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Cleaving CC Bonds in Cyclopropenium Ions

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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 C_3R_3 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 reaction.

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.[2,3]

(2)

$$C_3Ph_3^+ + IrCl(CO)(PR_3)_2 \longrightarrow \text{[complex 1]} \quad (1)$$
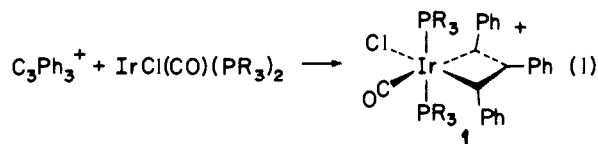
If coordination of the ring is a likely initial step, one is led to think about the ways in which a three-membered ring may be bound. Cyclopropenium complexes are not common, but we do have available structures in which the ring is η^3, **3**,[4-8] η^2, **4**,[9] and η^1, **5**.[10]

On the completely ring-opened or metallocyclobutadiene
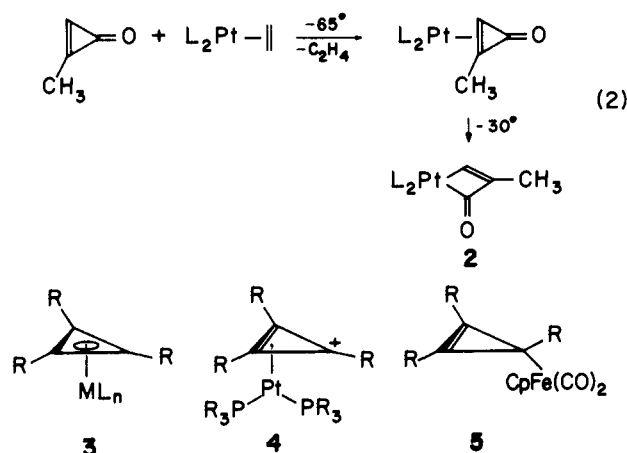
side we have the previously mentioned complexes **1** (and an analogous $RhCl_2(PMe_2Ph)_2(C_3Ph_3)$[12]) and **2**. Then we encounter a fascinating group of bi- or polynuclear complexes with C_3R_3 or C_2R_2CO units sitting atop them (**6**,[13] **7**,[14] **8**,[15] **9**,[16] and **10**[17]).

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

6 R = Ph

7

R = Ph   **8**   R' = NC^{t}Bu

9 M = Pd, Pt

10
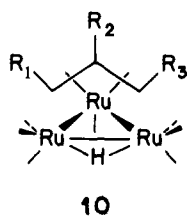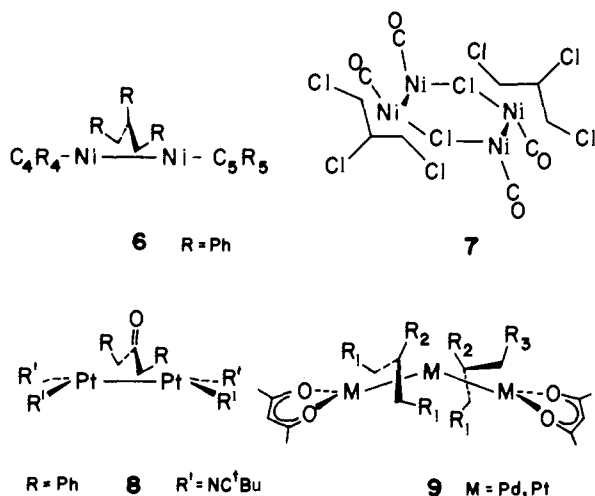
in the η^3 complexes, sometimes in that plane in the ring-opened metallocyclobutadienes. There are a number of ways of specifying this degree of freedom. We have chosen a parameter suited to a discussion of puckering on the metallocycle side, namely, the dihedral angle between the C_1MC_3 and $C_1C_2C_3$ planes, φ. These variables are shown in **11**. Of course they do

11
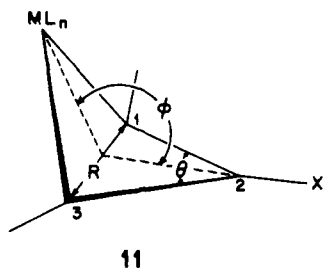
not determine fully the geometry of the complex. Other distances and structural changes are interesting, for instance, the way the flanking bonds C_1C_2 and C_2C_3 follow the opening and the disposition of the substituents at C_1 and C_3. But we think that the deformation is well described by θ, R, and φ, and for the known structures these are listed in Table I.

In the binuclear complexes two φ angles are given, corresponding to the two kinds of metallocycle linkages that one could think of forming. It is clear from the structural data that the binuclear complexes are ring opened (θ and R just as great as in the metallocyclobutadienes) and yet φ is not 180°. These C_3 units straddle metal-metal bonds, as structures **6-10** indicate, an orientation that allows maximum interaction with both metals. They will be considered separately.

The number of mononuclear cyclopropenium complexes caught in the middle of the reaction, i.e., with $60 < \theta < 100°$, $1.45 < R < 2.10$ Å, is small. Nevertheless the data clearly suggest a reaction coordinate, CC bond breaking, drawn in **12**.

12
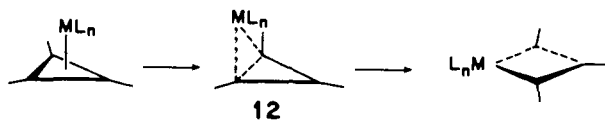
The metal bonding partners differ in their capacity for pushing the three-membered ring to a definite place along that reaction

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

molecule	θ, deg	R, Å	φ, deg	ref
CpNi(C_3Ph_3)	60	1.43	38	5b
py$_2$ClNi(C_3Ph_3)	60	1.42	38	5c
(CO)$_3$Co(C_3Ph_3)	60	1.42	37	8
(PPh$_3$)$_2$Pt(C_3Ph_3)$^+$	69	1.58	111	9
(acac)$_2$Pd$_3$(C_3Ph(p-MeOC$_6$-H$_4$)$_2$)$_2$	97.5	2.12	155, 108	16b
(CN^{t}Bu)$_4$Pt$_2$((CPh)$_2$CO)	99	2.18	129	15
[(CO)$_2$Ni$_2$Cl(C$_3$Cl$_3$)]$_2$	100	2.13	129	14
(PPh$_3$)$_2$Pt((CPh)$_2$CO)	100	2.12	180	3
Cl$_2$(PMe$_2$Ph)$_2$Rh(C_3Ph_3)	100	2.16	180	12
Cl(CO)(PMe$_3$)$_2$Ir(C_3Ph_3)$^+$	102	2.15	180	1
(C$_5$Ph$_5$)(C$_4$Ph$_4$)Ni$_2$(C_3Ph_3)	105	2.24	98, 112.5	13

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 $C_3H_3^+$, 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**,

13
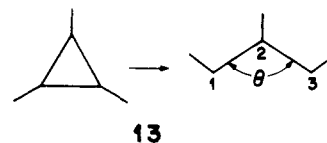
coupled through the side CC bond length (1.40 Å) to the 1,3 separation R. The hydrogens at C_1 and C_3 were coupled to this motion by specifying that the $H_1-C_1-C_2$ and $H_3-C_3-C_2$ angles vary as $180° - \frac{1}{2} \theta$. The computed Walsh diagram (Figure 1) is a classical example of simple perturbation theory at work.[19] At $\theta = 60°$ the π orbitals of cyclopropenium fall into the familiar a_2'' 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 D_{3h} to C_{2v}. 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 σ and σ^* cross—this is a well-understood consequence of through-bond coupling.[19a] 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 nonbonding region: σ, σ^*, and π_2^*. Any bonding partner to the opened C_3R_3 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, ML_n, and their isolobal replacements. More specifically we will examine bonding with C_{4v} ML_5, C_{2v} ML_4, C_{3v} ML_3, and C_{2v} ML_2, as well as with their analogues in which a cyclopentadienyl ring replaces three carbonyls, $M'L_2Cp$, $M'LCp$, and $M'Cp$. 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 ML_5, ML_4, and ML_3 there are three levels down below, the remnants of the octahedral t_{2g} set, and one, two, or three higher lying orbitals, the delocalized symmetry-adapted equivalents of the hybrids pointed toward the missing octahedral sites. Angular
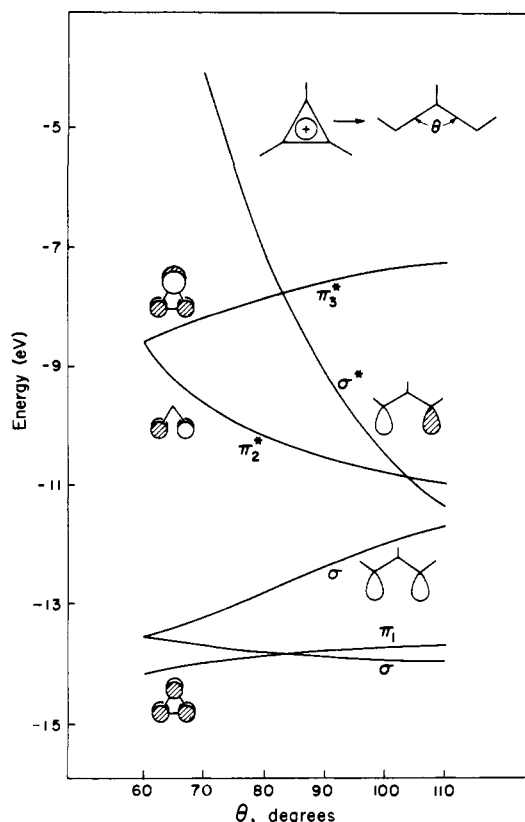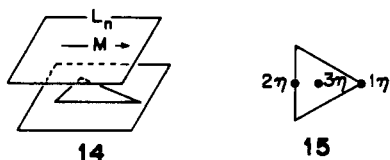
Figure 1. A Walsh diagram for cleaving a single CC bond in a cyclopropenium ion by opening up the angle opposite.

Figure 2. The frontier orbitals of ML_5, ML_4, ML_3, and ML_2 fragments.

ML_2 is different, having four low-lying orbitals and two hybrids above these. There is a second isolobal relationship between d^{10} ML_2 and d^8 ML_4,[20f] best approached by thinking about adding two axial ligands to ML_2 or removing them from ML_4. 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.[21] Consider an ML_n group in transit across the face of a cyclopropenium, **14**. 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 η^1, η^2, and η^3 coordination implied.

The ML_n group will adopt the optimum position where there is most bonding interaction, and this will depend on the orbital pattern of ML_n and the electron count. Consider, for instance, $Co(CO)_3$ or the isolobal $NiCp$. The higher lying $2a_1$ and $2e$ orbitals of these fragments are a perfect match for a_2'' and e'' π orbitals of cyclopropenium if, and only if, the ML_n fragment is η^3 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 $C_3H_3^+$ and $NiCp^-$, for in the one-electron molecular orbital theory we use the electron partitioning has no effects.

Were the MCp or $M(CO)_3$ fragment moved off center to 2η or 1η sites, part of the important π-type interaction between
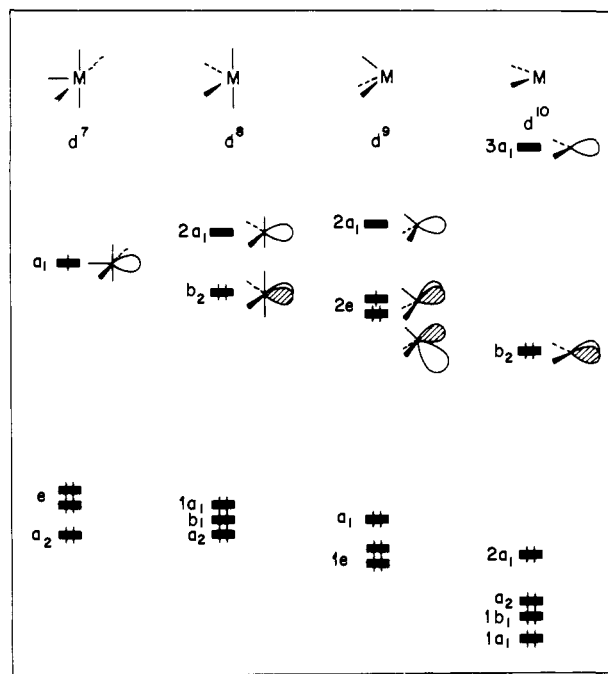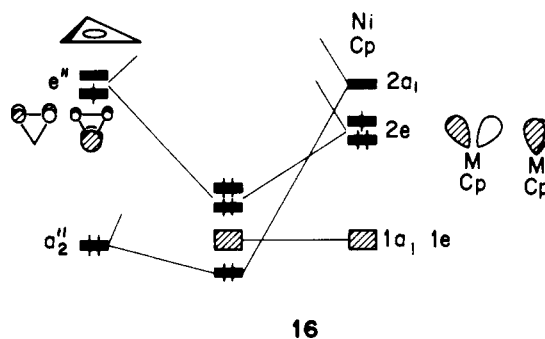

16

the e orbitals would be lost. The trihapto bonding type is well represented by C_3R_3 complexes with $CpNi$, py_2ClNi, and $Br(CO)_2Ni$.[4-8] Incidentally a CH group will do as well, since it is isolobal with d^9 ML_3. Which is hardly a surprise—we are discussing a peculiar way to form a tetrahedrane, a highly strained but respectable molecule.[22]

Now suppose that ML_n is $Mn(CO)_5$. This has one electron more than $Cr(CO)_5$ (Figure 2) and that electron is in a nicely oriented a_1 hybrid. As ML_n makes a transit across a cyclopropenium ring it always interacts with a_2'', but does so with one component of e'' only when it is off-center, and optimally so in the η^1 site. This is shown schematically in **17**. The molecular type exists, not yet as $(C_3R_3)Mn(CO)_5$ but as the isolobal η^1 $(C_3R_3)Fe(CO)_2Cp$.[10]
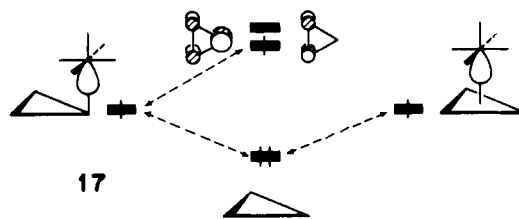
17

The ML_4 or ML_2 cases are interesting because they are in principle intermediate between those discussed above. Where ML_5 had a single σ-type orbital and ML_3 had a σ and two π's, ML_2 and ML_4 have one σ and one π. The result is a fairly soft surface for motion across the cyclopropenyl ring, with an
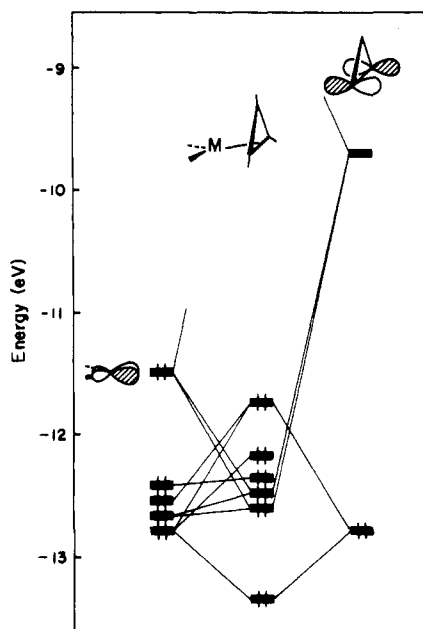
Figure 3. Interaction diagram for $(C_3R_3)ML_2$.

equilibrium geometry as in **18**. A complete discussion of the intricate surface for the interconversion of η^2 structures is given elsewhere.[23] The observed structure of $(PPh_3)_2Pt(C_3Ph_3)^+$ is indeed of the η^2 type, with two Pt-C distances of 2.09 and one of 2.48 Å.[9] Other $(C_3R_3)ML_2$ complexes are known.[5,24]

Metal-Assisted Ring Opening

Let us backtrack a moment to the $(C_3R_3)ML_2$ complex, for it will have been noticed from Table I that it is the only structurally well-characterized example that we have which has θ and R 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 η^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 e'' π_2^* as shown in **19**. Transfer of electrons to that π^* is what stretches the C_1-C_3 bond to 1.58 Å, actually a distance somewhat longer than that observed in many d^{10} ML_2 (olefin) complexes in which a similar interaction dominates.
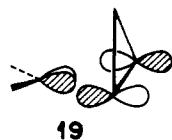
Why does not the CC bond stretch any further? Let us compare the energies of the frontier orbitals of the two fragments in Figure 4. This reproduces the C_3R_3 levels along a bond-breaking coordinate and indicates the ML_2 b_2 level position by a dashed line. The orbitals which interact strongly carry a circle. If θ 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 η^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.
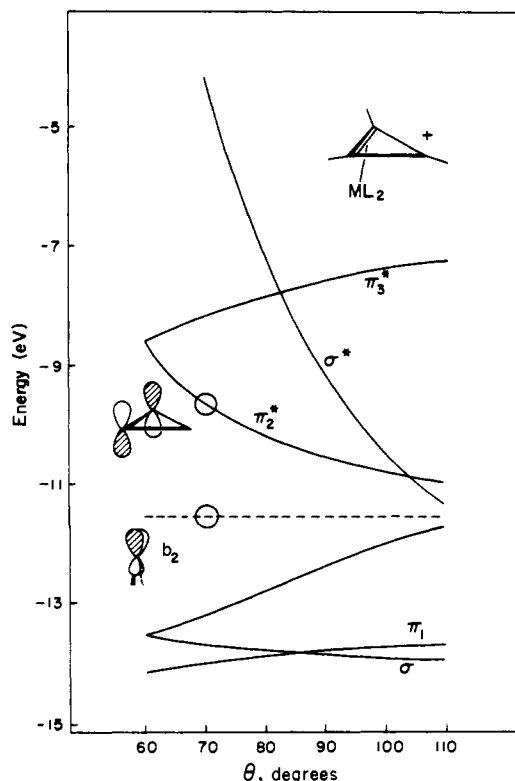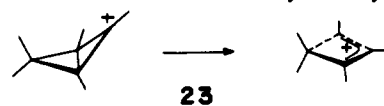

Figure 4. C_3R_3 levels as a function of θ, solid lines, and the ML_2 b_2 level, dashed line. Circles identify interacting orbitals at observed geometry.

d^8 ML_4 reagents of the Vaska's complex type break the CC bond in a three-membered ring completely, achieving the metallocyclobutadiene geometry, **20**.[1,12] We have modeled their electronic structure by $(CO)_4Co(C_3H_3)^{2+}$. The d^8ML_4 fragment has the three below two pattern exhibited in Figure 2. The important b_2 orbital can interact with π_2^*, as in **21**, when the ring plane is approximately orthogonal to the M-ring axis ($\varphi \sim 90°$). When φ approaches $180°$, the interaction is with σ^*, **22**. At intermediate φ π_2^* and σ^* mix through this interaction. It is clear that in the initial stages of the interaction, small θ, the energy proximity criterion of perturbation theory[19] favors π_2^*. At $\theta \sim 104°$ σ^* and π_2^* are of equal energy. Now the overlap criterion comes into play. At $\theta = 100°$ the group overlaps are $\langle b_2|\pi_2^* \rangle = 0.239$ ($\varphi = 90°$), $\langle b_2|\sigma^* \rangle = 0.272$ ($\varphi = 180°$). Increasing φ is favored. The match of fragment orbitals in the metallocycle is shown in Figure 5.
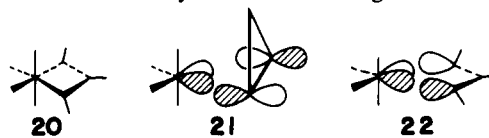
The process by which an η^2-bonded cyclopropenium complex of d^8ML_4 or $d^{10}ML_2$ is converted to a metallocycle, i.e., the increase in θ and φ along reaction path **12**, is similar in detail to the disrotatory opening of a bicyclobutyl cation to cyclobutenyl cation, **23**. This parallel has been noted by others as well.[8] It is supported by the isolobal analogy[20] that pairs CH_2 with $Fe(CO)_4$ or any d^8ML_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

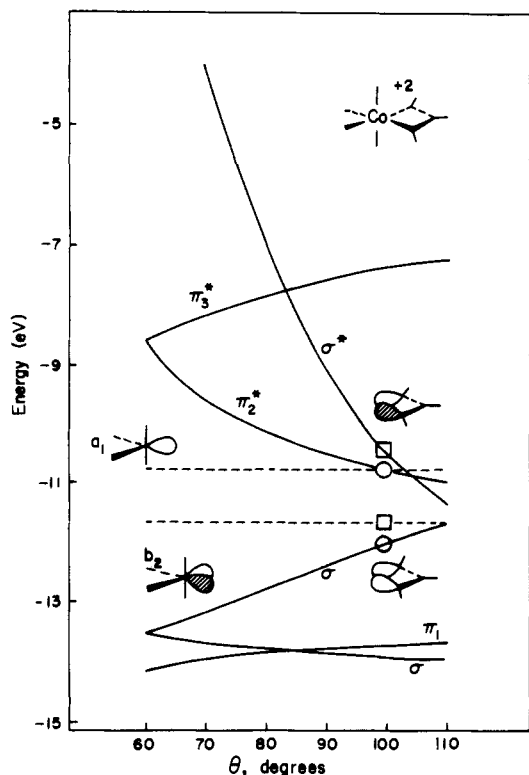The binuclear or polynuclear complexes **6-10** obviously do an effective job of breaking a carbon-carbon bond: θ ranges

Figure 5. C_3R_3 levels as a function of θ, solid lines, and the ML_4 frontier levels, dashed lines. Circles and squares identify interacting orbitals.
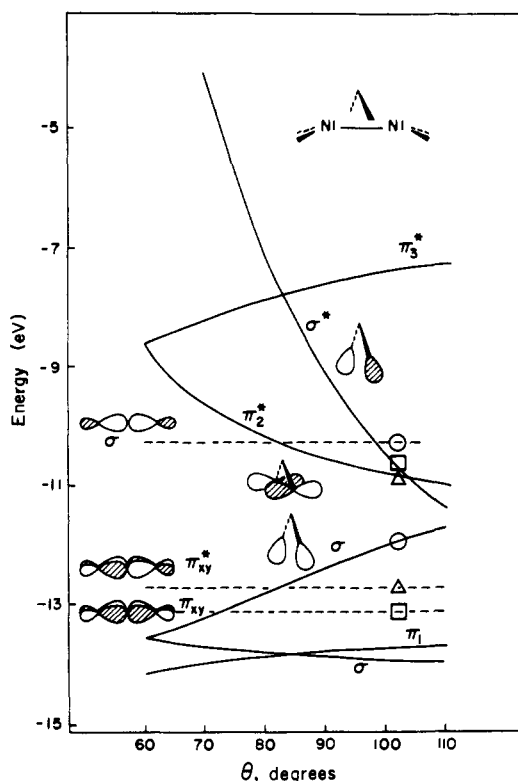

Figure 7. C_3R_3 levels as a function of θ, solid lines, and the $Ni_2(CO)_4$ frontier orbitals, dashed lines. The symbols identify interacting orbitals in the ring-opened geometry.
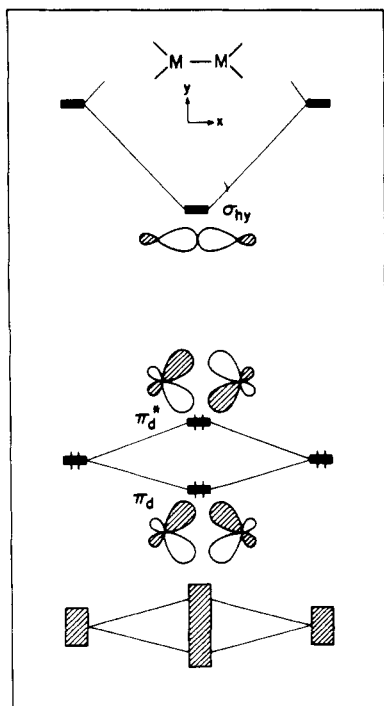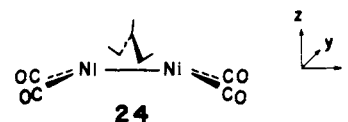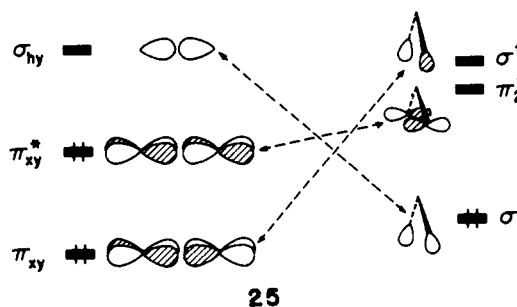

Figure 6. Construction of the orbitals of $Ni_2(CO)_4$. The lower shaded blocks contain four filled orbitals in the monomer, eight in the dimer.

24

The frontier orbitals of a d^{10}-d^{10} L_2MML_2 system are easily constructed from two ML_2 fragments (Figure 6); in fact we have already done this in the context of a discussion of $Pt(0)$-$Pt(0)$ dimers.[25] The ML_2 b_2 orbitals form two combinations that are metal-metal π bonding and antibonding, respectively. Another valence orbital comes from a σ bonding combination of the $3a_1$ MOs which we will call σ_{hy} to distinguish it from σ of $C_3H_3^+$. That the σ_{hy} combination in the dimer is much lower than in the monomer is important in the bonding picture. These three M_2L_4 orbitals, two filled, find a lovely match in three frontier orbitals of a ring-opened $C_3H_3^+$, 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 $C_3H_3^+$ less open than was found experimentally.

25

from 97.5 to 105° and R from 2.12 to 2.24 Å. In most cases the C_3R_3 unit nicely straddles the metal-metal bond, but this is not always so—notice the two disparate φ angles in the Pd_3 case, **9**.[16b] The structures known are so complicated (and therefore intriguing) and unsymmetrical that we have had to limit ourselves to a symmetrical idealized complex, $(CO)_4$-$Ni_2(C_3H_3)^+$, **24**, a model for **7** and **8**.

Several alternative geometries were explored for $(CO)_4$-$Ni_2(C_3H_3)^+$. 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 C_3H_3 or cyclopropenone and an acetylene. These systems are in a sense isolobal, as shown in **26** below. At left are

26
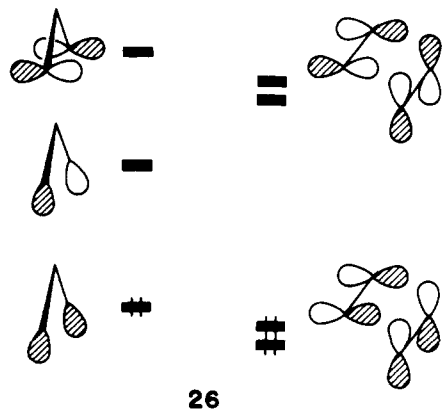
three valence orbitals of the three-membered ring at large θ, at right the four valence orbitals of an acetylene. The similarities jump to one's attention. One of the acetylene π's seems to have no cyclopropenium counterpart, but even that is not so—for the analogue is to be found in π_1, of $C_3H_3^+$. There should be a chemistry of C_3R_3 and cyclopropenones as rich as that of acetylenes.

Supplementary Material Available: A discussion of cyclopropenone, cyclopropene, and cyclopropane complexes as well as alternative $(C_3H_3)M_2L_4$ geometries (Table 2) (7 pages). Ordering information is given on any current masthead page.

Appendix

All calculations were performed using the extended Hückel method.[26] The H_{ii}'s and orbital exponents were taken from previous work.[27] The geometry of $(PH_3)_2PtC_3H_3^+$ (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 CCoC angle of 86°. The $Ni_2(CO)_4$ fragment in **24** had the following bond lengths and angles: Ni–Ni = 2.52 Å, Ni–C = 1.8 Å, C–O = 1.14 Å, angle NiNiC = 120°, angle CNiC = 117°. The C_3H_3 geometry corresponded to various points in Figure 1 (C–C = 1.4, C–H = 1.08 Å).

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