4. A Class of Trinuclear Clusters with Carbonyl Bridging

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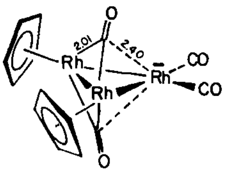
Summary

The impetus for this work was the structure of a trinuclear complex with two carbonyl groups showing incipient triple bridging - $Cp_2Rh_3(CO)_4^-$. Its structure, barrier to rotation of one $Rh(CO)_2^-$ piece *vs.* the rest of the molecule, and the nature of the bridging carbonyl interaction are analyzed. Isolobal analogies form an interesting connection between this complex and a bridged isomer of the recently synthesized carbene complexes, $Cp_2Rh_2(CO)_2CR_2$, one isomer of $Cp_2Rh_3(CO)_3$, and hypothetical carbyne complexes $Cp_2Rh_2(CO)_2CH^{+,-}$. A general bonding model for $Cp_2Rh_2(\mu\text{-}CO)_2X$ complexes is constructed. The model, rich in geometrical detail, allows minima for the bridging carbonyl groups bending toward and away from the bonded ligand X.

Introduction. - Interest and expediency, two of the motive forces of science, lay behind the initiation of this work. The interest was provided by the preparation and structure determination of $Cp_2Rh_3(CO)_4^-$ (**1**) by *Bergman et al.* [1][2]. We were intrigued by the semi-triply bridging disposition of two carbonyl groups in **1**. In transition metal clusters there exists a spectrum of terminally bonded, doubly bridging, semi-doubly bridging, and triply bridging carbonyl groups [2] [3]. The complex **1** is a so far unique example of a molecule caught between the doubly



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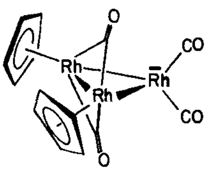

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[2] Throughout this paper we use the abbreviation Cp for an η^5-cyclopentadienyl ring.

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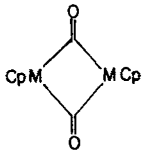

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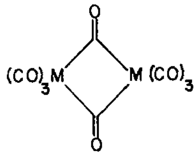
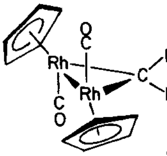


3b

bridging and triply bridging extremes. Moreover there is an interesting orientational choice made in **1** - the $Rh(CO)_2$ unit is coplanar with the two other Rh-atoms, rather than perpendicular, as in **2**, a choice that might have seemed better on steric grounds.

The expediency was grounded in a study we had just completed of $CpM(\mu\text{-}CO)_2MCp$ and $(CO)_3M(\mu\text{-}CO)_2M(CO)_3$ complexes (**3a** and **3b**) focusing on the planarity or puckering of the inner rhomboid and the metal-metal interaction [4]. The orbitals of a $Cp_2Rh_2(CO)_2$ were thus fresh in mind. That structural unit is obviously a piece of the trirhodium cluster **1**. It was a simple matter to think about constructing the orbitals of **1** or **2** from $Cp_2Rh_2(CO)_2$ and a $Rh(CO)_2^-$ fragment.

This was done, and the details will be given below. At this point another incentive appeared in the perception of a connection between $Cp_2Rh_3(CO)_4^-$ and a beautiful series of compounds prepared by *Herrmann*'s group and structurally characterized by *Bernal et al.*, the carbene complexes of type **4** [5]. A second step took us to a hypothetical symmetrical $Cp_3Rh_3(CO)_2$ with two triply bridging carbonyl groups.



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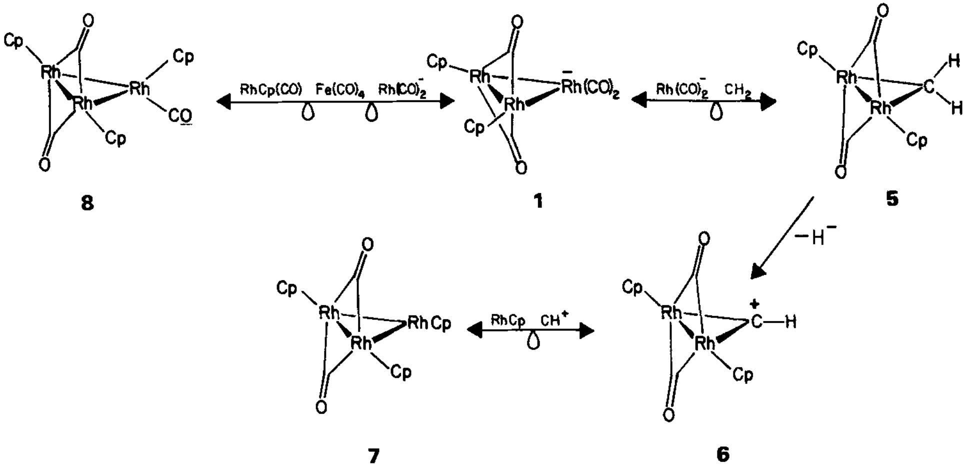
The chain of reasoning that we followed may be worth presenting at this point. We [6] and others [7] have established the utility of an isolobal analogy between the orbitals of transition metal carbonyl (or cyclopentadienyl) fragments and pieces of organic molecules. The analogy pairs $Mn(CO)_5$ with CH_3, $Fe(CO)_4$ with CH_2, $Co(CO)_3$ with CH. A cyclopentadienyl anion, Cp^-, obviously takes the place of three carbonyl groups, so further identifications of $Co(CO)_3$ with NiCp, $Fe(CO)_4$ with CoCp(CO) are possible. An extension of the analogy [6d] shows that the orbitals of a d^8ML_4 are similar to those of a $d^{10}ML_2$. Let us apply several of these isolobal transformations to **1** *(Scheme 1)*.

A $d^{10}ML_2$ fragment is isolobal with methylene. This replacement leads us back from **1** to **5**. Compound **5** is not the observed structure of *Herrmann*'s complexes, but could represent a bridged carbonyl group waypoint in a hypothetical carbonyl groups pathway in these molecules. This is apparently a high energy process [5c, d].

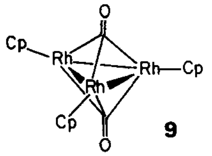
Let us next remove a hydride ion from the bridging methylene to give a hypothetical bridging carbyne complex, $Cp_2Rh_2(CO)_2CH^+$ (**6**). Isolobal replacement of

Scheme 1

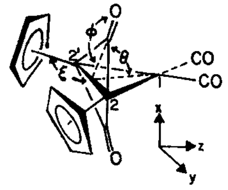


CH^+ by RhCp produces $Cp_3Rh_3(CO)_2$ (**7**). Another isolobal replacement, that of the $d^{10}Rh(CO)_2^-$ by RhCp(CO) (both similar to a d^8ML_4), leads one to the real structure of one isomer of $Cp_3Rh_3(CO)_3$ (**8**).

The $Cp_3Rh_3(CO)_2$ structure is drawn unsymmetrically in the scheme, to bring out its relationship to **1**. However, one can inquire whether the structure can be symmetrized by having the carbonyl groups move into fully symmetrical triply bridging positions, as in **9**. This compound is not known. Our calculations indicate a triply bridging structure for it, with some interesting possibilities for deformation.



$Cp_2Rh_3(CO)_4^-$. - A series of extended *Hückel* calculations, parameters specified in the Appendix, were carried out. In these we optimized independently the three variables shown in **10**. The dihedral angle between the Rh_1-Rh_2-$Rh_{2'}$ and the $Rh_{2'}$-C-Rh_2 planes is designated by θ; the bending of the Cp groups away from the y axis is given by ξ, the Rh_2-$Rh_{2'}$-Cp midpoint angle; and φ is the tilting of the bridging CO away from Rh_1. The optimized values were $\theta = 74°$, $\xi = 157°$, $\varphi = 176°$. These agree quite well with the experimental values of $\theta = 77.5°$, $\xi = 159.4°$, $\varphi = 170°$ [1]. The Rh-C(O) overlap populations shown in **11** indicate significant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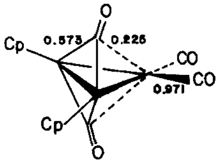

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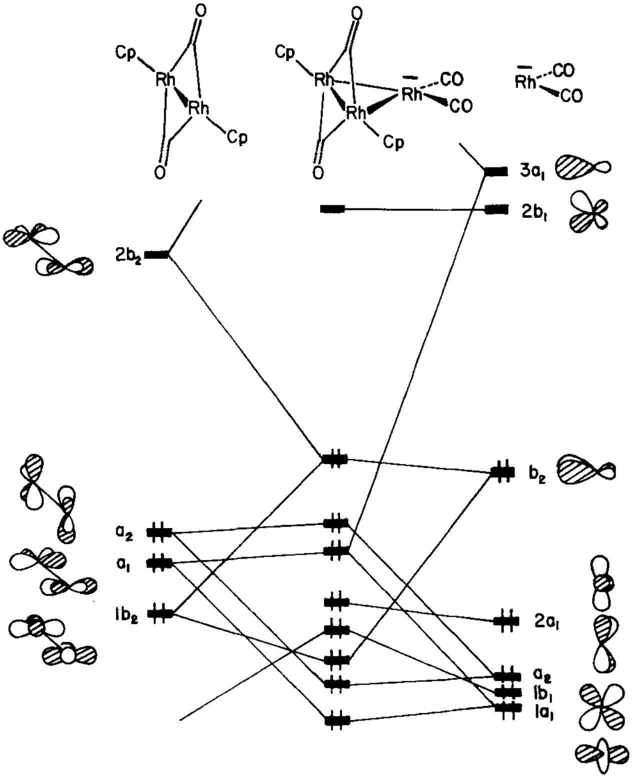
Scheme 2. *Construction of the orbitals of* $Cp_2Rh_3(CO)_4^-$ *from* $Cp_2Rh_2(CO)_2$ *at left and* $Rh(CO)_2^-$ *at right*



interaction between the bridging carbonyl groups and Rh_1, although the other two types of Rh-C(O) bonding are substantially larger. When the two carbonyl groups are placed in a more idealized doubly bridging geometry, $\theta = 90°$, $\xi = \varphi = 180°$, the Rh_1-C(O) overlap population is diminished to 0.083, while that for Rh_2-C(O) increases to 0.617.

Let us construct the orbitals of $Cp_2Rh_2(CO)_4^-$ from those of $Cp_2Rh_2(CO)_2$ and $Rh(CO)_2^-$, for simplicity taking a doubly-bridging reference geometry, $\theta = 90°$, $\xi = \varphi = 180°$. This is done in *Scheme 2*. The valence orbitals of a $d^{10}ML_2$ fragment analogous to $Rh(CO)_2^-$ have been fully described elsewhere [6b,e] [8] [9]. Basically there is a nest of four low-lying orbitals, $1a_1$, $1b_1$, a_2, and $2a_1$, which are largely nonbonding. Their resemblance to the four occupied orbitals of a square-planar, d^8ML_4 is obvious. At higher energy is b_2. This is comprised of metal **yz** and **y**[3]) in such a way that the orbital is hybridized out away from the carbonyl ligands. At still higher energy is $2b_1$, an orbital largely of carbonyl π^* character with some metal **xz** and **x** mixed in an antibonding and bonding manner, respectively.

Because $2b_1$ does not carry a heavy metal contribution, it will be much less active in π interactions with a ligand than b_2. Highest in the scheme is a well-

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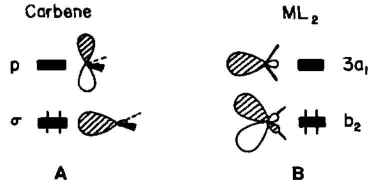
[3]) Throughout this paper we use the notation z^2, x^2-y^2, xy, xz, yz for the nd orbitals, s, x, y, z for (n+1) s and p.

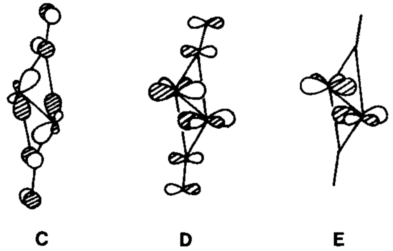
Scheme 3



directed hybrid of metal s, z and z^2. The orbitals of $Rh(CO)_2^-$ which figure in the isolobal analogy to methylene, *i.e.* those which are analogous to a CH_2 σ and p orbital [10] are $3a_1$ and b_2 respectively. This is shown below in **A** and **B** *(Scheme 3)*. Note the energy ordering in the metal fragment differs from that in the carbene.

The orbitals of $Cp_2Rh_2(CO)_2$ are a bit more complicated. The reader is referred to our detailed analysis [4], while here we sketch the outlines of the story. Two MCp fragments, each with three low-lying orbitals and three high-lying directed hybrids, combine to give a nest of six low-lying levels and six higher valence orbitals. One of the latter six, the MMσ^*, is very high in energy. The bridging carbonyl lone pairs destabilize two of the remaining five valence orbitals. There remain behind the six low-lying metal centered orbitals (the highest of these, $1b_2$, appears in *Scheme 2*) and three valence orbitals, a_1, a_2 and $2b_2$. In the d^8-$d^8Cp_2Rh_2(CO)_2$ fragment the six lower orbitals plus a_1 and a_2 are occupied. There is a great differentiation in energy between a_2 and a_1, both stabilized by bridging carbonyl π^* mixing, as shown in **C** and **D**, and $2b_2$, **E** *(Scheme 4)*, which does not have the right symmetry for that stabilization.

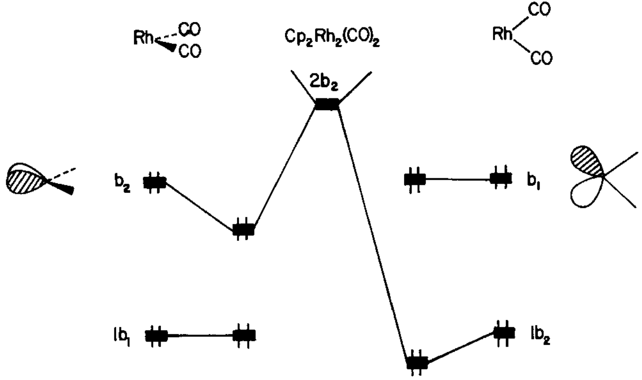
Scheme 4



Application of the eighteen electron rule leads one to a Rh-Rh double bond in this fragment. We dont find much metal-metal bonding, a typical result for carbonyl group bridged systems where the bonding in the bridging region is highly delocalized [6c] [11]. But note that the $2b_2$ orbital of $Cp_2Rh_2(CO)_2$ is clearly a π^* orbital, available for acceptance of electrons from another fragment.

This π interaction is in fact the major bonding factor in the trinuclear complex (see *Scheme 2*). The interaction is slightly complicated by the further involvement of the $1b_2$ orbital of the Rh_2 fragment. These three orbitals ($1b_2$, $2b_2$ of $Cp_2Rh_2(CO)_2$, b_2 of Rh $(CO)_2^-$) interact, producing three molecular orbitals - one at low energy, one high (not shown in the *Scheme 2*), one nonbonding. The two lower orbitals are filled, producing a net stabilization. Further bonding is provided by donor a_1 of $Cp_2Rh_2(CO)_2$ and acceptor $3a_1$ of $Rh(CO)_2^-$.

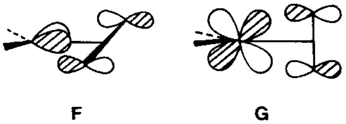
Scheme 5



The way is now clear to an understanding of the conformational preference for the observed geometry **1** over **2**. An interaction diagram similar to that of *Scheme 2* but with the $Rh(CO)_2^-$ fragment rotated by 90° could be constructed. The orbitals remain, of course, the same, but in that ML_2 fragment the symmetry labels b_1 and b_2 switch. The net result, sketched schematically in *Scheme 5*, is dramatic. The ML_2 fragment donor orbital, b_2 in orientation **1**, becomes uncoupled from the bonding in conformation **2**, since it is now b_1. Its place in the interaction with $Cp_2Rh_2(CO)_2$ is taken by a more distant and less effectively overlapping lower energy orbital. In the observed trimer geometry we calculate a rigid rotation barrier of 21 kcal/mol.

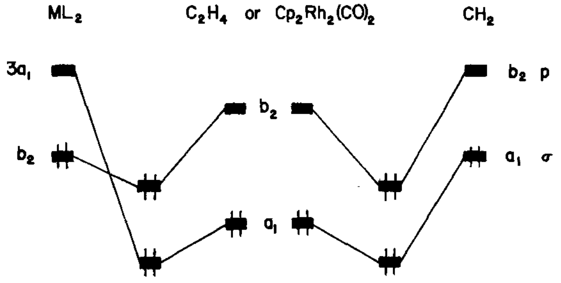
What we have described here for the conformational preference in $Cp_2Rh_3(CO)_4^-$ is analogous to what occurs in the rotational barrier of d^{10} ethylene-ML_2 complexes [6d]. The ethylene π^* orbital has a choice of interacting with either b_2 in a $d^{10}ML_2$ fragment, isoelectronic with $Rh(CO)_2^-$, as in **F** or b_1 in **G** *(Scheme 6)*. The geometry **F** is greatly favored for the same reasons as those that were described in the previous paragraph: larger overlap and smaller energy gap. The relationship between $Cp_2Rh_3(CO)_4^-$ and ethylene-ML_2 does not stop here. The bonding in both molecules could be described in terms of a classical *Dewar-Chatt-Duncanson* scheme *(Scheme 7)* in which $3a_1$ and σ on the one hand and b_2 and p, on the other, play analogous roles. The bonding in both complexes is entirely analogous to that in cyclopropane. At this point the reader might also compare our previous analysis of the $L_4Pt_2CR_2$ system [6e].

Scheme 6



The actual geometry of the $Cp_2Rh_2(CO)_2$ fragment in the Rh_3 complex differs substantially from the idealized structure with $\theta = 90°$, $\xi = \varphi = 180°$ in which the CpRhRhCp axis is linear and the bridging carbonyl groups do not lean toward the third rhodium. Bending the carbonyl groups over (reducing θ and φ) does not decrease the total energy. Stabilization ensues upon simultaneous bending back

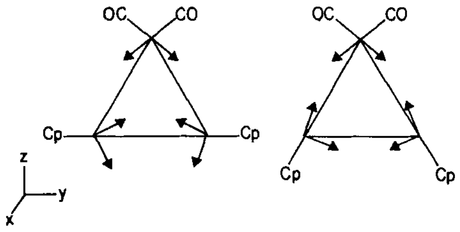
Scheme 7



of the Cp rings (reducing ξ). Motion of the Cp units is inextricably coupled to the puckering of the bridging carbonyl rhombus. We have examined this motion previously for the $Cp_2M_2(CO)_2$ complexes themselves [4], and will have something further to say about it below.

For the trimer the consequences of puckering, which involves simultaneous reduction of ξ and θ, has important stabilizing consequences. These enter through an energy lowering of the $Cp_2Rh_2(CO)_2$ fragment $2b_2$ orbital (through mixing of carbonyl π^*'s, absent in the planar rhomboid, turned on with puckering [4]) and a reorientation of that orbital for better overlap with the $Rh(CO)_2^-$ fragment. The latter factor is shown schematically in *Scheme 8* where the main lobes of the interacting b_2 orbitals are drawn as arrows. The important b_2 coupling overlap increases from 0.120 to 0.205.

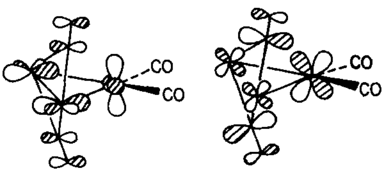
Scheme 8



$\xi = 180°, \theta = 90° \rightarrow \xi = 157°, \theta = 74°$

We return to the question of incipient triple bridging of the carbonyl groups. As θ is decreased there are several stabilizing interactions turned on between the bridging carbonyl group and Rh_1. Energetically this effect is smaller than that described previously. It is also partially masked by intermixing between the many lower-lying orbitals of the same symmetry which have been left out of *Scheme 2* and slight destabilization of the dimer levels themselves with the distortion. How-

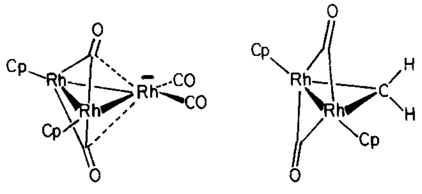
Scheme 9



ever, a fragment analysis allows a partial tracing of the interaction. Significant portions of it are to be found in the a_1 and b_2 orbitals shown in *Scheme 9*. $Rh(CO)_2^-$ lone pair interactions with bridging CO π^*, not the reverse charge transfer from carbonyl π to the 16-electron Rh-center, are implicated. We will return to the general problem of semi-bridging carbonyl groups in a separate paper.

Carbene complexes. - The introduction indicated succinctly how the isolobal analogy connects a hypothetical carbonyl bridged isomer of *Herrmann*'s carbene complexes **5** to *Bergman*'s compound **1**. The correspondence carries over in substantial detail, as *Scheme 11*, an interaction diagram for $Cp_2Rh_2(CO)_2CH_2$ constructed from $Cp_2Rh_2(CO)_2$ and CH_2, shows.

Scheme 10



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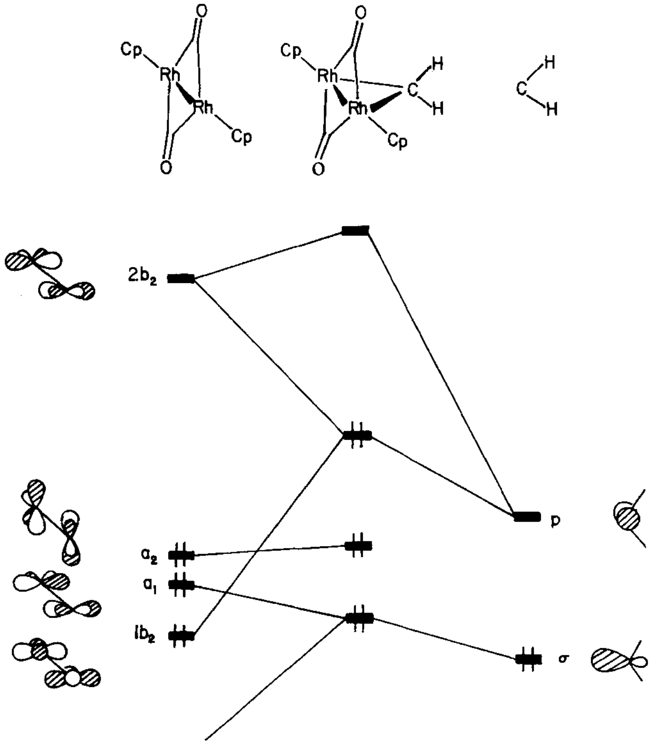
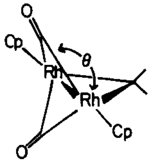
Scheme 11. *Construction of orbitals of $Cp_2Rh_2(CO)_2(CH_2)$ from $Cp_2Rh_2(CO)_2$ at left and CH_2 at right*



Even though the carbene begins with its σ orbital below the p, it is the bonding combination of carbene p with $Cp_2Rh(CO)_2$ $2b_2$ that is occupied. The three highest occupied levels in *Scheme 11*, b_2, a_2, a_1, are very similar to the three highest levels in *Scheme 2*, the $Rh(CO)_2^-$ case. The isolobal analogy is a very strong one.

Some differences emerge. When the flap angle θ (see **10**) is allowed to vary, the carbonyl groups bend *away* from the CH_2 group (see **12**) quite opposite to what happened in the *Bergman*'s compound, where the carbonyl groups bent *toward* the $Rh(CO)_2^-$. In the methylene complex θ optimizes at 115°. This value is quite insensitive to the Cp orientation, as measured by ξ.

We now have a curious feature. The bridging carbonyl groups bend one way in the $Rh(CO)_2^-$ complex, the other way in the methylene compound. Why that is so will be discussed in the next section.



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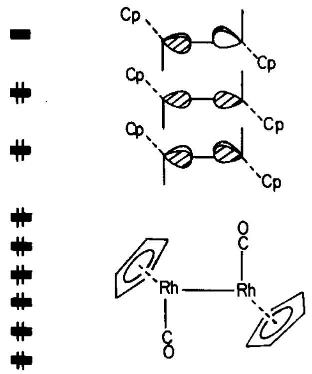
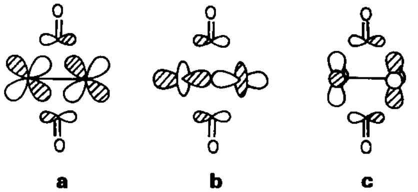
Let us not forget that the *Herrmann*'s compounds in fact do not have bridging carbonyl groups, but terminal ones (**4**). What is their electronic structure, and how is it related to the hypothetical bridging isomer discussed by us up to this point? The electronic structure of unbridged $Cp_2Rh_2(CO)_2(CH_2)$ has been treated in detail by one of us [12]. It is appropriate to write for the $Cp_2Rh_2(CO)_2$ fragment of it a double bonded structure, for above a nest of six metal centered orbitals the unbridged dimer has occupied levels of π and σ symmetry (as well as a low-lying π^* level), as shown in *Scheme 12*.

Scheme 12



The unbridged $Cp_2Rh_2(CO)_2$ may have a nice double bond, but it is unstable with respect to bridging. There are a couple of ways to see this. First, second-order *Jahn-Teller* considerations [13] turn our attention to the low-lying π^* orbital in the unbridged form. Second a detailed examination of the levels on each side shows a

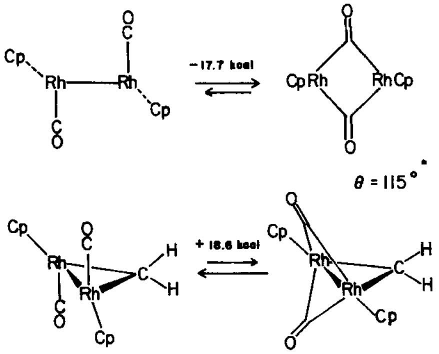
Scheme 13



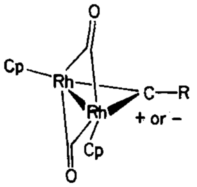
general stabilization on the bridged side through carbonyl stabilization of formally metal-metal antibonding orbitals such as **a**, **b**, **c** in *Scheme 13.* A detailed discussion will be given elsewhere [12b]. Here it will suffice to say that the bridged form is calculated to be more stable by some 21.7 kcal/mol when $\theta = 90°$, 17.7 kcal/mol for $\theta = 115°$.

While the unbridged Cp_2Rh_2 fragment is the less stable one, it is far better set up to bind a methylene than the bridged isomer. To a great extent this is the consequence of the low-lying π^* orbital (see *Scheme 12*) so beautifully set up to interact with a carbene p. The unbridged $Cp_2Rh_2(CO)_2$ interaction with CH_2 is not shown in detail here [12], but it is a lovely case of metallocyclopropane formation. The way the energetics of bridging-unbridging is coupled with carbene addition is summarized in *Scheme 14.*

Scheme 14



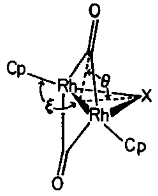
Carbyne complexes. – While **6** served just as a waypoint in an isolobal analogy in *Scheme 1,* perhaps it should be given more serious consideration, for other carbyne complexes are known. We have computed a potential energy surface for carbonyl bending in both the cation and anion of $Cp_2Rh_2(CO)_2CH$ (**6a**).



6a

The cation is relatively undistorted, $\theta = 175°$ (see **10** for the definition of the angle). The anion shows a rather different picture. In a curious mixture of the behaviour of the $Rh(CO)_2^-$ and CH_2 complexes, the hypothetical $Cp_2Rh_2(CO)_2(CH)^-$ has two well defined minima. In one the carbonyl bridges bend toward the CH^-, $\theta = 70°$, $\xi = 155°$; in the other they bend away, $\theta = 120°$, $\xi = 175°$. These geometries are 4.5 kcal/mol apart in energy, with the one bent away from the carbonyl groups being more stable. Secondary interactions between the carbanion lone pair and bridging carbonyl π^* orbitals are clearly identifiable in the low θ minimum. There is high C(O)–C(H) overlap population of +0.62 there. The barrier between the minima is approximately 13 kcal/mol. It would be most interesting to obtain such a carbyne complex and explore its structure and dynamics.

A general bonding pattern for $Cp_2Rh_2(\mu\text{-}CO)_2X$ complexes. - So far we have discussed several compounds, one real one with $X = Rh(CO)_2^-$, and several hypothetical ones with $X = CH_2$ or CH^+, CH^-. Still another known species remains, X = RhCp(CO), but even before we discuss its structure we must face up to the curious geometrical conclusion of the previous sections, namely that for $X = Rh(CO)_2^-$ the bridging carbonyl groups bend toward X, $\theta < 90°$, while for $X = CH_2$ the bridge is calculated to bend away from X, $\theta > 90°$ (see **13** for a reminder of the definition of the angles).



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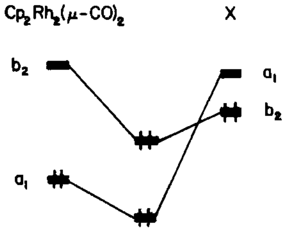
The explanation of this phenomenon is to be found in a general analysis of the bonding of a $Cp_2Rh_2(\mu\text{-}CO)_2$ fragment to a fragment X, where $X = Rh(CO)_2^-$, CH_2, $Fe(CO)_4$, RhCp(CO) or an isolobal group. As we have already said, the bonding pattern carries the usual *Dewar-Chatt-Duncanson* features of metal-ligand interaction, namely forward and back donation, involving orbitals of a_1 and b_2 symmetry *(Scheme 15)*.

Scheme 15



When we analyze the carbonyl bending in our two $Cp_2Rh_2(CO)_2X$ complexes, much of the driving force for bending is to be found in the HOMO, b_2. It is stabilized as θ increases or decreases from 90°. Why? The reasons are discussed in detail in our earlier paper [4]. At $\theta = 90°$, a planar $M_2(CO)_2$ rhomboid, this orbital

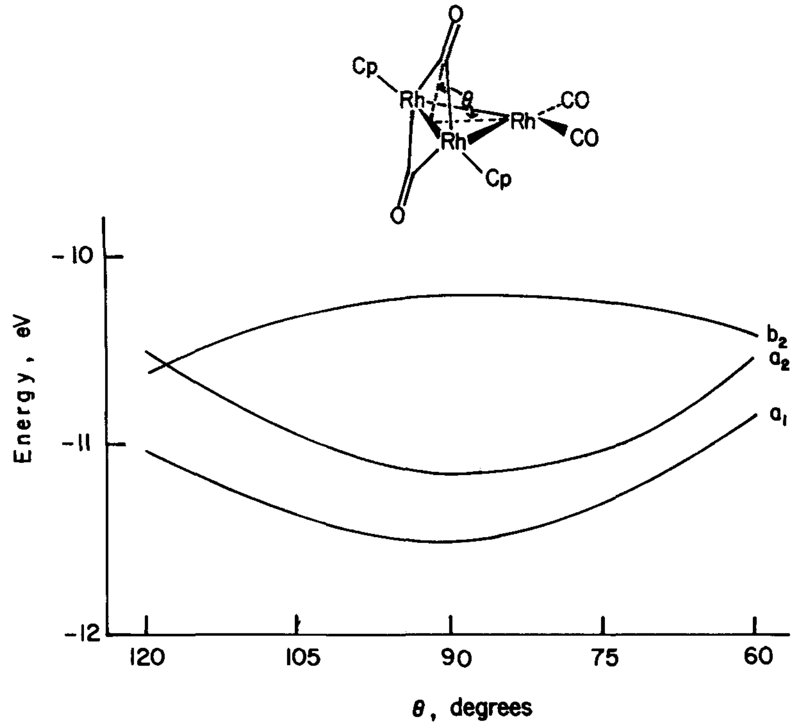


Fig. 1. *Frontier orbitals of* $Cp_2Rh_3(CO)_4^-$ *as a function of* θ. Both bridging carbonyls are bending.

cannot interact with the carbonyl π^*'s by symmetry. As the rhomboid puckers this favorable, stabilizing interaction becomes increasingly important.

In the d^8-$d^8Cp_2Rh_2(CO)_2$ this b_2 orbital, which favors bending, is *not* occupied. But, as *Scheme 2* and *11* clearly show, interaction with $Rh(CO)_2^-$ or CH_2 populates this orbital. *Figure 1* indicates the evolution of the higher occupied orbitals in $Cp_2Rh_3(CO)_4^-$ at $\xi = 180°$ as θ is varied. Note how the b_2, which favors puckering, is stabilized approximately equally as θ departs to greater or smaller angles than 90°. The lower orbitals counteract this trend.

The case at hand, $X = Rh(CO)_2^-$, is perturbed by further steric (Cp-carbonyls on unique Rh) and electronic (bridging CO-unique Rh) interactions. But quite generally if these secondary interactions are minimized we expect the primary potential energy curve for puckering in $Cp_2Rh_2(CO)_2X$ to resemble that for a $Cp_2M_2(CO)_2$ fragment with the b_2 orbital occupied, *i.e.* a broad flat minimum in a deformation coordinate in which θ and ξ are coupled. This is the dashed line in *Figure 2*.

In a hypothetical partitioning of interactions, the next factor to consider is the electronic role of the X group. As it interacts with $Cp_2Rh_2(CO)_2$ it will seek out maximum overlap with the a_1 and b_2 orbitals of the binuclear fragment. The directionality or hybridization of $Cp_2Rh_2(CO)_2$ a_1 and b_2 is a function of ξ, as shown below in *Scheme 16*, and as we discussed earlier. This will shift the minimum of *Figure 2* to smaller θ and ξ, the solid line.

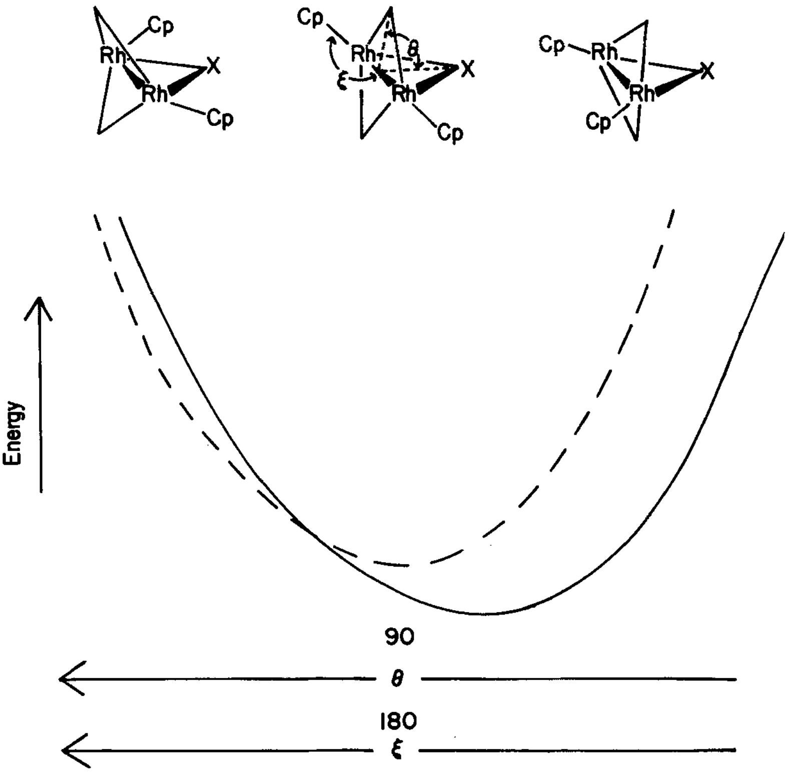
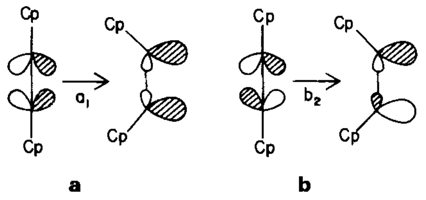


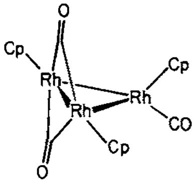
Fig. 2. *A schematic potential energy surface for carbonyl and cyclopentadienyl bending in $Cp_2Rh_2(CO)_2X$ complexes.* The dashed line is the hypothetical curve resulting from simple transfer of electrons to the b_2 orbital, while the solid line represents schematically the result of including rehybridization of a_1 and b_2 for better bonding to X. θ and ξ increase to the left.

Scheme 16



Superimposed upon this basic picture are weak attractive (secondary orbital interaction) and variable, often strong repulsive (steric) factors. These are highly encumbered geometries, and relatively small variations of θ and ξ bring on unacceptable steric contacts. In the case of $X=CH_2$ a decrease of θ brings the bridging carbonyl groups too close to the methylene. The minimum shifts to $\theta > 90°$. The hypothetical $Cp_2Rh_2(CO)_2CH^-$ has transformed the deformable surface into a double minimum curve with shallow wells, the one for small θ created by secondary interactions between CH^- and the bridging carbonyls. For $X=Rh(CO)_2^-$ the region of small θ and ξ is doubly deepened, by the secondary interactions between the bridging carbonyls and the unique Rh, and by the severe steric difficulties for $\xi > 180°$. We will soon see another example of the steric effects at work.

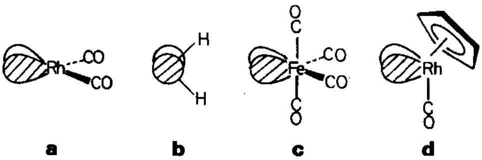
$Cp_3Rh_3(CO)_3$. - Another compound obtained by isolobal replacement of $Rh(CO)_2^-$ in **1** by RhCp(CO) is $Cp_3Rh_3(CO)_3$ (**8**). There are in fact two compounds of this stoichiometry obtained from the photolysis of $CpRh(CO)_2$. One has a symmetric structure with three bridging carbonyl groups [14], the other geometry **8** [15].



8

At first sight it seems that the RhCp(CO) fragment orientation is different from that of $Rh(CO)_2^-$. So it is, but in fact the orientation is entirely consistent with the isolobal analogy. Recall that the cruical bonding feature in these $Cp_2Rh_2(CO)_2X$ molecules is the interaction with a_1 and b_2 orbitals of the X group. The b_2 interaction sets the orientational preference. The low-lying b_2 orbitals of $Rh(CO)_2^-$ and CH_2 are shown in *Scheme 17* (**a** and **b**). RhCp(CO) is isolobal with $Fe(CO)_4$. The latter has a well-known valence active b_2 orbital (*Scheme 17*, **c** [5d]), and, not suprisingly, so does the $d^8MCp(CO)$ fragment **d** (*Scheme 17*, [12]). We have deliberately oriented all of these orbitals in the same way, the mode in which they should enter bonding with a $Rh_2Cp_2(CO)_2$ fragment coming from the left.

Scheme 17

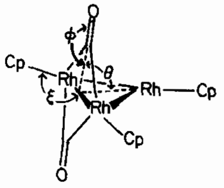


So the observed geometry of isomer **8** of $Cp_3Rh_3(CO)_3$ is, in fact, a consequence of an electronic fit. Calculations on **8** confirm this. An estimate of the barrier to rotation of the RhCp(CO) fragment is difficult to obtain because of steric crowding of Cp groups in the Rh_3 plane in the rotated form. We calculate a barrier of 36 kcal/mol even when the positions of the Rh_2 Cp rings are adjusted.

In the observed structure of **8** the $Cp_2Rh_2(CO)_2$ carbonyl groups are bent *away* from the third rhodium ($\theta = 95°$), in contrast to the $Cp_2Rh_3(CO)_4^-$ structure. We are reasonably certain that this is a steric effect, that decreasing θ below 90° is precluded by crowding between the bridging carbonyl groups and the CO and Cp on the third rhodium.

Our knowledge of the bridging tendencies in these molecules is far from complete. $Cp_3Rh_3(CO)_3$ opts for the two structures mentioned above. $Cp_3Co_3(CO)_3$ finds its equilibrium geometry in the solid state in a third isomer, which has two doubly bridging carbonyl groups (on distinct edges), and one triply bridging CO [16]. Yet in solution its infrared spectrum is indicative of structure **8a** [16].

$Cp_3Rh_3(CO)_2$ and other hypothetical molecules. - A second application of the isolobal analogy led us, in the Introduction, to an initially unsymmetrical $Cp_3Rh_3(CO)_2$ cluster, which has the appealing possibility of achieving three-fold symmetry through a small motion of the carbonyls into a fully triply bridging geometry, **7**→**9**. A discussion of this pathway follows.



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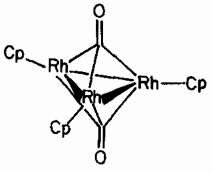
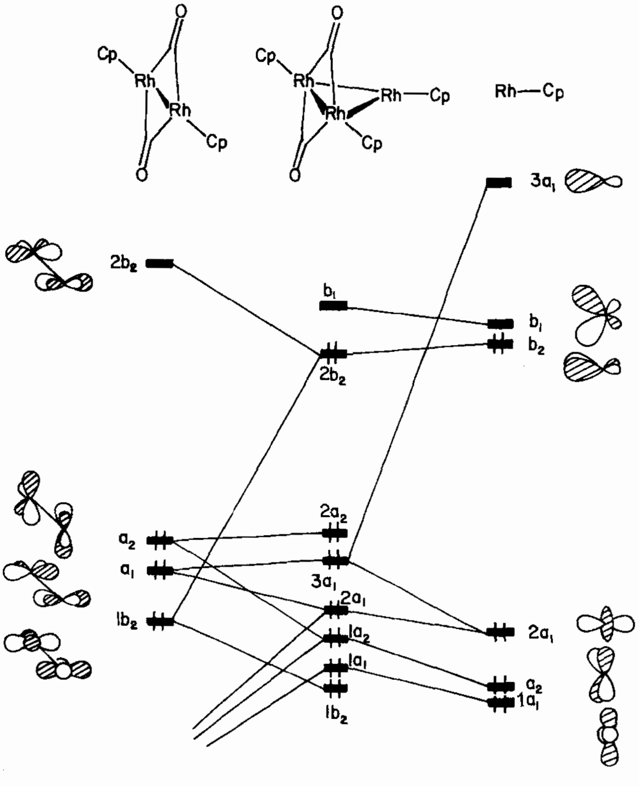


9

The interaction diagram for an unsymmetrical trimer, $\theta = 90°$, $\xi = 180°$, $\varphi = 180°$ is given in *Figure 5*. The orbitals of an MCp fragment, isolobal to $M(CO)_3$, have been discussed previously [6a, c]. They consist of three low-lying levels, $1a_1$, a_2, $2a_1$,

Scheme 18. *Construction of the orbitals of $Cp_3Rh_3(CO)_2$ from $Cp_2Rh_2(CO)_2$ at left and CpRh at right*



remnants of the octahedral t_{2g} set, and three high-lying levels, b_2, b_1 and $3a_1$, which are hybridized away from the Cp unit. Upon interaction the lower set of three are destabilized slightly by lower $Cp_2Rh_2(CO)_2$ orbitals. a_2, a_1, $1b_2$ and $2b_2$ in the dimer fragment interact in a familiar way, as we have seen previously for $Cp_2Rh_3(CO)_4^-$ and $Cp_2Rh_2(CO)_2CH_2$. The nonbonding molecular orbital labelled $2b_2$ is the HOMO of the complex. The b_1 level of the CpRh fragment is now high-lying. It forms a three orbital interaction with b_1, a primarily carbonyl π^* level, and its bonding counterpart, not shown in the diagram. Note that b_1 remains a low-lying LUMO.

Next we studied the approach to triply bridging. A *Walsh* diagram for a symmetrical cut of the potential surface varying θ, ξ and φ is presented in *Figure 3.* As ξ decrease the interaction between $2b_2$ of the dimer and b_2 of CpRh increases and the HOMO $2b_2$ drops. Also as the bridging carbonyl groups move to the triply bridging positions, a strong stabilization in the CpRh b_1 orbital is turned on. Thus

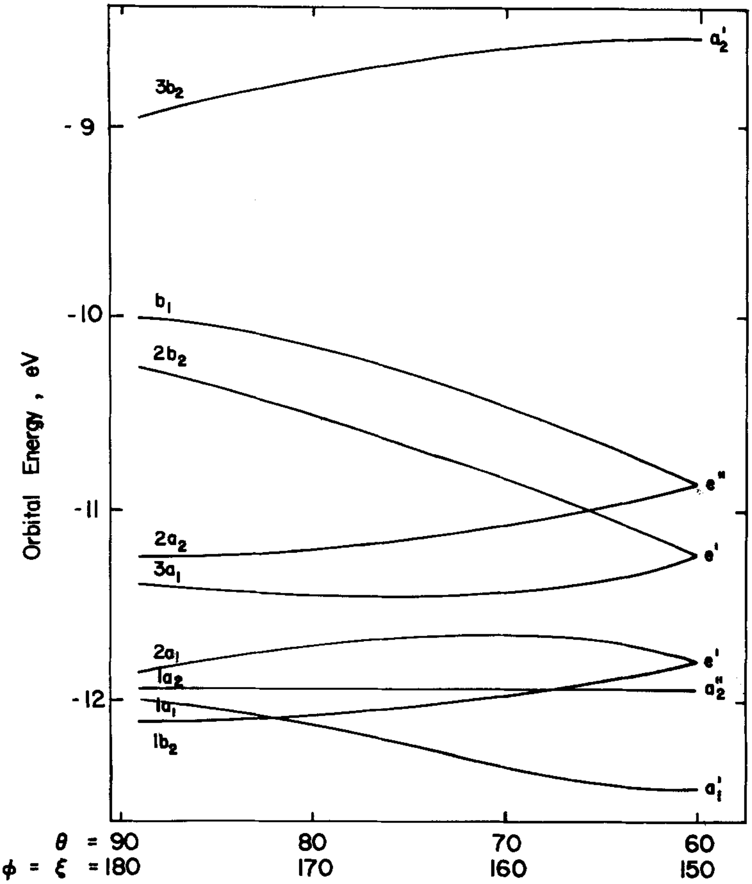


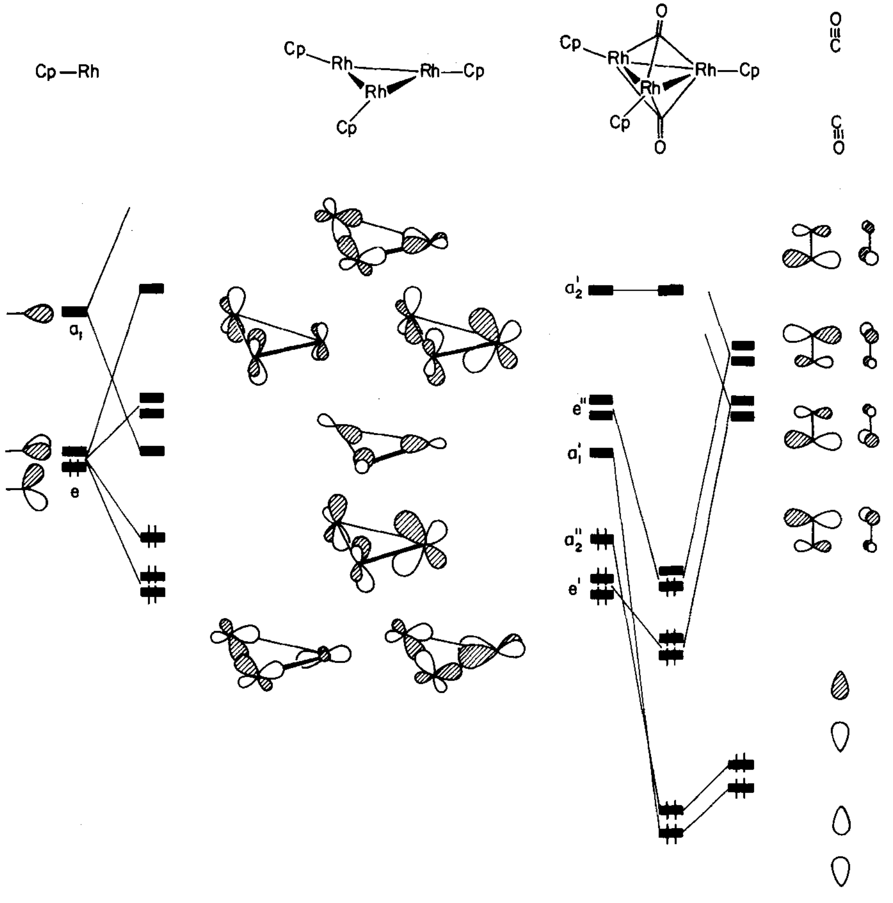
Fig. 3. *A* Walsh *diagram for an approach to the symmetrical triply bridging structure of $Cp_3Rh_3(CO)_2$.* The starting point, at left, is the doubly bridging structure with $\theta = 90°$.

the molecular b_1 level also falls. $2a_2$ rises in energy because some of the carbonyl π^* bonding is lost. Finally $3a_1$ remains relatively constant in energy until the later stages of distortion where it undergoes an avoided crossing with $2a_1$. $1a_1$ falls in energy because its interaction with lower orbitals of the dimer decrease as the Cp rings are canted back. The other valence levels of the molecule do not change much along this path.

The effective symmetry of the triply bridging $Cp_3Rh_3(CO)_2$ is D_{3h} even though the maximal real symmetry is C_{3v}. The levels at the right side of *Figure 3* are labelled according to D_{3h}.

The constitution of the trimer orbitals is better seen from an alternative construction, which begins from a three-fold symmetric $(CpRh)_3$ triangle, and adds two carbonyl groups. This is done in *Scheme 19.* At left are the seven valence orbitals of $(CpM)_3$ lying above a nest of nine metal orbitals, which are not shown in the scheme, but which have room for 18 electrons. The Cp_3M_3 system is isolobal to

Scheme 19. *At left the orbitals of a symmetrical Cp_3Rh_3 are built up from three CpRh units, at right two carbonyl groups are added to Cp_3Rh_3*

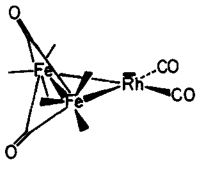


$M_3(CO)_9$ and the reader is referred to our paper on that system [17] for a detailed discussion of the $(M(CO)_3)_3$ or $(MCp)_3$ orbitals as they are built up from three $M(CO)_3$ or MCp units. Two capping carbonyl groups are brought in from right. Of the seven starting orbitals of the Rh_3 fragment two, a_2'' and a_1', are destabilized by the symmetric and antisymmetric carbonyl lone pair combinations. Four orbitals, e' and e'', are stabilized by carbonyl π^*. This leaves us with a_2', which does not find a partner among the carbonyl orbitals. There are two electrons in each CpRh e set (over and above a d^6 count) giving a total of six electrons for the valence orbitals in $Cp_3Rh_3(CO)_2$. Four go into e', leaving two for e''.

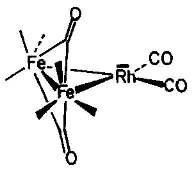
Thus the D_{3h} triply bridged $Cp_3Rh_3(CO)_2$ is an open shell complex. The molecule itself is not known, but there are some related species. With three electrons more, one reaches the known paramagnetic $Cp_3Ni_3(CO)_2$ [18]. A diamagnetic molecule with two electrons more is $(C_6H_6)_3Co_3(CO)_2^-$ [19]. Related species with triply bridging chalogens are $Cp_3Co_3S_2$ [20], its cation [21], $Fe_3(CO)_9As_2$ [22], $Fe_3(CO)_9Se_2$ [23], $Fe_3(CO)_9S_2$ [24] and $Cp_3Co_3(CO)(O)$ [25].

As a consequence of its electronic structure, two electrons in a degenerate orbital, $Cp_3Rh_3(CO)_2$ has several options open to it. It could remain a symmetrical high-spin species, as does the $Cp_3Co_3S_2$ system with four electrons less [20]. A second possibility is deformation of the Cp rings, such as that observed in a number of *Jahn-Teller* active metallocenes [26]. The degeneracy of e'' could be lifted in a number of ways. One metal-metal bond may stretch or contract, as in the $Fe_3(CO)_9X_2$ structures [22-24]. Alternatively the molecule may pause somewhere between the doubly and triply bridging structures, while keeping the metal-metal separations approximately constant, an excursion along the reaction coordinate of *Figure 3*. We have explored this last possibility, optimizing θ, φ and ξ independently. The energy is minimized at $\theta = 65°$, $\varphi = 158°$, $\xi = 150°$ (the C_{3v} structure is defined by $\theta = 60°$, $\varphi = 150°$, $\xi = 150°$). This geometry is only 2.4 kcal/mol below the symmetrical triply bridging structure and has a gap between filled and unfilled levels of 0.4 eV. We have not optimized the metal separations, and it could well be that the molecule, when it is made, will combine in its structure several of these distortions.

Isolobal replacements can be applied in the dirhodium fragment as well. For instance, let us consider the substitution of two RhCp units by $Fe(CO)_3$. Two possible conformations of $Fe_2Rh(CO)_{10}^-$, **14** and **15**, were considered.



14

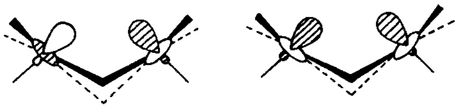


15

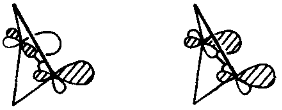
Based on our previous work [4], we realized that the tendency for the bridging carbonyl groups to pucker should be much larger in the $Fe_2(CO)_8$ fragment itself compared with $Cp_2Rh_2(CO)_2$. Furthermore, the sense of the puckering is tied to the orientation of the terminal carbonyl groups. The bridging carbonyl groups distort so as to stagger the terminal carbonyl groups. Optimization of θ, defined in an analogous manner to that in **10**, was consistent with this idea. For **14** θ was found to be 109° while for **15** it was 74°, similar to that in the triply bridging $Cp_2Rh_3(CO)_4^-$. The Rh-C overlap population for the bridging carbonyl group was again quite large - 0.266 in **15**.

While the Rh_3 system bent the bridging carbonyl groups toward the unique Rh, this does not happen here. The stability of **15** is calculated to be 59 kcal/mol *less* than that of **14**. The reason behind this is fairly simple. There is a relatively low-lying b_2 orbital **I** *(Scheme 21)*, in the $Fe_2(CO)_6$ fragment, analogous to $2b_2$ in $Cp_2Rh_2(CO)_2$. It is hybridized away from the bridging carbonyl groups [4]. Therefore, its overlap is much larger when b_2 of $Rh(CO)_2^-$ is brought in from the right side of **I** *(Scheme 20)* rather than the left. There is also a high-lying filled orbital in $Fe_2(CO)_8$ of a_1 symmetry (**K** in *Scheme 21*), which is analogous to a_1 of $Cp_2Rh_2(CO)_2$. It is hybridized like the b_2 and interacts with the empty $3a_1$ of $Rh(CO)_2^-$ much more strongly in conformation **14** than in **15**.

Scheme 20



Scheme 21



I **K**

A simple way to view the hybridization in these two orbitals is the following: Consider the $Fe_2(CO)_8$ fragment as two coupled ML_5 units and disregard any potential Fe-Fe bond [27]. Each ML_5 unit will have an orbital basically derived from one member of the e_g set in octahedral ML_6 [6]. A top view of the linear combination of these two orbitals is shown in *Scheme 20.* The interaction of $Rh(CO)_2^-$ in conformation **14** restores the octahedron with the formation of one Rh-Fe bond at each ML_5 unit. It is a brief step from here to the orbitals of $Fe_3(CO)_{12}$. All one has to do is to bring in an $Fe(CO)_4$, isolobal to $Rh(CO)_2^-$.

We have also examined a series of complexes based on $Cp_2Rh_3(CO)_4^-$ in which the bridging carbonyl groups are replaced by SR, PR_2 and halide bridges. There are some comprehensible changes in the bonding pattern and conformational preferences in these molecules, but we will constrain ourselves from presenting them in detail here.

This paper presents a rational analysis of a number of the formula $Cp_2Rh_2(\mu\text{-}CO)_2X$. If the reader now feels comfortable with the electronic order now apparent in what seemed to be a confused picture of different conformations and diverse X=$Rh(CO)_2^-$, CR_2, RhCp, RhCp(CO), then we have accomplished our task.

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Appendix. - The molecular orbital calculations were of the extended *Hückel* type [28], with a weighted H_{ij} formula [29]. *Table* lists the parameters used. The H_{ii}'s and orbital exponents for Fe and Rh were taken from previous work [11, 30]. The bond lengths and angles in **1** and other molecules containing the $Cp_2Rh_2(CO)_2$ unit were based on the experimental crystal structure of $Cp_2Rh_3(CO)_4^-$ [1]. The geometry of **14** was based on that of $Fe_2(CO)_9$ [31], with the Fe-Rh distance set at the sum of the single-bonded radii, 2.42 Å.

Table. *Extended* Hückel *Parameters*

Orbital	H_{ii} eV	Exponents[a])	
		ζ_1	ζ_2
Rh 5s	− 8.09	2.135	
5p	− 4.57	2.10	
4d	− 12.50	4.29 (0.5807)	1.97 (0.5685)
Fe 4s	− 9.17	1.90	
4p	− 5.37	1.90	
3d	− 12.70	5.35 (0.5366)	1.80 (0.6678)
C 2s	− 21.40	1.625	
2p	− 11.40	1.625	
O 2s	− 32.30	2.275	
2p	− 14.80	2.275	
H 1s	− 13.60	1.30	

a) Two Slater exponents are listed for the d functions. Each is followed in parenthesis by the coefficients in the double zeta expansion.

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