendicular to the

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[13] Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076.

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[15] (a) Levi, B. A.; Blurock, E. S.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 5537–5539. (b) Hehre, W. J.; Hiberty, P. C. *Ibid.* **1974**, *96*, 302–304. (c) Hehre, W. J. *Acc. Chem. Res.* **1975**, *8*, 369–376. (d) Olah, G. A.; Spear, R. P.; Hiberty, P. C.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 7470–7475.

[16] (a) Saunders, M.; Siehl, H.-U. *J. Am. Chem. Soc.* **1980**, *102*, 6868–6869. (b) Staral, J. S.; Yavari, I.; Roberts, J. D.; Prakash, G. K. S.; Donovan, D. J.; Olah, G. A. *Ibid.* **1978**, *100*, 8016–8018.

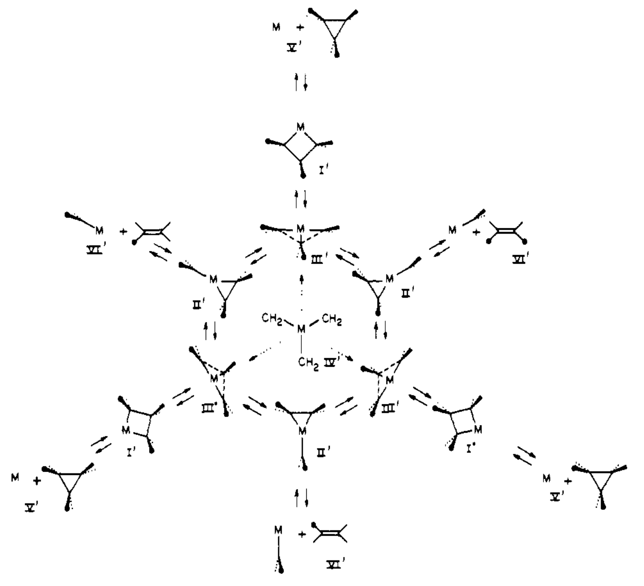
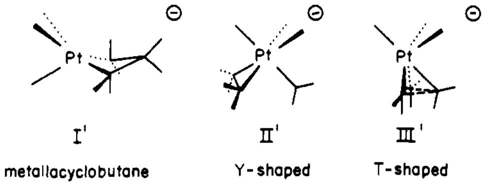


Figure 2. The interconversions of the $(\mathrm{Cl})_3\mathrm{Pt}(\mathrm{CH}_2)_3^-$ isomers: I', II', III', IV', V', and VI'. ● is a label to demonstrate the stereochemistry of the various isomerizations.

methylene planes) which fall into a two below one pattern and two electrons to place into these orbitals. A classical Jahn–Teller system results, a situation one has encountered several times before.[17] IV is atop a hill, a local maximum. The exchange of the III isomers must pass through II, not IV.

The isolobal inorganic complex should exhibit a pattern of rearrangements similar to those of $C_4H_7^+$. The overall reaction scheme is shown in Figure 2, and the specific intermediates or waypoints are shown in **15**. I' is close to the five-coordinate metallacyclobutane, **13**. II' is a d^8 Pt(II) five-coordinate 18-electron trigonal-bipyramidal complex containing an olefin and a carbene. III' is an unusual complex. The T-shaped arrangement contains a quasi-five-coordinate carbon. Moving from now on consistently from the less symmetrical $LPtCl_2$ to $PtCl_3^-$ (so as to simplify the orbital analysis and the potential energy surfaces), the orbitals of the three waypoints, **15**, are shown in Figure 3.



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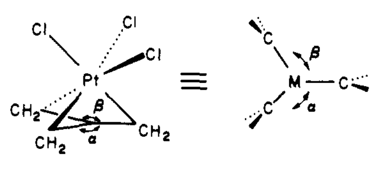
A rearrangement surface for $Cl_3Pt(C_3H_6)^-$ was computed. The primary active coordinates were chosen as the angles α and β defined in **16**. IV' is defined by α = 120° and β = 120°. Complex II' has $\alpha = \beta = 90°$. The calculated surface is shown in Figure 4. Three minima occur, for the Y-shaped geometries II', with a barrier to interconversion between them of 0.25–0.45 eV. Why are there nonequivalent Y-minima, and why does not Figure 4 have the threefold symmetry expected on the basis of Figure 2? The reason for this is that the $PtCl_3^-$ moiety is neither moved nor relaxed as α and β are varied. There are then two nonequivalent Y-type minima, **17** (dashed line is position of $PtCl_3^-$ and solid line position of the Pt–C bonds, both in projection). This is an unavoidable complication and makes life more difficult in the analysis of $Cl_3Pt(C_3H_6)^-$ vs. $HC(C_3H_6)^+$.



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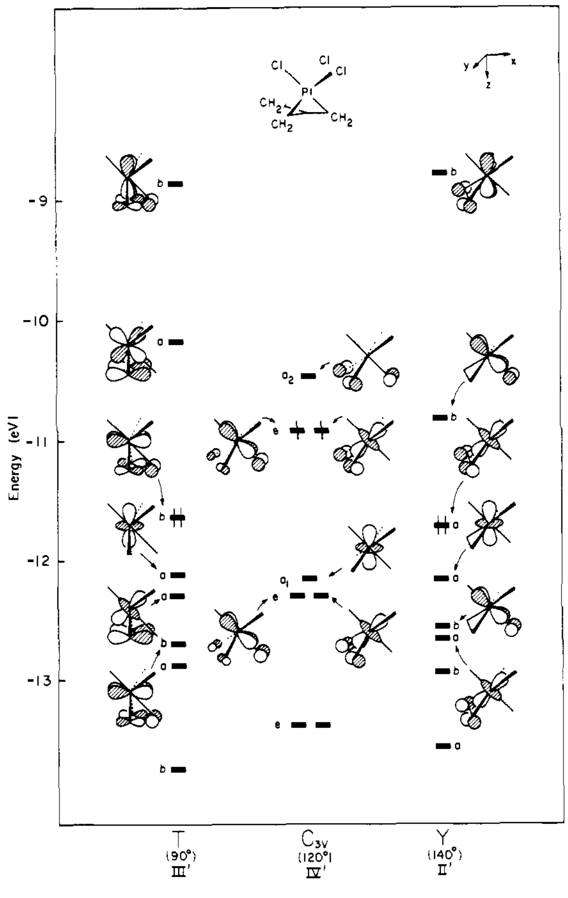


Figure 3. The orbitals of the T-, C_{3v} and Y-shaped complexes of d^8 $(\mathrm{Cl})_3\mathrm{Pt}(\mathrm{CH}_2)_3^-$.

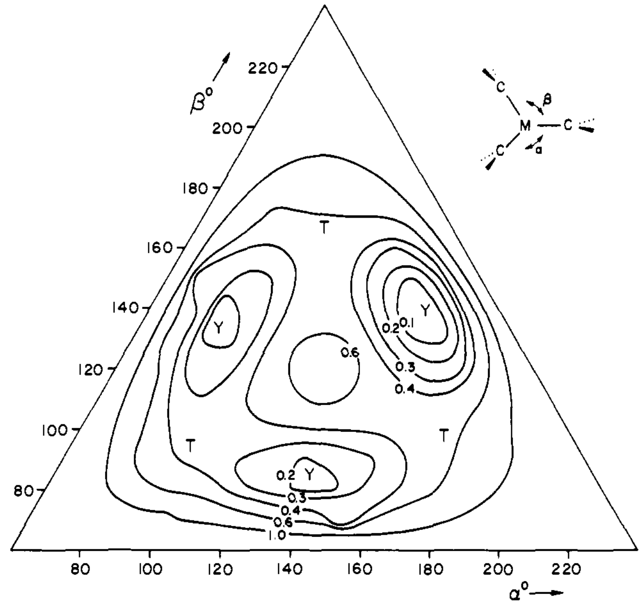
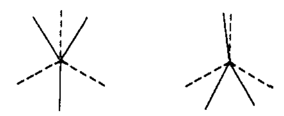


Figure 4. The potential energy surface of $(\mathrm{Cl})_3\mathrm{Pt}(\mathrm{CH}_2)_3^-$ for 0.1, 0.2, 0.3, 0.4, 0.6, and 1.0 eV energy contours. The locations of the T- and Y-shaped complexes are shown.



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[17] See for example: (a) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857–1867. (b) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255–7265; **1977**, *99*, 8440–8447. (c) Stohrer, W.-D.; Hoffmann, R. *Ibid.* **1972**, *94*, 1661–1668.

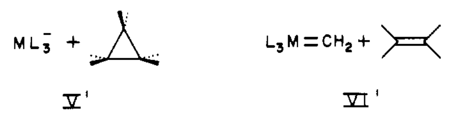
Table I. The Definition of Some Reaction Types on the $L_3M(C_3H_6)$ Surface

reaction type	most stable complex	most stable intermediate	stereochem of isomerizatn	chemistry
1	I′	II′ or IV′	lost (butane cis–trans)	metallacyclobutane isomerization with loss of cyclopropane stereochemistry
2	I′	III′	retained	Puddephatt rearrangement
3	II′	III′ or I′	lost (olefin cis–trans)	metathesis
4	III′	II′	retained	no effect on cyclopropane
5	IV′		lost (butane cis–trans)	

If the Y-shaped complexes were indeed the local minima, then the stereochemistry of the original metallacyclobutane would be lost. The transition state would consist of a set of rapidly equilibrating Y-shaped complexes which exit through the T-shaped complexes to the other metallacyclobutanes. In these Y-shaped complexes, the calculated rotation barrier of the carbene-like CH_2 moiety is very small, less than 0.01 eV. This would provide a mechanism for losing stereochemistry.

We know from experiment that the metallacyclobutane stereochemistry is maintained in these molecules. So the calculations seem incorrect. We think, however, that the general scheme of Figure 2 is correct and that the extended Hückel calculations, a most approximate procedure, are simply failing to predict properly the relative energies of the Y- and T-shaped geometries. The T-shaped structures are the likely intermediates, and in them the calculated CH_2 rotation barrier is indeed large, greater than 1.5 eV. Note that an apparently similar failure to predict the correct geometry occurs with better calculations for $C_4H_7^+$. The calculations predict the Y-shaped II as the local minimum,[15] but the experiment favors T-shaped III.[16]

The platinacyclobutane isomerization is just one piece of the chemistry possible on the surface of Figure 2. Two additional pathways that were not used by the isomerization are I′ to V′, a reductive elimination of a cyclopropane, and II′ to IV′, an explusion of an olefin, **18**. The path chosen by a particular



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organometallic complex through the surface depends upon the relative energies of the various species, I′–VI′. The five major reaction types are presented in Table I.

Table II. Preferred Reaction Types for Different Electron Counts

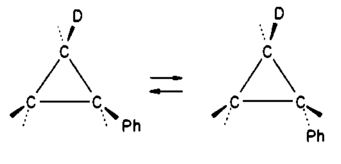
complex	electron count (carbenes neutral)	reactn type
$(Cl)_3Pt(CH_2)_3^{3-}$	d^{10}	1
$(Cl)_3Pt(CH_2)_3^{1-}$	d^8	2
$(Cl)_3Pt(CH_2)_3^{1+}$	d^6	1
$(Cl)_3Pt(CH_2)_3^{3+}$	d^4	1
$(Cl)_3W(CH_2)_3^{3-}$	d^6	5
$(Cl)_3W(CH_2)_3^{1-}$	d^4	3
$(Cl)_3W(CH_2)_3^{1+}$	d^2	2

Table III. Extended Hückel Parameters

orbital	H_{ii} (eV)	ζ_1	ζ_2	C_1[a]	C_2[a]
Pt 5d	−12.59	6.013	2.696	0.63338	0.55128
6s	−9.077	2.554			
6p	−5.475	2.554			
W 5d	−10.37	4.982	2.068	0.66854	0.54243
6s	−8.26	2.341			
6p	−5.17	2.309			
C 2s	−21.4	1.625			
2p	−11.4	1.625			
H 1s	−13.6	1.3			
P 3s	−18.6	1.6			
3p	−14.0	1.6			
Cl 3s	−30.0	2.36			
3p	−15.0	2.10			

[a] These are the double-ζ expansion coefficients.

Reaction type 1 is either a metal-catalyzed cis–trans isomerization of cyclopropane, **19**, or a cis–trans isomerization of a



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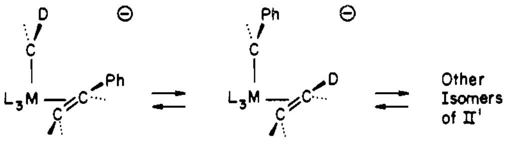
metallacyclobutane.[18] If olefin exchange with solvent is also accessible, II′ ⇄ VI′, then this pathway represents the cross-metathesis of cyclopropanes and olefins.[19] The isomerization of cyclopropane to propylene could proceed via an α-hydride abstraction from I′ or III′.[20,21]

Reaction type 2 is the platinacyclobutane isomerization discussed in this paper.[8]

Reaction type 3 is a possible metathesis pathway.[10,11] The reaction sequence VI′ ⇄ II′ ⇄ II′ ⇄ VI′ leads productively to the exchange of methylene groups between the metal and the olefin, **20**. Metallacyclobutane is not an intermediate in this



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metathesis mechanism, which then makes it a novel mechanism for this important reaction. We do not mean to imply that metallacyclobutanes are not metathesis intermediates but simply to raise the possibility that they might be bypassed.[22]

Reaction type 4 is the formation of T-shaped complexes from cyclopropane via the metallacyclobutane. The T-shaped complexes isomerize through the Y-shaped complexes. The reductive elimination yields the original cyclopropane with no loss of stereochemistry.

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(18) Metallacyclobutanes are known for metals other then platinum. For Ti: (a) $Cp_2Ti(CH_2C(Ph)C(Ph))$: Tebbe, F. N.; Parshall, G. W.; Overnall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074–5075. (b) $Cp_2Ti(CH_2CR_2CH_2)$: Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikarinya, T.; Straus, D. A.; Grubbs, R. H. *Ibid.* **1981**, *103*, 7358–7361. For Mo and W: (c) $Cp_2M(CH_2CHRCH_2)$: Al-Essa, R. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1980**, 45–47. (d) Ephritikhine, M.; Green, M. L. H. *Ibid.* **1976**, 926–927. For Fe and Rh: (e) $(CO)_4M$(dibenzosemibullvalene): Moriarty, R. M.; Chen, K.; Yeh, C.; Flippen, J. L.; Karle, J. *J. Am. Chem. Soc.* **1972**, *94*, 8944–8946. (f) Flippen, J. L. *Inorg. Chem.* **1974**, *13*, 1054–1057. (g) Tam, S. W. *Tetrahedron Lett.* **1974**, 2385–2388. (h) Johnson, B. F. G.; Lewis, J.; Tam, S. W. *J. Organomet. Chem.* **1976**, *105*, 271–279.

(19) Gassman, P. G.; Johnson, T. H. *J. Am. Chem. Soc.* **1976**, *98*, 6058–6059.

(20) Bishop, K. C., III *Chem. Rev.* **1976**, *76*, 461–468.

(21) Another example is metal catalyzed hydrocarbon skeletal rearrangements: (a) Garin, F.; Gault, F. G. *J. Am. Chem. Soc.* **1975**, *97*, 4466–4476. (b) O'Cinneide, A.; Gault, F. G. *J. Catal.* **1975**, *37*, 311–323. (c) Parshall, G. W.; Herskovitz, T.; Tebbe, F. N.; English, A. D.; Zeile, J. V. *Fundam. Res. Homog. Catal.*, [*Proc. Int. Workshop*] **1979**, *3*, 95–105.

(22) For another different suggestion of metathesis avoiding metallacyclobutane minima, see ref 12.

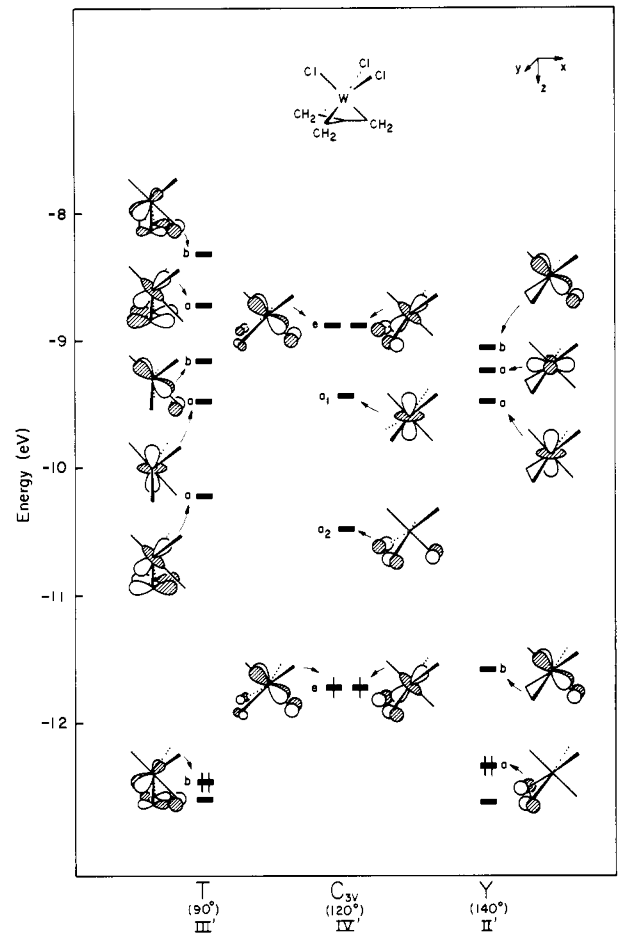

Figure 5. The orbitals of the T-, C_{3v}, and Y-shaped complexes of d^2 $(Cl)_3W(CH_2)_3^+$.

Reaction type 5 is just a stable tris(carbene) complex. There are such,[23] but of course not for a d^8 configuration.

Thus there is a wealth of chemistry available to organometallic complexes on the surface of Figure 2. The chemical behavior of a specific complex depends upon the energies of the various species involved, I'–VI'. The relative energies among these various species differ with a change of electron count, metal electronegativity, metal–ligand geometry, or methylene substituents. We explored some possibilities with detailed calculations on the $(Cl)_3M(CH_2)_3^n$ complex (M = W, $n = -3$ to $+1$; M = Pt, $n = -3$ to $+1$). The results are summarized in Table II.

When the metal is platinum, it is the metallacyclobutane **13** which has the lowest calculated energy. These complexes therefore follow either reaction type 1 or 2 depending upon the relative energies of II'/IV' and III'. For the d^8 $(Cl)_3Pt(CH_2)_3^-$ complex, an e orbital is half-filled and so the symmetric complex IV' sits atop a Jahn-Teller hill. For either two more or two less electrons, this is no longer so. Both d^{10} $(Cl)_3Pt(CH_2)_3^{3-}$ and d^6 $(Cl)_3Pt(CH_2)_3^{1+}$ belong to reaction type 1. d^4 $(Cl)_3Pt(CH_2)_3^{3+}$ removes two electrons from a metal-only orbital, $a_1(d_{z^2})$, unaffected by the motion of the CH_2 groups. This complex should behave similarly to d^6 $(Cl)_3Pt(CH_2)_3^{1+}$.

However, when the calculations were repeated with tungsten, a more electropositive metal, the metallacyclobutane was not calculated to be more stable than some of the carbene complexes, II'–IV'. The orbitals for the $(Cl)_3W(CH_2)_3^n$ complex are shown in Figure 5. The a_2 orbital of IV' is a ligand-only orbital, and consequently its energy remains unchanged from the platinum complex, Figure 3. The energy of the other orbitals, however, do change with a change of metal. The a_2 orbital is filled for d^6 $(Cl)_3W(CH_2)_3^{3-}$. Our calculations predict d^6 $(Cl)_3W(CH_2)_3^{3-}$ to have geometry IV' and reaction type 5.[24] For d^4 $(Cl)_3W(CH_2)_3^-$, the a_2 orbital is empty. The calculated geometry is Y-shaped and belongs to reaction type 4.[25] For d^2 $(Cl)_3W(CH_2)_3^+$, the two electrons are removed from an e orbital, leaving it half-filled. Again the symmetric complex IV' sits on a Jahn–Teller hill. The energy surface for the d^2 complex is shown in Figure 6. The T-shaped geometries are calculated to be the minima with the Y-shaped complexes serving as intermediates for the isomerization of the T-shaped complexes. The metallacyclobutane, however, is the global minimum and so belongs to reaction type 2.[26]

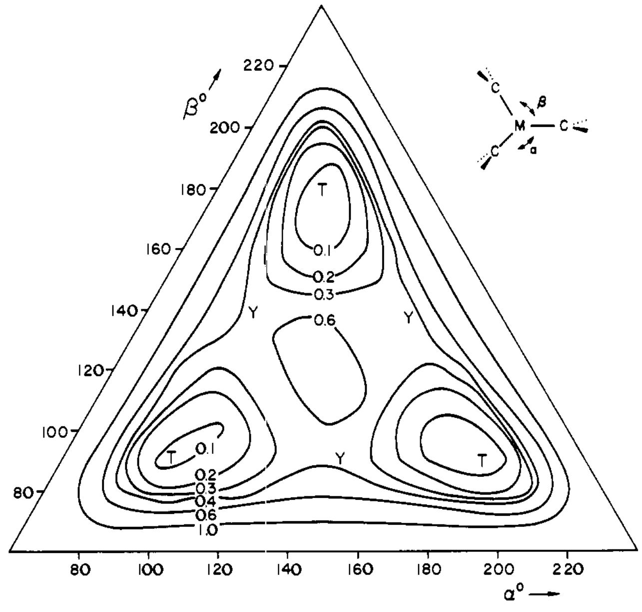

Figure 6. The potential energy surface of $(Cl)_3W(CH_2)_3^+$ for 0.1, 0.2, 0.3, 0.4, 0.6, and 1.0 eV energy contours. The locations of the T- and Y-shaped complexes are shown.

In conclusion, the five major reaction pathways (Table I) available to an L_3M(trimethylene) complex may be understood by recognizing the isolobal relationship between the d^8 organometallic complex and the organic $C_4H_7^+$. As the relative energies of the various isomers involved (I'–VI') are changed, the energy surface is modified, opening some pathways while closing others. In addition to a detailed understanding of the Puddephatt rearrangement this way of looking at the problem leads to the suggestion of an alternative metathesis pathway. But most satisfying is the beautiful parallelism between the organic and inorganic reaction mechanism that the isolobal analogy furnishes.

Acknowledgment. We are grateful to Richard Puddephatt for making some research results available to us before publication and the National Science Foundation for its support through Research Grant CHE 7828048. We thank J. Jorgensen for the drawings and E. Stolz for the typing.

Appendix

All calculations were performed using the extended Hückel method[27] with weighted H_{ij}'s.[28] The parameters are given in Table

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[24] All of the known tris(carbene)ML_3 complexes are d^6. See ref 23c and 23d.

[25] $(Et)(L)_2Ta(CR_2)(C_2H_4)$ is a d^4 Ta(I) carbene–olefin complex of this type. See: Fellmann, J. D.; Schrock, R. R.; Rupprecht, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5752–5758.

[26] $Cp_2Ti(C_3R_6)$ metallacyclobutane complexes are of this type. See: ref 18a and also ref 11b.

[27] (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412. (b) Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179–2195; **1962**, *37*, 2872–2883.

III. Idealized geometries were used to provide a bridge among the known experimental structures. The geometry of the CH_2 unit was fixed for its transits on the energy surfaces. The bond distances used throughout were C–H = 1.09 Å, M–C = 2.083 Å, M–Cl = 2.3 Å, M–P = 2.28 Å, P–H = 1.42 Å, and C–C (metallacyclobutane) = 1.535 Å. The geometry of the planar metallacyclobutane had ∠C–M–C = 67.3°, ∠M–C–C = 97.6°, and ∠C–C–C = 97.5°.

Registry No. $(Cl)_3Pt(CH_2)_3^{3-}$, 85957-26-2; $(Cl)_3Pt(CH_2)_3^{-}$, 85957-25-1; $(Cl)_3Pt(CH_2)_3^{+}$, 85957-27-3; $(Cl)_3Pt(CH_2)_3^{3+}$, 85957-28-4; $(Cl)_3W(CH_2)_3^{3-}$, 85957-29-5; $(Cl)_3W(CH_2)_3^{-}$, 85957-30-8; $(Cl)_3W(CH_2)_3^{+}$, 85957-31-9.

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(28) Ammeter, J. H.; Bürgi, H. B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686-3692.

The Mechanism of Fe–EDTA Catalyzed Superoxide Dismutation[1]

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Abstract: The catalysis of superoxide dismutation ($2O_2 + 2H^+ \rightarrow O_2 + H_2O_2$) by Fe^{3+}–EDTA and Fe^{2+}–EDTA has been examined. Potentiometric and spectrophotometric titrations of Fe^{3+}–EDTA revealed an ionization at $pK_a = 7.6$ consistent with the ionization of a bound water molecule. No other ionizations were detected below pH 10.7. Potentiometric titration of Fe^{2+}–EDTA revealed no ionizations in the pH range 5–11. We have studied the kinetic behavior of three reactions which constitute a catalytic cycle for O_2^- dismutation: $O_2^- + Fe^{3+}\text{–EDTA} \rightleftharpoons Fe^{2+}\text{–EDTA} + O_2$ (reaction 4), $O_2^- + Fe^{2+}\text{–EDTA} \rightleftharpoons Fe^{3+}\text{–EDTA–}O_2^{2-}$ (reaction 5), and $H_2O_2 + Fe^{3+}\text{–EDTA–OH}^- \rightleftharpoons Fe^{3+}\text{–EDTA–}O_2^{2-} + H_3O^+$ (reaction 6). Combining our data with that available in the literature we find that between pH 7 and pH 11 reaction 4 is described by the expression $k_{obsd} \approx 2 \times 10^6\ M^{-1}\ s^{-1}\ [H^+/(H^+ + K_a)]$ where $pK_a \approx 7.6$. Reaction 5 appears to be independent of pH and occurs with a velocity constant of 10^6–$10^7\ M^{-1}\ s^{-1}$. A mechanism has been derived for reaction 6 which accounts for the pH dependence of the individual rate constants, general-acid catalysis, and the pH dependence of the formation constant. The breakdown of the peroxo complex is catalyzed by both specific and general acids, and $k_{-6}/[H^+] \simeq 10^{10}\ M^{-1}\ s^{-1}$ in the absence of general acids. The rate of formation of the peroxo complex is independent of pH but is increased by general acids. This apparent general-acid catalysis is thought to arise from a combination of specific-acid and general-base catalysis. In the absence of general acids $k_6 \approx 350\ M^{-1}\ s^{-1}$. The pH dependence of the formation constant is due to the $1/[H^+]$ dependence of the dissociation rate. Fe–EDTA is demonstrated to be a catalyst of superoxide dismutation, and the above reactions account quantitatively for the observed catalysis. It is also shown that kinetic parameters derived from steady-state analyses of superoxide decay curves can be related to the individually determined rate constants.

Superoxide is formed to a small extent in the normal functioning of aerobic organisms, and during the past several years there has been much discussion of its role in biology.[1a-j,2a-d] However, extensive studies[3a-c] of the chemistry of this species have not as yet revealed how superoxide may affect biological systems. Proponents of the view that superoxide is an important mediator of oxygen poisoning[4] have argued that superoxide and hydrogen peroxide react with trace metal ions to form reactive hydroxyl radicals.[2a,d] In spite of certain shortcomings,[1f,2c] this concept deserves careful chemical study. The purpose of this work is to explore some of the reactions of oxygen, hydrogen peroxide, and superoxide with iron complexes of ethylenediaminetetraacetic acid (EDTA).

In aqueous solution superoxide is unstable toward hydrogen peroxide and dioxygen and dismutes via reaction 1. The

$$2O_2^- + 2H^+ \rightarrow H_2O_2 + O_2 \qquad (1)$$

mechanism of this process has been studied in great detail and is known to consist of two electron-transfer reactions (eq 2 and 3) and the ionization of HO_2 ($pK_a = 4.69$).[5a,b] Thus the rate of

$$2HO_2 \rightarrow H_2O_2 + O_2 \quad k_2 = 8.6 \times 10^5\ M^{-1}\ s^{-1} \qquad (2)$$

$$O_2^- + HO_2 \rightarrow HO_2^- + O_2 \quad k_3 = 1 \times 10^8\ M^{-1}\ s^{-1} \qquad (3)$$

reaction 1 is independent of pH below 2, increases to a maximum at the pK_a, and decreases tenfold for each pH unit increase above the pK_a.

Superoxide dismutation is catalyzed by various complexes of Cu, Fe, and Mn ions including a group of metalloproteins termed superoxide dismutases. Catalysis appears to require redox cycling,

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