Cleaving CC Bonds in Cyclopropenium Ions

Eluvathingal D. Jemmis and Roald Hoffmann*

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14853. Received September 19, 1979

Abstract: A cyclopropenium ion breaking one of its carbon—carbon bonds furnishes an orbital template which can be exploited by sundry mononuclear and binuclear transition metal fragments.

One of the many things that transition-metal complexes do, and we wish we knew better how to control it, is to cleave and form carbon—carbon bonds. In this paper one very specific CC bond breaking that in cyclopropenium cations and cyclopropenones, is investigated theoretically. The case is special, but the theoretical methodology developed here lends itself to obvious extension.

We chose these three-membered rings for study in part because we understand the electronic structure of the organic moiety well and in part because the body of structural information on C3R3 and cyclopropenone complexes is just reaching the critical stage, revealing a continuum of bonding modes which may trace out a reaction coordinate for the insertion of a metal atom, with its associated ligands, into a CC bond of a strained three-membered ring may occur (21).

The intrusion of a metal atom, with its associated ligands, into a CC bond of a strained three-membered ring may occur in either a single oxidative step, as in eq 1,1 or following prior coordination of the organic ligand. Equation 2 represents perhaps the best characterized instance of this sequence.2

(1) C9H92+ + IrCl2(CO)(PPh3)2 → ClIrCl(CO)(PPh3)2 + Ph3P (1)

If coordination of the ring is a likely initial step, one is led to think about the ways in which a three-membered ring may be bound. Cyclopropenonium complexes are not common, but we do have available structures in which the ring is η1, η3, η4, and η5.10

On the completely ring-opened or metalloocyclobutadiene side we have the previously mentioned complexes 1 (and an analogous RhCl2(PMe2Ph)2(C5H3)3)12) and 2. Then we encounter a fascinating group of bi- or polynuclear complexes with C3R3 or C2R2 units sitting atop them (6,13 7,14 8,15 9,16 and 1017).

Are the three-membered rings in these complexes completely or only partially opened up? As the cyclopropenium ring is cleaved one CCC angle, θ, opens up and the CC bond opposite, R, stretches. Less obvious, but important, is the fact that the orientation of the metal atom relative to the three-carbon plane changes. The metal is perpendicular to the plane.
Jemmis, Hoffmann / Cleaving CC Bonds in Cyclopropenium Ions

Table 1. Deformation Parameters (θ, R, and ϕ Defined in 11) for Cyclopropenium and Cyclopropenone Complexes

<table>
<thead>
<tr>
<th>molecule</th>
<th>θ, deg</th>
<th>R, Å</th>
<th>ϕ, deg</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpNi(C3Ph3)</td>
<td>60</td>
<td>1.43</td>
<td>38</td>
<td>5b</td>
</tr>
<tr>
<td>p2ClC2Ni(C3Ph3)</td>
<td>60</td>
<td>1.42</td>
<td>38</td>
<td>5c</td>
</tr>
<tr>
<td>(CO)3Co(C3Ph3)</td>
<td>60</td>
<td>1.42</td>
<td>37</td>
<td>8</td>
</tr>
<tr>
<td>(PPh3)2Pd(C3Ph3)+</td>
<td>69</td>
<td>1.58</td>
<td>11.1</td>
<td>9</td>
</tr>
<tr>
<td>(scacac)Pd3(C3Ph3)</td>
<td>97.5</td>
<td>2.12</td>
<td>155, 108</td>
<td>16b</td>
</tr>
<tr>
<td>(CN Bu)2Pt2((CPh)2CO)</td>
<td>99</td>
<td>2.18</td>
<td>129</td>
<td>15</td>
</tr>
<tr>
<td>[(CO)2NiCl(C3Cl3)]2</td>
<td>100</td>
<td>2.13</td>
<td>129</td>
<td>14</td>
</tr>
<tr>
<td>(PPh3)2Pt((CPh2)CO)</td>
<td>100</td>
<td>2.12</td>
<td>180</td>
<td>3</td>
</tr>
<tr>
<td>C2(NMe2)2Rh(C3Ph3)</td>
<td>100</td>
<td>2.16</td>
<td>180</td>
<td>12</td>
</tr>
<tr>
<td>Cl(CO)(PMe3)2Ru(C3Ph3)</td>
<td>102</td>
<td>2.15</td>
<td>180</td>
<td>1</td>
</tr>
<tr>
<td>(C3Ph5)(C2Ph4)Ni2(C3Ph3)</td>
<td>105</td>
<td>2.24</td>
<td>98, 112</td>
<td>13</td>
</tr>
</tbody>
</table>

coordinate. How this comes about is next explored by us, using extended Hückel calculations whose details are provided in the Appendix.18

Opening up a Cyclopropenium Cation

Our procedure is a transparent one. We will cleave a CC bond in C3H5+, the isolated organic molecule. The orbitals so obtained at various stages of the bond-breaking process will serve as electronic templates for transition metal fragment bonding partners. Sometimes we will turn the argument around, and ask what portion of the ring-opening surface will be stabilized by a specific metal fragment.

The geometrical change envisaged is an increase in θ, 13,

coupled through the side CC bond length (1.40 Å) to the 1,3 separation R. The hydrogens at C1 and C3 were coupled to this motion by specifying that the H1–C1–C2 and H3–C3–C2 angles vary as $180° - \frac{1}{2} \theta$. The computed Walsh diagram (Figure 1) is a classical example of simple perturbation theory at work.19

At θ = 60° the π orbitals of cyclopropenium fall into the familiar a* below e* pattern. Not far above the occupied π level the extended Hückel calculation places a degenerate e' σ level. As θ departs from 60°, the symmetry is lowered from D3h to C3v. The π* level splits, one component going up, one going down. The low-lying π level is not much affected. The degenerate σ level also splits. At large θ it is joined by a σ* level which has fallen rapidly in energy. At still greater θ the σ and σ* cross—this is a well-understood consequence of through-bond coupling.19 The destabilized σ and stabilized σ* levels can also be thought of as the in- and out-of-phase combinations of the radical lobes of a didehydroallyl cation. Note that on the ring-opened side there are three orbitals lodged in the non-bonding region: σ, σ*, and π*. Any bonding partner to the opened C2R3 must provide stabilizing interactions with these orbitals.

The hypothetical bonding partners that we would like to consider in the first instance are mononuclear transition metal fragments, MLn, and their isolobal replacements. More specifically we will examine bonding with C4n, ML2, C2, ML4, C3, ML, and C2, as well as with their analogues in which a cyclopentadienyl ring replaces three carbonyls, ML3Licp, M2Licp, and M3Licp. The orbitals of these fragments should by now be familiar to our readers,20 and they are sketched in Figure 2. In the octahedral fragment geometries of ML4, ML3, and ML2 there are three levels down below, the remnants of the octahedral t2g set, and one, two, or three higher lying orbitals, the delocalized symmetry-adapted equivalents of the hybrids pointed toward the missing octahedral sites. Angular
ML₂ is different, having four low-lying orbitals and two hybrids above these. There is a second isolobal relationship between d¹⁰ ML₂ and d⁹ ML₄, best approached by thinking about adding two axial ligands to ML₂ or removing them from ML₄. We are now ready for putting together the two pieces of the molecule.

Bonding with a Cyclopropenium without Ring Opening, or, Haptotropic Shifts across a Three-Membered Ring

The secondary title of this section refers to our study of sigmatropic shifts in cyclopentadienyl complexes. Consider an ML₅ group in transit across the face of a cyclopropenium. Its location can be approximately described by the projection of the metal onto the ring plane, spanning sites marked 1η, 2η, and 3η in 15 to form obvious mnemonic connections to the η¹, η², and η³ coordination implied.

The ML₅ group will adopt the optimum position where there is most bonding interaction, and this will depend on the orbital pattern of ML₅ and the electron count. Consider, for instance, Co(CO)₅ or the isolobal NiCp. The higher lying 2a₁ and 2e orbitals of these fragments are a perfect match for a₂⁺ and e⁻ π orbitals of cyclopropenium if, and only if, the ML₅ fragment is η³ bonded. The interaction diagram is shown schematically below in 16. The molecule is split up into neutral fragments. This is entirely arbitrary—we could just as well have interacted C₃H₃⁺ and NiCp⁻, for in the one-electron molecular orbital theory we use the electron partitioning has no effects.

Were the MCp or M(CO)₅ fragment moved off center to 2η or 1η sites, part of the important π-type interaction between the e orbitals would be lost. The trihapto bonding type is well represented by C₃R₃ complexes with CpNi, py₃CNI, and Br(CO)₂Ni⁺. Incidentally a CH group will do as well, since it is isolobal with d⁹ ML₃. Which is hardly a surprise—we are discussing a peculiar way to form a tetrahedrane, a highly strained but respectable molecule.

Now suppose that ML₅ is Mn(CO)₅. This has one electron more than Cr(CO)₅ (Figure 2) and that electron is in a nicely oriented a₁ hybrid. As ML₅ makes a transit across a cyclopropenium ring it always interacts with a₁⁻, but does so with one component of e⁻ only when it is off-center, and optimally so in the η¹ site. This is shown schematically in 17. The molecular type exists, not yet as (C₃R₃)Mn(CO)₅ but as the isolobal η¹ (C₃R₃)Fe(CO)₂Cp⁴⁺. The ML₄ or ML₂ cases are interesting because they are in principle intermediate between those discussed above. Where ML₅ had a single σ-type orbital and ML₃ had a σ and two π's, ML₂ and ML₄ have one σ and one π. The result is a fairly soft surface for motion across the cyclopropenyl ring, with an

---

**Figure 1.** A Walsh diagram for cleaving a single CC bond in a cyclopropenium ion by opening up the angle opposite.

**Figure 2.** The frontier orbitals of ML₅, ML₄, ML₃, and ML₂ fragments.
Jemmis, Hoffmann / Cleaving CC Bonds in Cyclopropenium Ions

equilibrium geometry as in 18. A complete discussion of the intricate surface for the interconversion of \( \eta^2 \) structures is given elsewhere.\textsuperscript{23} The observed structure of \((\text{PPPh}_3)_2\text{Pt}(\text{C}_3\text{H}_3)_2^+\) is indeed of the \( \eta^2 \) type, with two Pt–C distances of 2.09 and one of 2.48 Å.\textsuperscript{9} Other \((\text{C}_3\text{R}_3)\text{ML}_2\) complexes are known.\textsuperscript{5,24}

Metal-Assisted Ring Opening

Let us backtrack a moment to the \((\text{C}_3\text{R}_3)\text{ML}_2\) complex, for it will have been noticed from Table I that it is the only structurally well-characterized example that we have which has \( \theta \) and \( \varphi \) in the intermediate range. The ring is beginning to open up, though it has not gotten very far. Figure 3 shows an interaction diagram in the observed \( \eta^2 \) geometry. On top of several four-electron repulsive interactions the primary bonding is accomplished by the ML\(_2\) \( b_2 \) level and one component of the cyclopropenium \( \pi^* \) as shown in 19. Transfer of electrons to that \( \pi^* \) is what stretches the C\(_1\)-C\(_2\) bond to 1.58 Å, actually a distance somewhat longer than that observed in many d\(^8\) ML\(_4\) (olefin) complexes in which a similar interaction dominates.

Why does not the CC bond stretch any further? Let us compare the energies of the frontier orbitals of the two fragments in Figure 4. This reproduces the C\(_3\)R\(_3\) levels along a bond-breaking coordinate and indicates the ML\(_2\) \( b_2 \) level position by a dashed line. The orbitals which interact strongly carry a circle. If \( \theta \) is increased further, the difference in energy between these orbitals would diminish, which is one factor that would strengthen interaction. There are also some four-electron repulsive interactions which appear to combine to hold the observed structure at an \( \eta^2 \) bonded point. In principle there is nothing barring the system from going on to open the ring further. Let us discuss this channel through the known ring-opened ML\(_4\) complexes, whose orbitals resemble those of ML\(_2\), as mentioned above.

\(^{d8}\) ML\(_4\) reagents of the Vaska’s complex type break the CC bond in a three-membered ring completely, achieving the metalloyclobutadiene geometry, 20,12,21 We have modeled their electronic structure by \((\text{CO})_4\text{Co}(\text{C}_3\text{H}_3)_2^{2+}\). The \( d^8 \) ML\(_4\) fragment has the three below two pattern exhibited in Figure 2. The important \( b_2 \) orbital can interact with \( \pi_2^* \), as in 21, when the ring plane is approximately orthogonal to the M-ring axis (\( \varphi \sim 90^\circ \)). When \( \varphi \) approaches \( 180^\circ \), the interaction is with \( \sigma^* \). At intermediate \( \varphi \) \( \pi_2^* \) and \( \sigma^* \) mix through this interaction. It is clear that in the initial stages of the interaction, small \( \theta \), the energy proximity criterion of perturbation theory\textsuperscript{19} favors \( \pi_2^* \). At \( \theta \sim 104^\circ \) \( \sigma^* \) and \( \pi_2^* \) are of equal energy. Now the overlap criterion comes into play. At \( \theta = 100^\circ \) the group overlaps are \( (b_2|\pi_2^*) = 0.239 \) (\( \varphi = 90^\circ \)), \( (b_2|\sigma^*) = 0.272 \) (\( \varphi = 180^\circ \)). Increasing \( \varphi \) is favored. The match of fragment orbitals in the metallocycle is shown in Figure 5.

The process by which an \( \eta^2 \)-bonded cyclopropenium complex of \( d^8 \) ML\(_4\) or \( d^{10} \) ML\(_2\) is converted to a metallocycle, i.e., the increase in \( \theta \) and \( \varphi \) along reaction path 12, is similar in detail to the disrotatory opening of a bicyclobutyl cation to cyclobutenyl cation, 23. This parallel has been noted by others as well.\textsuperscript{9} It is supported by the isobelal analogy\textsuperscript{20} that pairs CH\(_2\) with Fe(CO)\(_4\) or any \( d^8 \) ML\(_4\). A correlation diagram connecting the extremes of the reaction path is also easily drawn, and shows that the reaction is symmetry allowed.

Bigger and Better

The binuclear or polynuclear complexes 6–10 obviously do an effective job of breaking a carbon–carbon bond: \( \theta \) ranges
from 97.5 to 105° and R from 2.12 to 2.24 Å. In most cases the C3R3 unit nicely straddles the metal–metal bond, but this is not always so—notice the two disparate ϕ angles in the Pd3 case, 9, 10b. The structures known are so complicated (and therefore intriguing) and unsymmetrical that we have had to limit ourselves to a symmetrical idealized complex, (CO)4-Ni*(C3H3)+, 24, a model for 7 and 8.

The frontier orbitals of a d10-L2M system are easily constructed from two ML2 fragments (Figure 6); in fact we have already done this in the context of a discussion of Pt(0)–Pt(0) dimers.25 The ML2 b2 orbitals form two combinations that are metal–metal σ bonding and antibonding, respectively. Another valence orbital comes from a 3a1 MOs which we will call σxy to distinguish it from σ of C3H3+*. That the σxy combination in the dimer is much lower than in the monomer is important in the bonding picture. These three M2L4 orbitals, two filled, find a lovely match in three frontier orbitals of a ring-opened C3H3+, one filled, as shown in 25. A comparison (Figure 7) of the energies of the frontier orbitals of the fragments tells us that the bonding would have been less strong were the C3H3+ less open than was found experimentally.

Several alternative geometries were explored for (CO)4-Ni*(C3H3)+. Details are given in the microfilm edition of the journal. All are at higher energy than 24, but for some metal and ligand sets some of these geometries may become competitive.
The supplementary material in the microfilm edition also contains a discussion of cyclopropenone, cyclopropene, and cyclopropane as ligands analogous to cyclopropenyl cation. Here it is worthwhile to draw a comparison between ring-opened C₃H₃ or cyclopropenone and an acetylene. These systems are in a sense isobal, as shown in 26 below. At left are three valence orbitals of the three-membered ring at large θ, at right the four valence orbitals of an acetylene. The similarities jump to one’s attention. One of the acetylene π’s seems to have no cyclopropenone counterpart, but even that is not so—for the analogue is to be found in π₁ of C₃H₃⁺. There should be a chemistry of C₃R₃ and cyclopropenones as rich as that of acetylenes.

Acknowledgment. We are grateful to T. A. Albright for some comments, to P. M. Maitlis, J. A. K. Howard, and F. G. A. Stone for bringing to our attention some of their fascinating compounds, and to the National Science Foundation for its support through Research Grant CHE 7828048.

Supplementary Material Available: A discussion of cyclopropenone, cyclopropene, and cyclopropene complexes as well as alternative (C₃H₃)M₂La geometries (Table 2) (7 pages). Ordering information is given on any current masthead page.

Appendix

All calculations were performed using the extended Hückel method. The H/’s and orbital exponents were taken from previous work. The geometry of (PH₃)₂PtC₃H₃⁺ (Figure 3) was adapted from the observed structure 4 by replacing the substituents on ligands by hydrogens (P-H = 1.4, C-H = 1.08 Å). The Co-C and C-O distances in the Co(CO)₄ fragment were 1.9 and 1.13 Å with an equatorial COOC angle of 86°. The Ni₂(CO)₄ fragment in 24 had the following bond lengths and angles: Ni-Ni = 2.52 Å, Ni-C = 1.8 Å, C-C = 1.14 Å, angle NiNiC = 120°, angle CNiC = 117°. The C₃H₃ geometry corresponded to various points in Figure 1 (C-C = 1.4, C-H = 1.08 Å).

References and Notes


11. We have not mentioned here some other compounds whose structures are not so well known, for instance, the (diphenylcyclopropenone)Ni(CO)₅ of Bird, G. W.; Hollins, E. M. Chem. Ind. (London) 1964, 1362, and compounds in which a cyclopropenone is thought to be bound through the oxygen: Fichtman, W. L.; Schmidt, P.; Ohrin, M. J. J. Orgnnomet. Chem. 1968, 12, 249–252.


23. (a) Albright, T. A., to be published. (b) Dobosh, P. A.; Lilly, C. P., to be published.


