Stabilities of Metallacyclobutadiene and Metallatetrahedrane Complexes

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Ab initio molecular orbital theory has been used to study the stabilities of isomeric metallacyclobutadiene and metallatetrahedrane complexes. In the metallacyclobutadienes, the C_3R_3 ligand is bonded to the transition metal in a ring-opened η^2-C_3R_3 coordination mode. In the metallatetrahedranes, the C_3R_3 coordinates as η^3-C_3R_3. In this paper, we examine the stability governing factors, such as the ligand environment, number of valence electrons, and type of transition metal. For most $L_5M(C_3R_3)$ complexes, the metallatetrahedrane structures are found to be more stable than the metallacyclobutadienyl ones because the former can be viewed as pseudo-octahedral d^6 compounds if one takes the C_3R_3 ligand as a single $[\eta^3\text{-}C_3R_3]^+$ cationic ligand. For most $L_4M(C_3R_3)$ complexes, however, the metallacyclobutadienyl structures are more stable than the metallatetrahedrane ones. If one takes the η^2 ligand as a bidentate $[\eta^2\text{-}C_3R_3]^-$ anion, these metallacyclobutadienyl complexes also can be viewed as octahedral d^6 compounds. For most $L_3M(C_3R_3)$ complexes, the metallatetrahedrane structures become more stable. By adopting metallatetrahedrane structures, these η^3-C_3R_3 complexes satisfy the 18-electron rule and can be viewed as late transition metal tetrahedral d^{10} complexes. Most metallacyclobutadienes are found to have symmetric bonds within the $M(\eta^2\text{-}C_3R_3)$ unit. The short–long–short–long bonds in the experimentally known $CpCl_2W(\eta^2\text{-}C_3R_3)$ complex are explained as a result of a compromise between steric and electronic factors. The former forces the C_3R_3 unit to twist and induces bond alternation; the latter favors a symmetric structure.

Introduction

The insertion of an η^2 bound olefin or acetylene into alkylidene or alkylidyne–metal bonds to form various metallacycles has attracted considerable interest.[1] Particular attention has been paid to metallacyclobutadienes (**1** or **2**) because they are believed to play an important role in the alkyne metathesis.[2] Several metallacyclobutadiene complexes with a molecular formula of $X_3WC_3R_3$ (X = Cl or OR′) have been isolated and structurally characterized.[2,3] In these complexes, the structures are highly symmetric (see **1**) with equal short M–C(1) and M–C(1′) bond lengths and a close M–C(2) contact. A closely related system, $CpCl_2W(C_3R_3)$,[4] shows alternate bonds (short–long–short–long) as in **2**. Surprisingly, when one more ligand is introduced, as in $Cp(PMe_3)Cl_2W(C_3R_3)$, the structure becomes a metallatetrahedrane, **3**, in which the C_3R_3 unit is bonded to the metal through a η^3 coordination mode.[5] A large number of other metallacyclobutadienes and metallatetrahedranes have been characterized and are listed in Table 1.

Table 1. Examples of Metallacyclobutadienes and Metallatetrahedranes

		no. of valence electrons[a]	ref
	Metallacyclobutadienes		
$L_5M(C_3R_3)$	$CpCl_2W[C_3(CMe_3)Ph_2]$	18	4
$L_4M(C_3R_3)$	$(CO)_4Re(C_3Ph_3)$	20	14
	$Cl_2(PMe_2Ph)Rh(C_3Ph_3)$	20	15
	$[Cl(CO)(PMe_3)_2Ir(C_3Ph_3)]^+$	20	16
$L_3M(C_3R_3)$	$X_3W(C_3R_3)$ (X = Cl, OR)	14	2, 3
	Metallatetrahedranes		
$L_6M(C_3R_3)$	$Cp(PMe_3)Cl_2W[C_3(CMe_3)_2Me]$	18	5
$L_5M(C_3R_3)$	$Cl_3[TMEDA]W[C_3Me_2(CMe_3)]$[b]	16	13
	$Cp(CO)_2Mo(C_3Ph_3)$	18	17
	$(CO)_2(bpy)BrMo(C_3Ph_3)$	18	18
	$CpX_2Ru(C_3R_3)$ (X = Cl, Br)	18	20
$L_3M(C_3R_3)$	$(CO)_2(NO)Fe(C_3Bu^tPh_2)$	18	19
	$(CO)_3M(C_3R_3)$ (M = Co, Rh, Ir)	18	21
	$CpNi(C_3Ph_3)$	18	22
	$Cl(py)_2Ni(C_3Ph_3)$	18	23
$L_2M(C_3R_3)$	$[(PPh_3)_2M(C_3Ph_3)]^+$ (M = Ni, Pd)	16	24

[a] A neutral η^2-C_3R_3 ligand contributes 5 valence electrons, while a neutral η^3-C_3R_3 ligand gives 3 valence electrons. [b] TMEDA = $Me_2N(CH_2)_2NMe_2$.

The nature of the bonding in the metallacyclobutadiene and the metallatetrahedrane have been examined theoretically.[6–9] Qualitative bonding analyses based on extended Hückel calculations have been given for several $L_nM(C_3R_3)$ complexes.[6] Both Fenske–Hall calculations[7] and nonlocal density functional theory[9] suggest that there is a weak M–C(2) bond in $L_3M(\eta^2\text{-}C_3R_3)$. However, it was

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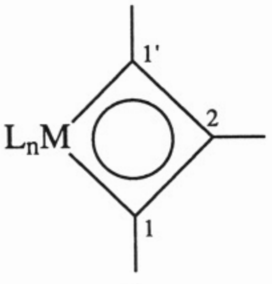

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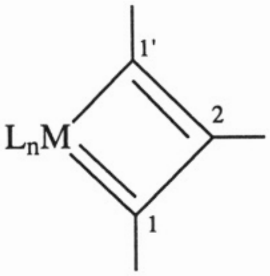

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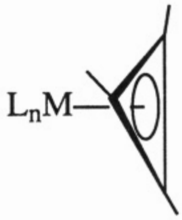

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concluded from GVB calculations of $Cl_3Mo(C_3H_3)$ that there is no significant Mo–C(2) interaction.[8] None of the theoretical studies to date provide enough insight to understand the factors that determine the relative stabilities of the metallacyclobutadiene structures (**1** and **2**) and its metallatetrahedrane isomer (**3**).

Theoretical Details

Effective core potentials were employed in all *ab initio* calculations. All geometries were optimized at the restricted Hartree–Fock (HF)[10] level. In this study, all aryl and alkyl groups were replaced by hydrogen atoms; i.e., PR_3 was replaced by PH_3. The H–P–H angle was fixed at 103.4° and the P–H bond distance was fixed at 1.44 Å. The C_5H_5 unit is also fixed as planar with C–C and C–H bond lengths of 1.41 and 1.08 Å, respectively. On the basis of the HF optimized geometries, energies were also calculated at the MP2 level.

In the effective core potentials[11a] (ECPs), the outermost core orbitals of the transition metals, which correspond to ns^2np^6 configuration, were treated explicitly along with the nd, $(n + 1)$s, and $(n + 1)$p valence orbitals. The ECP basis sets of the second and third transition series atoms were described with double-ζ representations for the $(n + 1)s/np/nd$ electrons, (541/41/31) and (541/41/21), respectively. For ligand atoms, the ECPs and double-ζ basis sets of Stevens, Basch, and Krauss[9b] were used. [He] and [Ne] configurations were taken as cores for the first and second row main group atoms, respectively. The Dunning–Huzinaga double-ζ basis set (31) was used for the hydrogen atom.[11c,d]

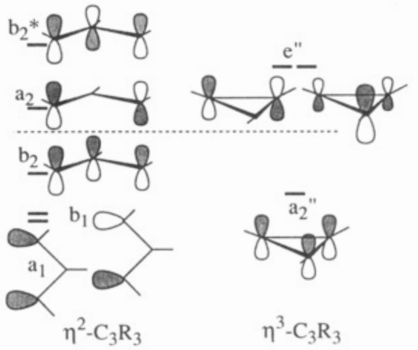

Figure 1. Molecular orbital diagrams for a C_3R_3 unit.

All ab initio calculations were performed with the GAMESS and Gaussian 92 software,[12] at the Cornell National Supercomputer Facility (CNSF) on an IBM ES9000, at the Supercomputer Center of Cray Research, Inc., on a Cray YMP-M98–4Gw-8, and on a Silicon Graphic Indigo workstation.

Results and Discussion

C_3R_3 Unit. In the metallacyclobutadiene and metallatetrahedrane complexes, the C_3R_3 adopts η^2 and η^3 coordination modes, respectively. The η^2-C_3R_3 ligand refers to the ring-opened ligand required for the metallacyclobutadienes, **1** or **2**, while the η^3-C_3R_3 ligand corresponds to the C_3 ring structure found in the metallatetrahedranes, **3**. Schematic molecular-orbital diagrams for these C_3R_3 ligands are presented in Figure 1. In the η^2-C_3R_3 unit (see left column of Figure 1), the lowest two orbitals ($a_1 + b_1$) are available to form two σ bonds with a metal atom, while the top three orbitals (b_2, a_2, and b_2*), which are π-bonding, π-nonbonding, and π-antibonding

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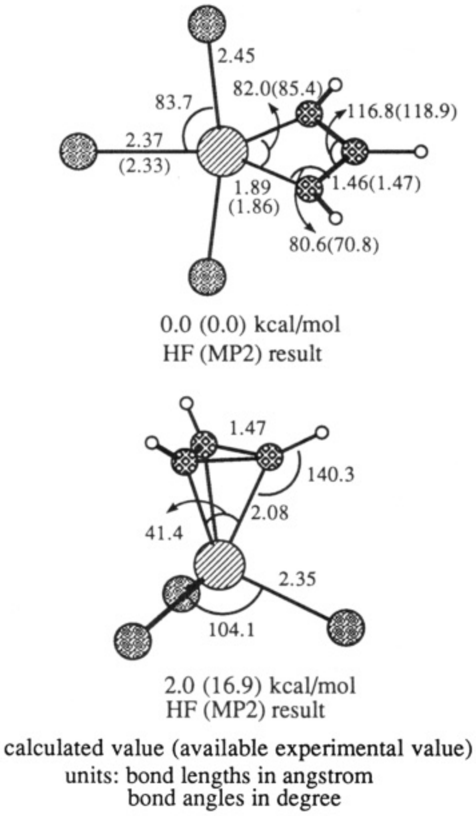


Figure 2. Optimized structures for two different isomers of the $Cl_3W(C_3H_3)$ molecule.

orbitals within the η^2-C_3R_3 unit, are available for metal–carbon π interactions. In the η^3-C_3R_3 unit (see right column of Figure 1), the lowest molecular orbital, which is C–C π-bonding, is available for a metal cyclopropenyl "σ" interaction while the top two π-antibonding molecular orbitals are of the correct symmetry for a metal–cyclopropenyl "π" interaction.

A major difference between the two coordination modes of the C_3R_3 unit is that the neutral η^2 ligand has up to five frontier orbitals and up to five valence electrons available for bonding with an L_nM fragment, while the η^3 ligand has available only three frontier orbitals and three valence electrons. If we draw a line in the MO diagrams to divide the HOMO and LUMO (see Figure 1), we can formally assign the η^2 ligand as a $[\eta^2\text{-}C_3R_3]^-$ anion and the η^3 one as a $[\eta^3\text{-}C_3R_3]^+$ cation.

These differences in the formal charges imply that the η^2 ligand can reserve more electrons than the η^3 ligand. In other words, the η^3-C_3R_3 is likely to donate more electrons to the transition metal when it interacts with a ML_n fragment. A late transition metal has more contracted d orbitals and allows more electrons localized in itself. Therefore, we might conclude that metallatetrahedrane (a η^3 coordination mode) complexes are favored among late transition metals. This general conclusion is supported, more or less, by many examples listed in Table 1 in which a large number of metallatetrahedrane complexes are found in the late transition metals. However, quite a few exceptions are also found in Table 1. These exceptions indicate that the ligand environment and number of d electrons are important factors in influencing the adoption of one isomer over the other.

Tungsten Complexes. As mentioned previously, tungsten complexes[4,5] provide examples of all these (**1**, **2**, or **3**)

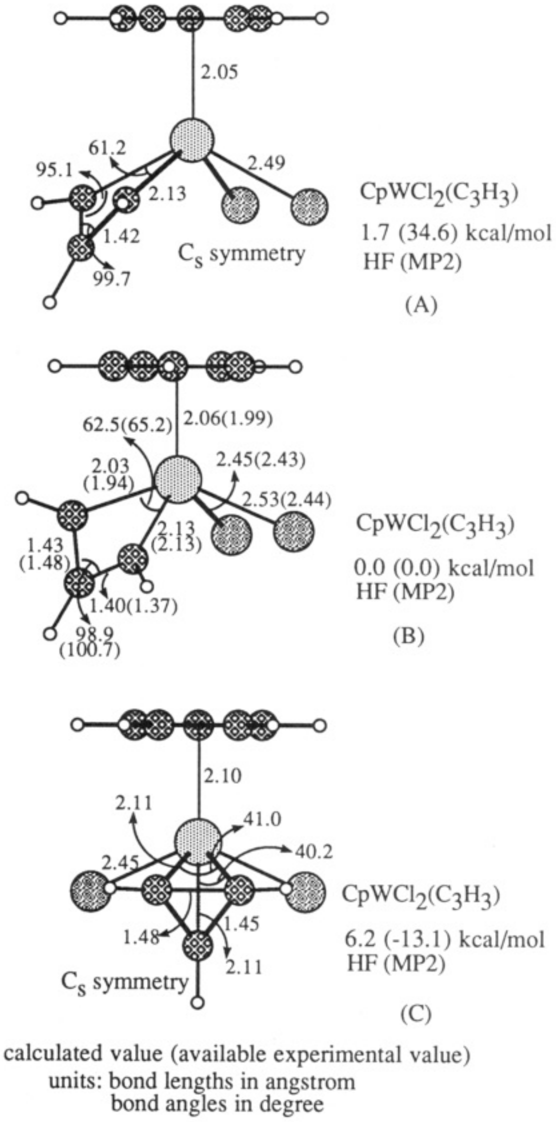
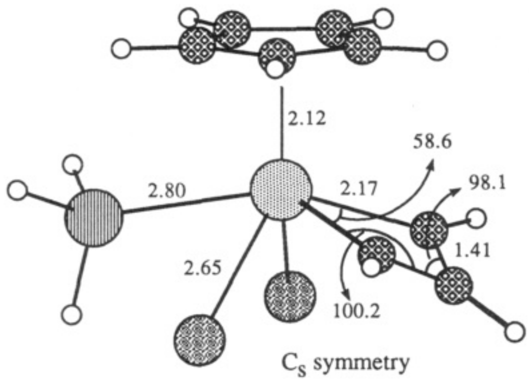


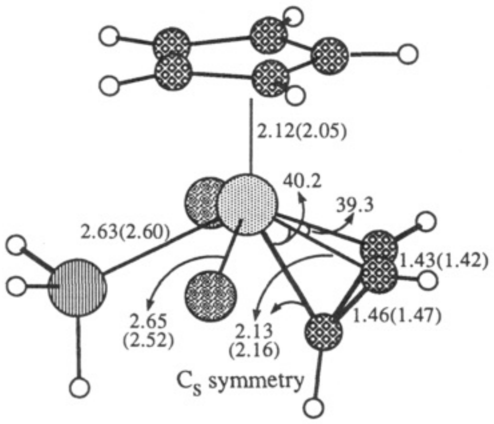
Figure 3. Optimized structures for three different isomers of the $CpCl_2W(C_3H_3)$ molecule.

structural patterns. Geometry optimizations have been performed on different isomers of $Cl_3W(C_3H_3)$, $CpCl_2W(C_3H_3)$ and $Cp(PH_3)Cl_2W(C_3H_3)$ model complexes. The results are shown in Figures 2–4 together with their relative energies of both HF and MP2 results. Our theoretical predictions at the HF level are satisfactorily consistent with the experimental observations in which $Cl_3W(C_3R_3)$ adopts isomer **1**, $CpCl_2W(C_3R_3)$ isomer **2**, and $Cp(PR_3)Cl_2W(C_3R_3)$ isomer **3** (see Figures 2–4). Energetically, the MP2 results do not give a correct prediction for $CpCl_2W(C_3R_3)$ (see Figure 3). Here, it should be noted that the perturbation theory may not provide reliable results for complexes with an unsaturated electronic configuration. For example, the conformer of Figure 3(C) is formally a 16-electron species. In such a 16-electron complex, there is a low-lying unoccupied molecular orbital which can cause significant error in the perturbation theory calculations. The calculated W-C_3H_3 geometries agree quite well with the experimental ones:[3–5] the metal–carbon bond lengths are within 0.06 Å, and bond angles are within 5° (see Figures 2–4).

$X_3W(\eta^2\text{-}C_3R_3)$ Complexes. A schematic molecular orbital diagram for the interaction between a T-shaped ML_3 fragment and an η^2-C_3R_3 unit is presented in Figure 5. As a result of the interactions between these two



(A) 18.9 (57.2) kcal/mol
HF (MP2) result

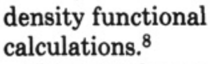


(B) 0.0 (0.0) kcal/mol
HF (MP2) result

calculated value (available experimental value)
units: bond lengths in angstrom
bond angles in degree

Figure 4. Optimized structures for two different isomers of the $Cp(PH_3)Cl_2W(C_3H_3)$ molecule.

fragments, two metal–carbon σ bonds (a_1 and b_1 molecular orbitals) and two metal–carbon π bonds (a_2 and b_2 molecular orbitals) are formed. The two metal–carbon π-bonding molecular orbitals are shown in **4** and **5**. The b_2 orbital (**4**) has a significant metal–C(2) positive overlap which implies a weak interaction between the metal and the distal carbon in the $Cl_3W(C_3R_3)$ complex and a very short W–C(2) distance (calculated 2.16 Å; experimental 2.12 Å). Our studies here agree with Fenske–Hall and density functional calculations,[7,9] but not with the GVB calculations.[8]



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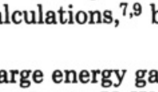

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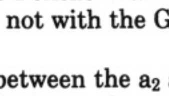

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Figure 5 shows a large energy gap between the a_2 and a_1^* molecular orbitals. In the $X_3W(C_3R_3)$ (X = Cl or OR) complexes the valence electrons occupy through the a_2 molecular orbital for a total electron count of 14. For complexes with more than 14 valence electrons, the additional electrons have to occupy molecular orbitals with slightly antibonding character. As an early transition metal with a low valence electron count, tungsten prefers complexes with a η^2-C_3R_3 coordination mode. This result conforms to the general rule discussed above.

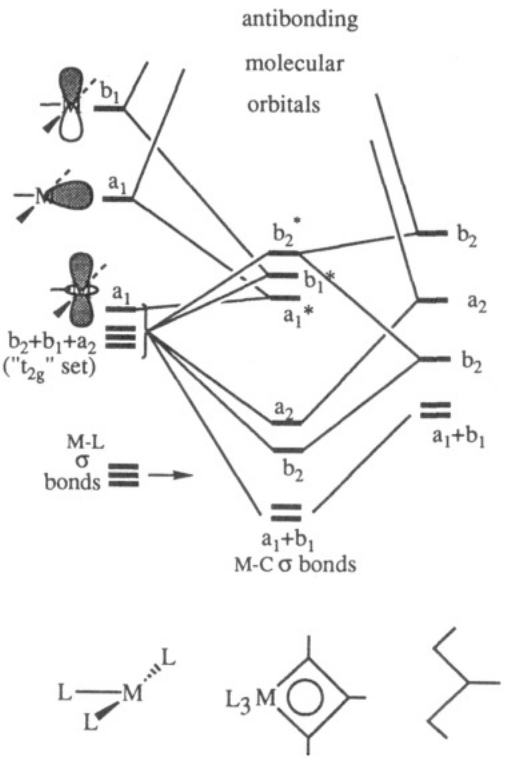


Figure 5. Orbital interaction diagram for the $L_3M(\eta^2\text{-}C_3H_3)$ complex.

Here, it should be noted that the nonlocal density functional calculations[9] on the corresponding Mo complex, $Cl_3Mo(C_3H_3)$, predict a more stable metallatetrahedrane structure by about 12 kcal/mol. Our calculations on the Mo complex (both at HF and MP2 levels) give similar results. This unanticipated change indicates that one should be very careful in using the result of calculations on second-row transition-metal complexes to understand or analyze corresponding third-row complexes.

$CpCl_2W(\eta^2\text{-}C_3R_3)$ Complex. Unlike the $X_3W(C_3R_3)$ (X = Cl or OR) complexes, $CpCl_2W(C_3R_3)$ adopts an unsymmetric structure (**2**). Since $CpCl_2W$ is isolobal with an ML_5 fragment, we first provide the schematic diagram shown in Figure 6 to illustrate the orbital interaction between an ML_5 fragment and an η^2-C_3R_3 unit. Again, the interaction between the two fragments results in the formation of two W–C σ and two W–C π bonds. A large energy gap occurs between the a_2 π-bonding orbital and b_2^* slightly antibonding orbital (see **6**).

As we can see from Figure 6, the interaction between the L_5M and C_3R_3 fragments is similar to that in $Cl_3W(\eta^2\text{-}C_3R_3)$. In both cases, two metal–carbon σ ($a_1 + b_1$) and two metal–carbon π ($b_2 + a_2$) bonds are formed within the metal–C_3 unit. Therefore, for a $L_5M(\eta^2\text{-}C_3R_3)$ complex where the L_5M fragment is derived from an octahedral ML_6 complex, distortion from the highly symmetric (**1**) structure is not expected unless a second-order Jahn–Teller (SOJT) distortion occurs. To prove that no SOJT distortion occurs in this case, we made calculations on a model complex, $Cl_3(CO)_2W(C_3H_3)$, in which a Cl and two carbonyls replace the Cp ligand. Geometry optimizations without any symmetry restriction were performed on the two structures shown in **7**. Results of the two calculations gave no indication of distortion within the $W(\eta^2\text{-}C_3H_3)$ unit.

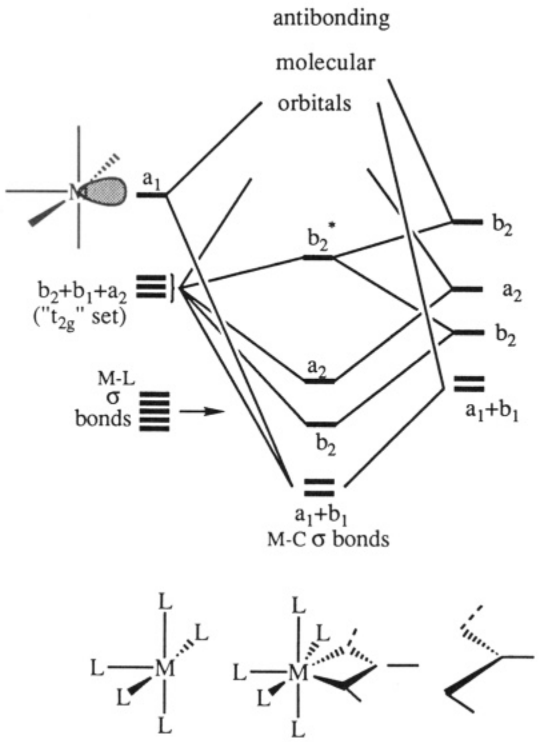
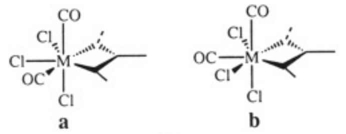


Figure 6. Orbital interaction diagram for the $L_5M(\eta^2\text{-}C_3H_3)$ complex.



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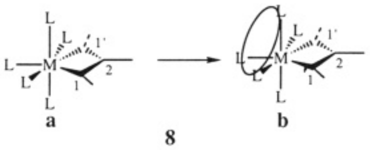
Since the SOJT effect is not responsible for the short–long–short–long distortion observed in $CpCl_2W(\eta^2\text{-}C_3R_3)$, we examine the importance of steric factors. When three L ligands are replaced by a Cp ligand (see **8**), the symmetric structure becomes sterically unfavorable because the Cp ring crowds C(1). By rotating the C_3R_3 unit along the M–C(2) axis to relieve this crowding, the molecule rearranges to a "four-legged" piano stool-like structure. Such a rearrangement, however, destroys both the b_2 (**4**) and a_2 (**5**) strong metal–C π interactions shown in Figure 6. A compromise is seen in the crystal structure of $CpCl_2W[\eta^2\text{-}C_3(CMe_3)(Ph)_2]$[4] and in the calculated structure of $CpCl_2W(\eta^2\text{-}C_3H_3)$ (Figure 3B). In an "idealized" undistorted structure, as in **8b**, Cp–M–C(1) is about 102° while Cp–M–C(1′) is ca. 142°. In the calculated structure **8b**, we see one stronger W–C(1) interaction (2.03 Å) with the Cp–W–C(1) angle of 108° and one weaker W–C(1′) (2.13 Å) with the Cp–W–C(1′) angle of 132°. In the experimental structure, W–C(1) is 1.94 Å and Cp–W–C(1) is 111.2° while W–C(1′) is 2.13 Å and Cp–W–C(1′) is 120.7°. The calculated geometric trends agree well with the experimental results, and we can conclude here that the alternate bonds (short–long–short–long) within the $W(\eta^2\text{-}C_3R_3)$ unit in the crystal structure of $CpCl_2W[\eta^2\text{-}C_3(CMe_3)(Ph)_2]$ are a result of a compromise between steric and electronic factors. The former forces the C_3R_3 unit to twist and induces bond alternation while the latter favors a symmetric structure.



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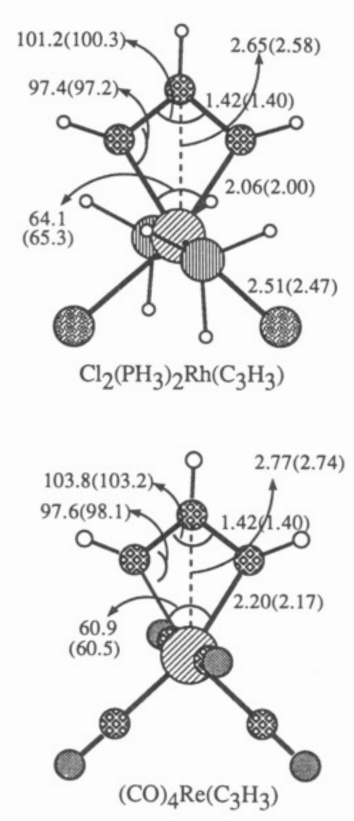
$Cp(PR_3)Cl_2W(\eta^3\text{-}C_3R_3)$ Complex. In the two examples discussed above, the $\eta^2\text{-}C_3R_3$ ligand requires four metal orbitals to form two σ and two π bonds (see Figures 5 and 6). For an ML_6 fragment, such as $Cp(PR_3)Cl_2W$, the transition metal uses six of nine available orbitals to form six M–L σ bonds. Therefore, the $Cp(PR_3)Cl_2W$ fragment has only three available orbitals to form bonds with the C_3R_3 unit. For this electronic reason, the $Cp(PR_3)Cl_2W$ fragment bonds to the C_3R_3 unit through a η^3 coordination mode rather than through a η^2 coordination mode (see Figure 4 for the optimized structures).

$L_3M(C_3R_3)$ Complexes. Except for the $X_3W(C_3R_3)$ (X = Cl or OR) complexes adopting a metallacyclobutadiene (**1**) structure, all other $L_3M(C_3R_3)$ complexes listed in Table 1 have a metallatetrahedrane structure (**3**) with a pseudooctahedral arrangement where $\eta^3\text{-}C_3R_3$ occupies three vertices. In this class of metallatetrahedranes, all complexes conform to the 18-electron rule. Alternatively, if we take the η^3 ligand as a $[\eta^3\text{-}C_3R_3]^+$ cation occupying one vertex in a polyhedral geometry, these complexes can be described as d^{10} tetrahedral complexes. In either description, these complexes adopt a structure significantly different from the one (pseudo-trigonal-bipyramidal (TBP) structure) observed for the $X_3W(C_3R_3)$ (X = Cl or OR) complexes. This difference is not too surprising if we examine the pseudo-TBP orbital interaction diagram in Figure 5 where a significant HOMO–LUMO gap is seen for a 14-electron complex. The other complexes discussed here all have 18 valence electrons and are isoelectronic and isostructural with the d^{10} $Ni(CO)_4$ complex.

$L_4M(C_3R_3)$ Complexes. Three $L_4M(C_3R_3)$ complexes have been characterized structurally (Table 1), and all adopt a metallacyclobutadienyl structure. Surprisingly, all three of these complexes have 20 valence electrons, 2 more electrons than the usual 18. Figure 7 shows the calculated and experimental structural parameters for $Cl_2(PR_3)_2Rh(C_3R_3)$ and $(CO)_4Re(C_3R_3)$ complexes. The calculated and experimental values agree extremely well for this level of calculation. An orbital interaction diagram is shown in Figure 8 to illustrate the interaction between the ML_4 and $\eta^2\text{-}C_3R_3$ fragments. Apparently, these complexes represent a situation where the slightly antibonding b_2^* molecular orbital (see **6** and Figure 8) is occupied. The occupation of this weakly antibonding molecular orbital results in a significant lengthening in the distance between the metal and the β-carbon in the MC_3 four-membered ring. In **9**, the two tungsten complexes represent a situation where the b_2^* molecular orbital is not occupied. In the remaining three complexes with 20 valence electrons, the b_2^* orbital is occupied.

Because an $\eta^2\text{-}C_3R_3$ unit contributes 2 more valence electrons to the metal–ligand interactions than an $\eta^3\text{-}C_3R_3$ unit, one wonders why the three $L_4M(C_3R_3)$ complexes adopt a metallacyclobutadienyl structure with a total of 20 valence electrons instead of choosing a metallatetrahedrane with 18 valence electrons. In view of the nature of the b_2^* molecular orbital (**6**), the MC_3 rhombus framework in a metallacyclobutadiene provides the flexibility of lengthening the metal–C(2) (see **1** for the numbering) distance so that an additional electron pair can localize exclusively at C(2) of the $\eta^2\text{-}C_3R_3$ unit and



calculated value (experimental value)
units: bond lengths in angstrom
bond angles in degree

Figure 7. Calculated and experimental structures for the $Cl_2(PH_3)_2Rh(C_3H_3)$ and $(CO)_4Re(C_3H_3)$ molecules.

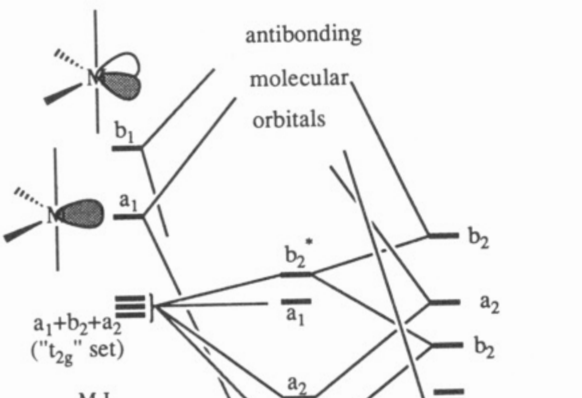
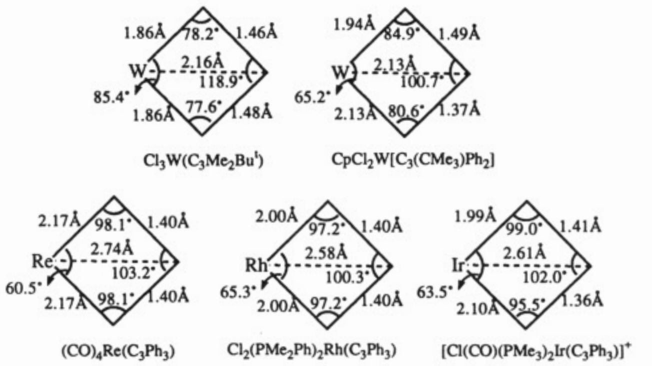


Figure 8. Orbital interaction diagram for the $L_4M(\eta^2\text{-}C_3H_3)$ complex.

retain only a very weak interaction with the central metal atom. Thus, these complexes essentially conform to the 18-electron rule although they formally have 20 electrons.



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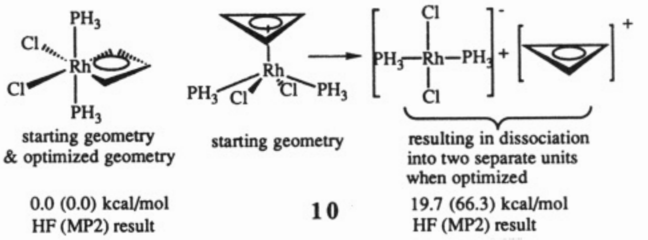
If we take the η^2 ligand as an $[\eta^2\text{-}C_3R_3]^-$ anion, these complexes can be formally viewed as d^6 octahedral complexes which are generally a particularly stable class.

The reason for not adopting a metallatetrahedrane for the three complexes discussed above can be also appreciated as follows. If we start geometry optimization on $Cl_2(PR_3)_2Rh(C_3R_3)$ in the structure shown in the center of **10** (a pseudo four-legged piano stool-like structure), the system begins to dissociate into two units, a square planar $[Cl_2Rh(PR_3)_2]^-$ complex and a cyclopropenyl cation. This is not surprising because most Rh d^8 complexes prefer a 16-electron configuration. The iridium complex is very likely to behave in the same manner. For the $(CO)_4Re(C_3Ph_3)$ complex, a geometry optimization with a four-legged piano stool-like structure as a starting geometry gave a pseudo-trigonal-bipyramidal structure (see **11**). The resulting complex $(CO)_4Re(\eta^3\text{-}C_3R_3)$ can be formally viewed as a d^8 complex. We have not found a stable Re d^8 trigonal-bipyramidal complex in the literature. Our calculations predict this one to be 57.1 kcal/mol at the HF level (22.7 kcal/mol at the MP2 level), higher in energy than its η^2 isomer (see **11**).



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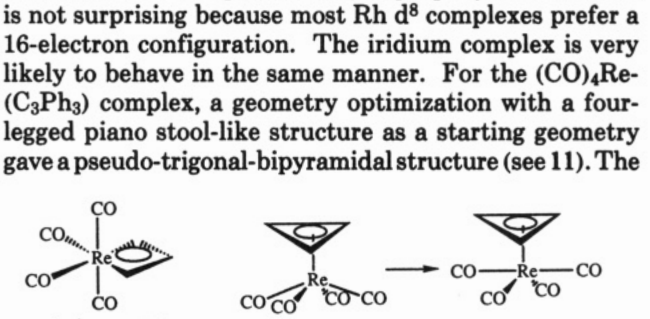

11

$L_5M(C_3R_3)$ Complexes. Except for the $CpCl_2W[(C_3(CMe_3)Ph_2]$ complex discussed above, most $L_5M(C_3R_3)$ complexes adopt a metallatetrahedrane structure (see Table 1). Since $\eta^3\text{-}C_3R_3$ can be taken as a ligand occupying a single vertex in a polyhedron, it is expected that many $L_5M(C_3R_3)$ complexes will adopt a pseudooctahedral structure. An orbital interaction diagram is shown in Figure 9 to illustrate the interaction between an ML_5 fragment and the $\eta^3\text{-}C_3R_3$ unit. Formally, one can see that the metal forms one σ and two π bonds with the η^3-

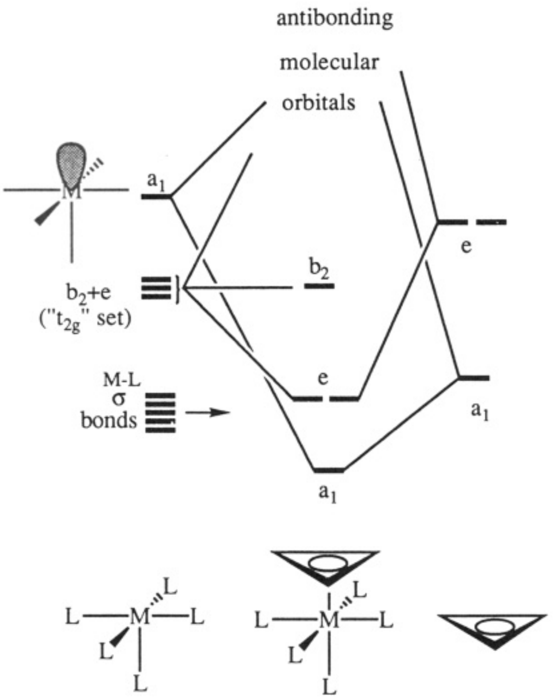

Figure 9. Orbital interaction diagram for the $L_5M(\eta^3\text{-}C_3H_3)$ complex.

C_3R_3 unit. The electronic structure of these pseudooctahedral complexes is similar to a complex consisting of a ML_5 fragment and a potentially triple bond ligand (T) such as a carbyne. Thus, this complex could be classified as one of the (T)ML_5 complexes, which forms part of a recent review.[25]

Unlike $CpCl_2W[C_3(CMe_3)Ph_2]$, which adopts a metallacyclobutadienyl structure, $Cl_3[TMEDA]W[C_3Me_2(CMe_3)]$ (see Table 1) is a 16-electron species which adopts a metallatetrahedrane structure. In this example the b_2 molecular orbital is not occupied (see Figure 9). As we have discussed above, a $\eta^2\text{-}C_3R_3$ unit can provide 2 more valence electrons than a $\eta^3\text{-}C_3R_3$ unit for metal–ligand bonding. In principle this complex could adopt the metallacyclobutadienyl structure (**8a**) and satisfy the 18-electron rule. However, larger ligand–ligand repulsions in the pentagonal–bipyramidal structure (**7a**) probably prevent this. In the $CpCl_2W[C_3(CMe_3)Ph_2]$ complex, the smaller Cp ligand provides less steric hindrance than the combination of a Cl and the TMEDA ligands. Therefore it can adopt a metallacyclobutadienyl structure which can be also described as a four-legged piano-stool structure,[26] as shown in Figure 3B. Our theoretical calculations on model complex $Cl_3(NH_3)_2W(C_3H_3)$ did not give clear support for this rationale. In the calculations, the metallatetrahedrane is predicted to be about 10.0 kcal/mol less stable at the HF level than its metallacyclobutadiene isomer while the metallatetrahedrane is predicted to be about 15.0 kcal/mol more stable at the MP2 level. These conflicting results can only be resolved at higher levels of theoretical calculations which should be investigated further in a future paper. Again, these results raise further caution in using MP2 energies for electronically unsaturated transition-metal complexes.

All other $L_5M(\eta^3\text{-}C_3R_3)$ complexes in Table 1 conform to the 18-electron rule where the b_2 orbital (see Figure 9) is fully occupied. When we take the $\eta^3\text{-}C_3R_3$ unit as a single $[\eta^3\text{-}C_3R_3]^+$ cationic ligand, these 18-electron complexes again belong to the class of d^6 octahedral transition metal complexes.

Conclusion

A C_3R_3 unit is coordinated to transition-metal atom either through a η^2 mode (metallacyclobutadiene) or a η^3 mode (metallatetrahedrane). The relative stabilities of these isomers are determined by several factors, such as ligand environment, number of valence electrons and type of transition-metal atom in the complex. In the aspect of electron count, a neutral $\eta^2\text{-}C_3R_3$ ligand contributes formally 5 valence electrons in the metal–ligand interaction while a neutral $\eta^3\text{-}C_3R_3$ ligand has 3 valence electrons. On the basis of this electron counting, most metallacyclobutadiene and metallatetrahedrane complexes conform to the 18-electron rule.

$L_5M(C_3R_3)$ complexes, except $CpCl_2W[C_3(CMe_3)Ph_2]$, adopt a pseudooctahedral metallatetrahedrane structure in which the $\eta^3\text{-}C_3R_3$ ligand occupies one vertex of an octahedron. $L_4M(C_3R_3)$ complexes again adopt an octahedral structure with an $\eta^2\text{–}C_3R_3$ (metallacyclobutadiene) coordination mode. The octahedral structure for these complexes is particularly stable because they can be formally viewed as d^6 compounds if one takes the η^2 ligand as a $[\eta^2\text{-}C_3R_3]^-$ anion and the η^3 ligand as a $[\eta^3\text{-}C_3R_3]^+$ cation. $L_3M(C_3R_3)$ complexes, except $X_3W(C_3R_3)$ (X = Cl or OR) with 14 valence electrons, adopt a pseudotetrahedral metallatetrahedrane structure and satisfy the 18-electron rule. The high stability of this pseudotetrahedral structure for these $L_3M(C_3R_3)$ complexes can be understood by considering them as late transition-metal d^{10} complexes with a $[\eta^3\text{-}C_3R_3]^+$ cationic ligand.

The alternate bonds (short–long–short–long) within the $W(\eta^2\text{-}C_3R_3)$ unit of $CpCl_2W(\eta^2\text{-}C_3R_3)$ are a result of a compromise between steric and electronic factors. Electronically, the molecule favors a symmetrical arrangement within the $W(\eta^2\text{-}C_3R_3)$ unit, while sterically, because of the Cp presence, an unsymmetric ligand environment forces the molecule to rearrange so that a maximum metal–ligand interaction is preserved.

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