

pumping efficiency in the critical region near the source exit slit such as by constructing the first ion lens (closest to the ion source) from transparent screen.

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Cyclobutadiene Complexes and the Role of Ligand Nonbonding or Peripheral Orbitals

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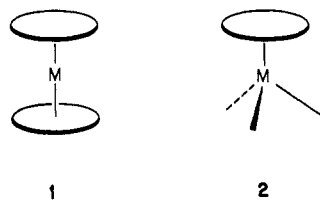
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A molecular orbital construction of the levels of $(C_nH_n)M(CO)_3$ and $(C_nH_n)_2M$, where $n = 4, 5$, or 6 and M is a transition metal, shows that the second ring provides little extra stabilization over the first one. There is on Cb_2M a high-lying orbital, localized on the cyclobutadiene ligands. The presence and role of similar orbitals is traced in other complexes. The conditions for the stabilization of Cb_2ML_n complexes are explored; there should be an extensive set of these analogous to Cp_2ML_n . The cyclobutadiene rotational barrier in $Cb_2Mo(CO)_2$ and related d^2 complexes is analyzed. An inverse sandwich mechanism for cyclobutadiene transfer reactions is suggested. Such structures provide again nonbonding orbitals localized on the periphery of what is now a transition state for a reaction. Such peripheral orbitals provide a convenient way for bypassing situations of high electron density by storing them in orbitals that are in proximity to each other but nonoverlapping by symmetry.

Cyclobutadiene is by now a common ligand in transition-metal chemistry.^{1,2} It is one of a series of possible cyclopolyene or cyclopolyenyl partners for a metal fragment. There are obvious similarities in the electronic structure of $(C_nH_n)ML_n$ complexes, and there are some differences. In this article we examine several unique aspects of cyclobutadiene complex chemistry, from a theoretical perspective.

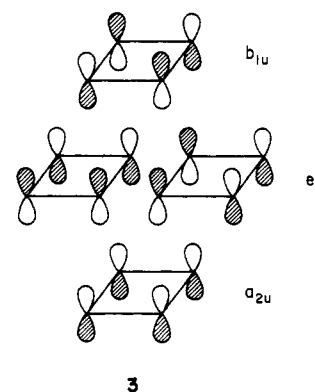
Bonding in Cyclobutadiene Complexes

The general features of cyclobutadiene (Cb) bonding are well understood, from the seminal work of Longuet-Higgins and Orgel³ to the incisive analysis of Bursten and Fenske.⁴ Because we would like to make a comparison to cyclopentadienyl (Cp) and arene (Ar) complex chemistry we begin with the two series Cb_2Ni , Cp_2Fe , and Ar_2Cr , 1, and



$CbFe(CO)_3$, $CpMn(CO)_3$, and $ArCr(CO)_3$, 2.

For the $(C_nH_n)_2M$ series 1, the obvious construction is from the well-known cyclopolyenyl orbitals⁵ and the naked metal atom. A generalized interaction diagram is shown in Figure 1 for Cb_2Ni .⁶ Each Cb monomer carries the familiar π set of 3. Two eclipsed monomers prepared for metal binding double these levels, to give (a_{1g}, a_{2u}) , (e_g, e_u) , and (b_{1g}, b_{1u}) pairs. The a_{1g} , a_{2u} , and e_g ligand orbitals are nicely stabilized by metal s , p_z (z) and $d_{xz,yz}$ (xz, yz), respectively. Three orbitals on the metal (z^2 , xy , $x^2 - y^2$)



remain relatively unaffected by the ligands, if for different reasons.^{7,8} The z^2 level has the correct symmetry to interact with the ligand a_{1g} combination, but the relevant overlap is small, the ligand π orbitals sampling the node of the z^2 . xy is stabilized only weakly by overlap with the highest energy Cb orbital, and $x^2 - y^2$ does not find a match

(1) For some reviews of the chemistry of cyclobutadiene see: (a) T. Bally and S. Masamune, *Tetrahedron*, **36**, 343 (1980); (b) S. Masamune, *Pure Appl. Chem.*, **44**, 861 (1975); (c) W. T. Borden and E. R. Davidson, *Acc. Chem. Res.*, **14**, 69 (1981).

(2) The transition-metal complex chemistry of cyclobutadiene is summarized in (a) A. Efraty, *Chem. Rev.*, **77**, 691 (1977); (b) R. Pettit, *J. Organomet. Chem.*, **100**, 205 (1975); (c) P. M. Maitlis, *ibid.*, **200**, 161 (1980); (d) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York, 1967; (e) P. M. Maitlis and K. W. Eberius in "Nonbenzenoid Aromatics", J. P. Snyder, Ed., Academic Press, New York, 1971.

(3) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

(4) B. E. Bursten and R. F. Fenske, *Inorg. Chem.*, **18**, 1760 (1979).

(5) See, for example, F. A. Cotton, "Chemical Applications of Group Theory", Wiley-Interscience, New York, 1971, p 141.

(6) A similar interaction diagram for Cb_2Ni is also given by L. H. Hall, "Group Theory and Symmetry in Chemistry", McGraw-Hill, New York, 1969, p 269.

(7) For a general discussion of molecular structure and bonding in the 3d metallocenes see the recent review by A. Halland, *Acc. Chem. Res.*, **12**, 415 (1979).

(8) J. C. Green, *Structure Bonding (Berlin)*, **43**, 37 (1981).

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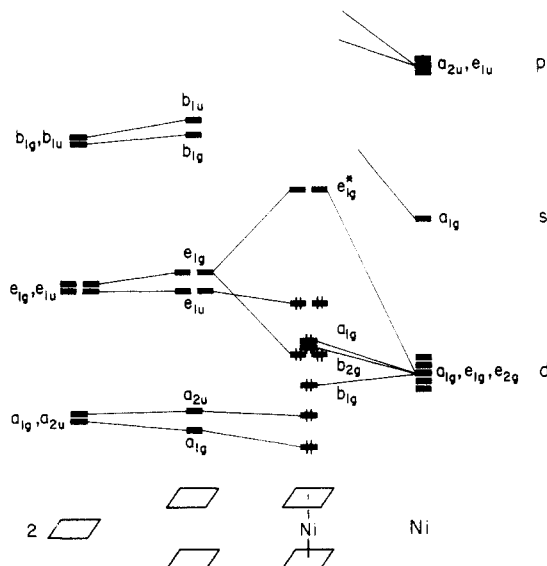


Figure 1. Interaction diagram for Cb_2Ni . Two cyclobutadienes (left) are brought together and interact with a Ni atom.

at all in the Cb π system. These three orbitals remain more or less nonbonding, forming the “ t_{2g} ” set of this electronically pseudo-octahedral complex.⁹

Throughout this paper we use a nonstandard group theoretical notation. Even though the D_{4h} e representations are not distinguished by subscripts 1 or 2, we label them e_1 so as to form a continuity of notation that encompasses not only Cb but also Cp and Ar complexes, where the distinction between e_1 and e_2 is crucial.

Most interesting for the sequel is the ligand e_{1u} set. It interacts only weakly with metal x and y , and in essence retains its free monomer ligand form.¹⁰ In Cb_2Ni the total of $2(4) + 10 = 18$ electrons fills the bonding a_{1g} , a_{2u} , and e_g and the nonbonding “ t_{2g} ” and e_{1u} sets.

The general features of Cp_2M and Ar_2M interaction are no different.^{11a} Each ligand carries a a_1 and e_1 orbitals which play the role of the Cb a_1 and e_1 set. Cp and Ar have an e_2 set, but its interaction with metal xy and $x^2 - y^2$ is not great. The 18 electrons in each complex enter bonding a_{1g} , a_{2u} , and e_g orbitals, leaving behind a nonbonding “ t_{2g} ” set composed mainly of metal z^2 , xy , and $x^2 - y^2$ and a largely ligand-based e_{1u} orbital.

To be sure, there are differences in the $(\text{C}_n\text{H}_n)_2\text{M}$ series, stemming from the different energy of the ligand π orbitals. For instance, the composition of the metal–ligand bonding orbitals changes along the series, but the most dramatic effect, to be seen in the comparison of energy levels of $(\text{C}_n\text{H}_n)_2\text{M}$ in Figure 2, is the positioning of the ligand-based nonbonding orbital, e_{1u} , relative to the t_{2g} set. It rises substantially above the t_{2g} set in Cb_2Ni , consistent with its parentage in a nonbonding orbital of cyclobutadiene.^{11b}

A recent SCF calculation by Pitzer, Goddard, and Schaefer on Cb_2Ni ¹² also places the e_{1u} level in one-electron

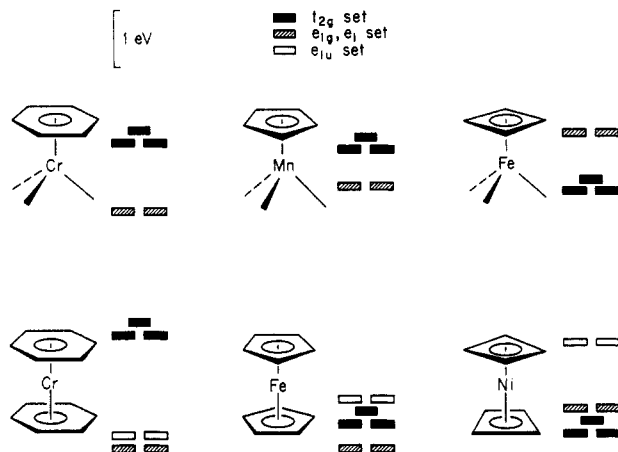


Figure 2. Orbital energies of metal t_{2g} set and C_nH_n e set(s) in $(\text{C}_n\text{H}_n)\text{M}(\text{CO})_3$, top, and $(\text{C}_n\text{H}_n)_2\text{M}$, bottom.

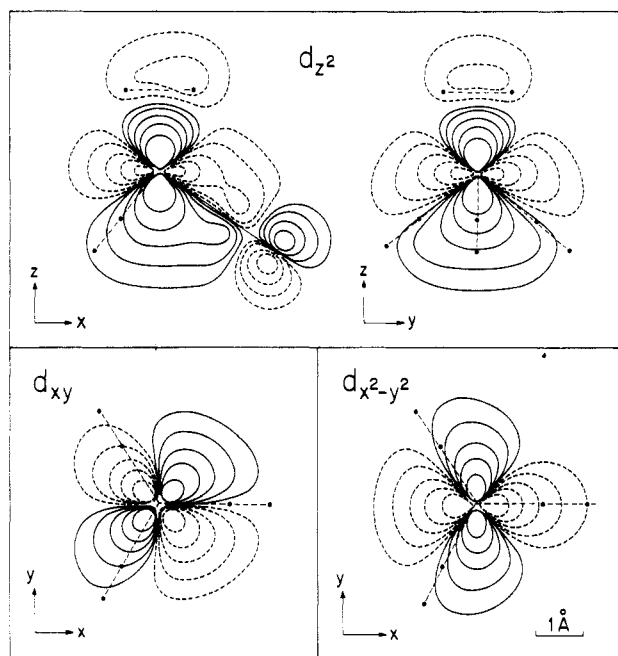
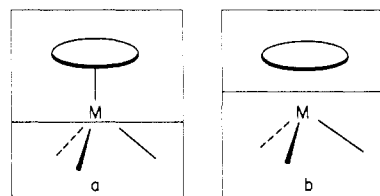


Figure 3. The three occupied d-type orbitals of $\text{CbFe}(\text{CO})_3$. The $d_{x^2-y^2}$ and d_{xy} are shown in xy plane, and d_{z^2} is shown in both xz and yz plane. The contour values of Ψ are $\pm 0.2, 0.1, 0.055, 0.025,$ and 0.01 .

energy substantially above the d block. But when ionization potentials are correctly calculated, taking into account electron relaxation, the e_{1u} is comparable to the d block.

For the $(\text{C}_n\text{H}_n)\text{ML}_3$ complexes two modes of construction suggest themselves, 4a and 4b, and indeed both types



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appear in the literature.^{4,8} The reader is referred especially to the very nice analysis of Bursten and Fenske on the $\text{CbFe}(\text{CO})_3$ system.⁴ The binding is accomplished through orbitals of a_1 and e_1 pseudosymmetry. Furthermore, consistent with the 18-electron pseudo-octahedral electronic configuration, a set of primarily metal-based (but

(9) The “ t_{2g} ” set in electronically pseudo-octahedral complexes is discussed by (a) R. Hoffmann, *Science*, 211, 995 (1981); (b) R. Hoffmann, T. A. Albright, and D. L. Thorn, *Pure Appl. Chem.*, 50, 1 (1978).

(10) From our molecular fragment analysis, the overlap between ligand e_{1u} and metal p is not small, but about 0.2. The large energy gap between the two orbital sets, about 6 eV, results in a weak stabilization of e_{1u} set, only 0.3 eV from metal p mixing. The metal character in the composite orbital is small, approximately 10%.

(11) (a) See, for example, p 235 and p 237 in ref 5. (b) The t_{2g} and e_{1u} sets in ferrocene are nearly degenerate, and in fact switch order with M–Cp distance. The t_{2g} – e_{1u} separation has been exaggerated in Figure 2 for reasons of clarity.

(12) R. M. Pitzer, J. D. Goddard, and H. F. Schaefer, III, *J. Am. Chem. Soc.*, 103, 5681 (1981).

TABLE I: Some Orbital Energies (eV)

	C ₆ H ₆	C ₅ H ₅	C ₄ H ₄
free ligand e ₁	-12.8	-12.0	-10.8
e ₁ in (C _n H _n)M(CO) ₃	-13.3	-12.8	-11.9
e _{1g} in (C _n H _n) ₂ M	-13.2	-13.2	-12.5

TABLE II: e₁ Set Orbital Energies and Their d Character in the Systems (C_nH_n)₂M, (C_nH_n)M, and C_nH_n

	e ₁ orbital energy	e _{1u} orbital energy in (C _n H _n) ₂ M	net (d _{xz} , d _{yz}) population at M
Ar ₂ M	-13.3	-13.0	(0.50, 0.50)
ArM	-13.3		(0.42, 0.42)
Ar	-12.8		
Cp ₂ M	-12.8	-12.2	(0.62, 0.62)
CpM	-12.7		(0.57, 0.57)
Cp	-12.0		
Cb ₂ M	-12.0	-10.9	(0.79, 0.79)
CbM	-11.7		(0.78, 0.78)
Cb	-10.8		

substantially delocalized to carbonyl π* orbitals is recognizable to a "t_{2g}" set. These frontier orbitals are also shown in Figure 3.

Let us try to get an estimate of the stabilization of two C_nH_n rings relative to one. This is not easy, since for two of the three pairs of complexes in Figure 2 the metals differ. But perhaps we can proceed as follows. The e_{1g} orbital in (C_nH_n)₂M is responsible for a substantial part of the bonding between C_nH_n and the metal. The same is true for the e₁ orbital in (C_nH_n)M(CO)₃. So let us compare the stabilizations of these orbitals relative to the free e₁ orbital of the uncomplexed ligand. The numbers are collected in Table I.

Putting aside for the moment the Ar₂Cr case, where a lower-lying σ orbital of the benzene ring gets involved in metal-ring bonding, it is clear that the second ring gains some over one ring, but not twice as much. This is a typical three-orbital vs. two-orbital interaction result.¹³ Still another way to probe the effect of the second ring is to examine directly the changes on going from C_nH_n to M(C_nH_n) to M(C_nH_n)₂. This is done in Table II for the same metal, Ti.

It appears there is much less gain in energy with the coordination of the second ligand in the process LM + L → L₂M. To be specific, the stabilization is 0.0, 0.1, and 0.3 eV along the Ar, Cp, and Cb series compared with 0.5, 0.7, and 0.9 eV for the first coordination process L + M → LM. To make a more accurate comparison, one should use the difference between two sums, the sum of orbital energies in L₂M (e_{1g} + e_{1u}), and the sum of the relevant orbital energies in LM and free L as a measure of the energy gain in the second coordination process. These values are 0.2, 0.3, and 0.4 eV, about one-half the values corresponding to the first coordination. The considerable similarity between the d orbital populations in L₂M and LM systems indicates that the coordination of the second ring simply completes and shares the d orbitals which play their major role in the first coordination.

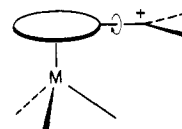
Previously we showed explicitly the nonbonding nature of the ligand e_{1u} set in (C_nH_n)₂M, most prominently displayed in Cb₂Ni. When this is coupled with the conclusion that the second C_nH_n ring gains little in stabilization over one ring, one is led to a rationalization of a number of

seemingly disparate experimental findings.

(1) Ar₂Cr is much less stable than ArCr(CO)₃, and does not survive under electrophilic conditions.¹⁴

(2) Biscyclobutadiene complexes are scarce. (Ph₄C₄)₂Ni and -Pd have been synthesized,¹⁵ but their detailed molecular structure is not yet known. Perhaps they are sterically protected, for we would have predicted great kinetic reactivity toward acids for a compound in which four electrons occupy a high-energy cyclobutadienoid nonbonding orbital e_{1u}.

(3) The relatively high position of the Cb-M bonding orbitals in CbM(CO)₃, not to speak of the Cb₂M dimer, are indicative of superior π-electron-donating capability.¹⁶ This shows up in the rate of hydrolysis of the chloromethyl CbFe(CO)₃ derivative, 10⁸ times faster than benzyl.¹⁷ Also influenced is the calculated barrier to internal rotation of an external carbonium ion center 5. The coplanar geom-



5

etry is preferred by 0.78 eV in CbFe(CO)₃, 0.46 eV in CpMn(CO)₃, and 0.24 eV in ArCr(CO)₃. There are some known biscyclobutadiene carbonium ion systems which are locally planar.¹⁷ CbFe(CO)₃ is acylated more easily than ArCr(CO)₃¹⁸ and in CbCoCp and CbRhCp the Cb ring is easier acylated.¹⁹

It should be mentioned here that there is some disagreement in the literature concerning the positioning of the e₁ levels in CbFe(CO)₃, relative to the t_{2g} set. Photoelectron spectra yield an assignment such that the first ionization is from the t_{2g} set, with the metal-ring bonding orbitals at slightly lower energy.²⁰ SCF calculations have the one-electron energies of the t_{2g} much below the e₁ level, but a ΔE SCF procedure brings them close to each other.¹² The calculations of Bursten and Fenske⁴ place the t_{2g} set some 1.6 eV above e₁. This disagrees with our ordering, but we think that even if we are wrong there is no doubt that the metal-ring bonding orbitals lie relatively high in energy.

Cb₂ML_n Complexes

Given the remarkable variety of Cp₂ML_n complexes, n = 1, 2, or 3,²¹ it is interesting that there is but a single

(14) See, for example, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, 1972, p 746.

(15) (a) H. Hoberg, R. Krause-Göing, and R. Mynott, *Angew. Chem., Int. Ed. Engl.*, **17**, 123 (1978); H. Hoberg and C. Fröhlich, *J. Organometal. Chem.*, **168**, C52 (1979); (b) H. Hoberg and C. Fröhlich, *ibid.*, **197**, 105 (1980).

(16) For correlation of frontier orbital indices of polyene-M(CO)₃ complexes with SN1 and nucleophilic substitution activities, see (a) D. A. Brown, N. J. Fitzpatrick, and N. J. Mathews, *J. Organomet. Chem.*, **88**, C27 (1975); D. A. Brown, J. P. Chester, and N. J. Fitzpatrick, *ibid.*, **155**, C21 (1978); (b) D. M. P. Mingos, S. G. Davies, and M. L. H. Green, *Tetrahedron*, **34**, 3047 (1978).

(17) R. E. Davis, H. D. Simpson, N. Grice, and R. Pettit, *J. Am. Chem. Soc.*, **93**, 6688 (1971).

(18) See, for instance, G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds", Methuen, London, 1968, p 181.

(19) (a) R. G. Amiet and R. Pettit, *J. Am. Chem. Soc.*, **90**, 1059 (1968); M. Rosenblum, B. North, D. Wells, and W. P. Giering, *ibid.*, **94**, 1239 (1972); (b) S. A. Gardner and M. D. Rausch, *J. Organomet. Chem.*, **56**, 365 (1973).

(20) (a) M. B. Hall, I. H. Hillier, J. A. Connor, M. F. Guest, and D. R. Lloyd, *Mol. Phys.*, **30**, 839 (1975); (b) S. D. Worley, T. R. Webb, D. H. Gibson, and T.-S. Ong, *J. Organomet. Chem.*, **168**, C16 (1979).

(21) See, for instance, (a) P. C. Wailes, R. S. P. Coutts, and H. Weigold, "Organometallic Chemistry of Titanium, Zirconium and Hafnium", Academic Press, New York, 1974; (b) M. L. H. Green, "Organometallic Compounds", Vol. 2, 3rd ed., Methuen, London, 1968, p 90.

(13) See J. K. Burdett and T. A. Albright, *Inorg. Chem.*, **18**, 2112 (1979); N. Rösch and R. Hoffmann, *ibid.*, **13**, 2656 (1974).

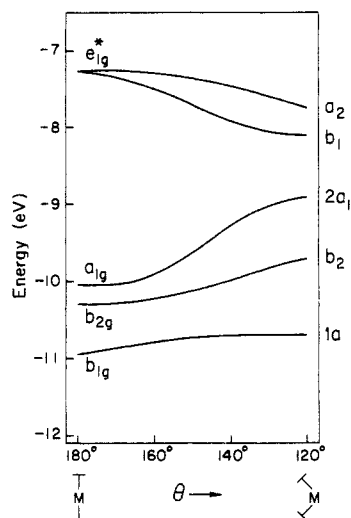
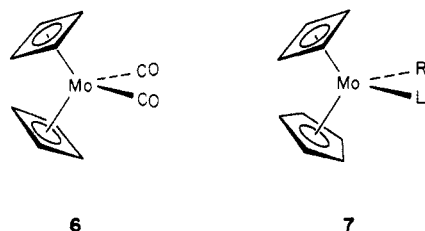
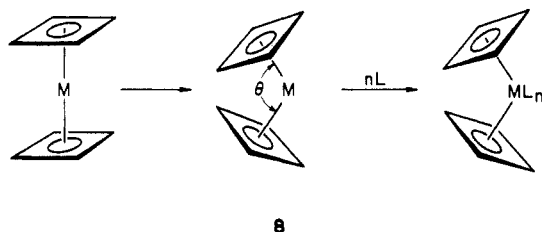


Figure 4. Cb_2Mo orbitals as a function of the bending angle θ from an eclipsed D_{4h} geometry.

representative of the corresponding cyclobutadiene class, $(\text{C}_4\text{Ph}_4)_2\text{Mo}(\text{CO})_2$, **6**.²² Mixed Cb, Cp complexes, such as $\text{CbCpMo}(\text{CO})(\text{H})$, $\text{CbCpMo}(\text{CO})(\text{Cl})$, $\text{CbCpMo}(\text{dtc})$, $\text{CbCpMo}(\text{RC}\equiv\text{CR})\text{L}$, $\text{CbCpV}(\text{CO})_2$, **7**, are better represented.²³⁻²⁷



Is there some electronic problem with Cb_2ML_n complexes? To answer this question we undertook an exploration of the electronic structure of molecules of this type. Figure 4 shows how the d block orbitals of a D_{4h} Cb_2Mo are affected by bending to C_{2v} geometry, **8**. The



D_{4h} Cb_2M levels have been discussed above. In the present case the Cb-localized e_{1u} levels and the Cb-M bonding e_{1g} set are below the " t_{2g} " levels and are not shown in the figure. The three lower metal-centered orbitals are e_{2g} (xy , $x^2 - y^2$) and a_{1g} (z^2). On deformation C_{2v} these reduce as follows: $e_{2g} \rightarrow a_1 + b_2$, $a_{1g} \rightarrow a_1$. The a_1 orbitals mix

(22) A. Efraty, J. A. Potenza, L. Zyontz, J. Daily, M. H. A. Huang, and B. Tohy, *J. Organomet. Chem.*, **145**, 315 (1978).

(23) $\text{CbCpMo}(\text{CO})(\text{H})$: R. B. King and A. Efraty, *Chem. Commun.*, 1370 (1970).

(24) (a) $\text{CpCbMo}(\text{CO})(\text{Cl})$: P. M. Maitlis and A. Efraty, *J. Organomet. Chem.*, **4**, 172 (1965); (b) $\text{CpCbMo}(\text{CO})(\text{Br})$: A. Efraty, *Can. J. Chem.*, **47**, 4695 (1969).

(25) $\text{CbCpMoS}_2\text{Cn}(\text{Me})_2$: J. L. Davidson, *Chem. Commun.*, 113 (1980).

(26) $\text{CbCpMo}(\text{RC}\equiv\text{CR})(\text{CO})$: A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and Yu T. Struchkov, *Chem. Commun.*, 739 (1969).

(27) $\text{CbCpV}(\text{CO})_2$: (a) A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov, *Dokl. Akad. Nauk. SSSR*, **185**, 610 (1969); (b) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. A. Pasynskii, *ibid.*, **182**, 112 (1968).

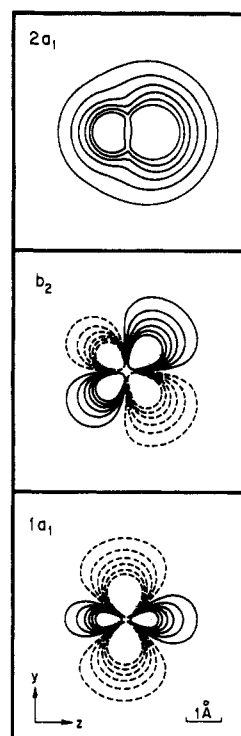
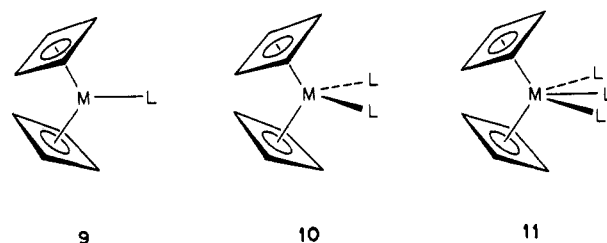


Figure 5. Contour diagrams of $2a_1$, b_2 , and $1a_1$ orbitals of Cb_2Mo , $\theta = 136^\circ$, in the yz plane. The contour values of Ψ are ± 1.2 , 1.0, 0.8, 0.4, and 0.2.

strongly with each other, $1a_1$ remains approximately constant in energy, and $2a_1$ rises with bending of the Cb-M-Cb axis. All this is quite analogous to the Cp_2M case,²⁸ as is the shape of the resulting orbitals, shown in Figure 5.

Even at this stage the similarities between Cp_2M and Cb_2M are so clear that we are led to expect a Cb_2M chemistry quite analogous to Cp_2M . This was confirmed by the detailed construction of level diagrams for **9-11**.



The interaction diagrams for $\text{Cb}_2\text{Mo} + n\text{L}$ are nearly indistinguishable from those for $\text{Cp}_2\text{Ti} + n\text{L}$, $\text{L} = \text{H}^-$, $n = 1, 2, 3$ (Figure 6). With one ligand the primary interaction is with $\text{Cb}_2\text{M } 2a_1$. For two ligands, with donor orbitals ϕ_1 and ϕ_2 the symmetry adapted combinations of $a_1(\phi_1 + \phi_2)$ and $b_2(\phi_1 - \phi_2)$ symmetry find a match in metal $2a_1$ and b_2 . For three ligands all metal orbitals are accounted for. One would expect a series of compounds, 14-18 electrons for Cb_2ML , 16-18 electrons for Cb_2ML_2 , and 18 electron Cb_2ML_3 , of which the known $\text{Cb}_2\text{Mo}(\text{CO})_2$ is the sole example to date.²² We think others will be made and that in time a rich chemistry of these complexes will develop. All conclusions on Cp_2ML_n complexes should carry over, especially the interesting possibility of tuning the angle at the metal with d electron count,²⁸ and the preferred orientation of single-faced π -acceptor or -donor ligands.

(28) J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 1729 (1976), and references therein.

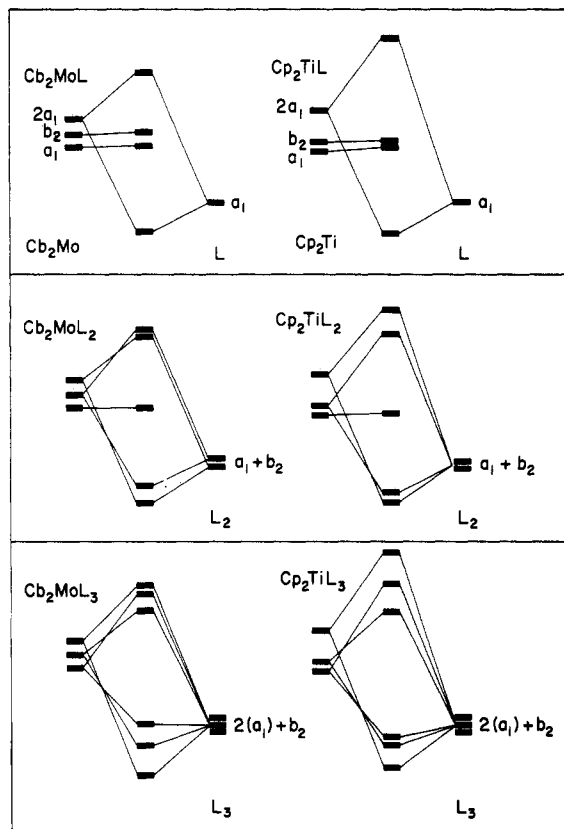
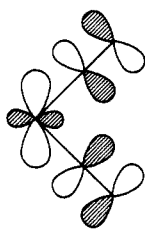


Figure 6. Interaction diagrams for $\text{Cb}_2\text{Mo} + n\text{H}^+$ compared with those for $\text{Cp}_2\text{Ti} + n\text{H}^+$, $n = 1, 2, 3$ and ring center-M-ring center bending angle of 140° .

There is a special feature of the Cb_2M complexes which is related to the relatively high energy of the Cb orbitals, discussed above for Cb_2Ni . Four such orbitals, derived from e_{1u} and e_{1g} in D_{4h} Cb_2M , remain at high energy as the Cb_2Mo is bent. The $1a_1$ orbital of a Cb_2MoH_2 is above these Cb orbitals. But if the two ligands are π acceptors, e.g., CO, the $1a_1$ is stabilized substantially by the interaction shown in 12.



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Figure 7, which compares the energies of several systems, shows that the $1a_1$ orbital of $\text{Cb}_2\text{Mo}(\text{CO})_2$ is down among the Cb-localized π levels. This is not so for $\text{Cp}_2\text{Ti}(\text{CO})_2$. A different mode of reactivity with acid might follow for the $\text{Cb}_2\text{Mo}(\text{CO})_2$ complexes—possibly attack at the Cb ring rather than the metal. It may also be that 16-electron $\text{Cb}_2\text{M}(\text{CO})_2$ systems will be high-spin complexes or undergo substantial distortions if they are low spin.

The analysis presented here is easily extended to mixed systems such as $\text{CbCpV}(\text{CO})_2$.²⁷ Their level pattern (see Figure 7) is a near superposition of the two previously discussed schemes.

Cb Rotational Barrier in $\text{Cb}_2\text{Mo}(\text{CO})_2$ and Related d^2 Complexes

There appears to be a strongly expressed conformational preference in d^2 Cb complexes. The solid-state structures

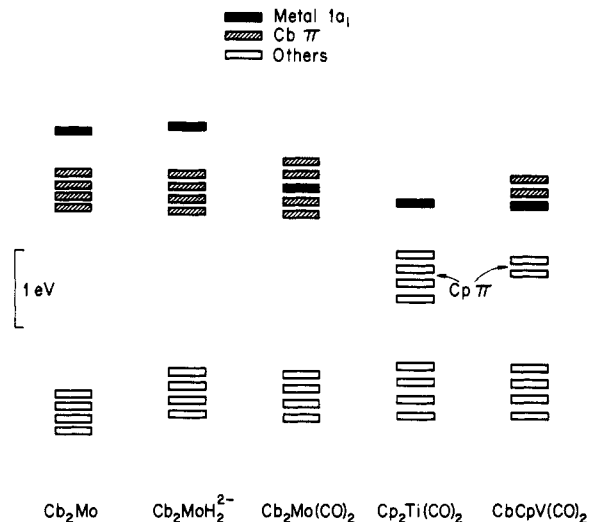
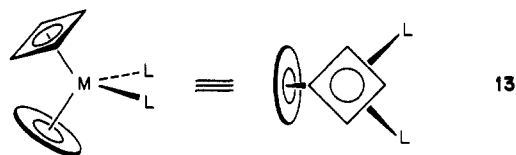
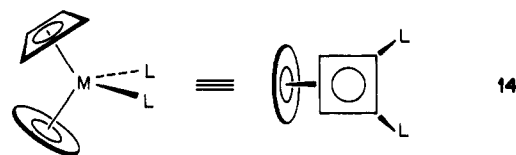


Figure 7. Orbital energy levels for Cb_2Mo , $\text{Cb}_2\text{MoH}_2^{2-}$, $\text{Cb}_2\text{Mo}(\text{CO})_2$, $\text{Cp}_2\text{Ti}(\text{CO})_2$, and $\text{CbCpV}(\text{CO})_2$, all at bending angle of 140° . The filled, lined, and unfilled level bars represent, respectively, the metal $1a_1$ orbital, a set of π orbitals on the Cb ring, and other orbitals.

of $\text{Cb}_2\text{Mo}(\text{CO})_2$ ²² and $\text{CbCpNb}(\text{CO})(\text{C}_2\text{H}_2)$ ²⁶ and the NMR-determined solution structure of $\text{CbCpMo}(\text{dte})$ ²⁵ all show the Cb ring staggered, 13, rather than eclipsed, 14.



13

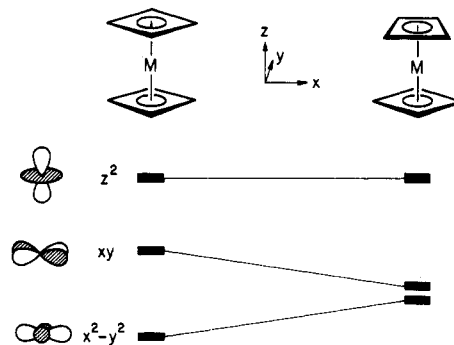


14

The reference is to the relative orientation of the MX_2 and the cyclobutadiene ligand.

When we do an extended Hückel calculation on a "linear" Cb_2Mo we obtain a substantial rotational barrier of 0.51 eV favoring eclipsing, D_{4h} . The source of this barrier is interesting, and related to the above-mentioned conformational preferences.

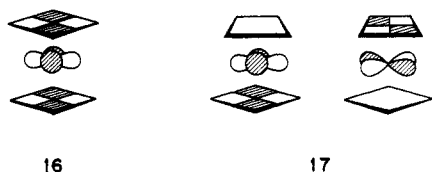
The three lower d-block orbitals in Cb_2M are xy , $x^2 - y^2$, and z^2 , as was shown in Figure 1. The evolution of these orbitals with Cb ring rotation is indicated in 15. In D_{4h}



15

only the $x^2 - y^2$ is stabilized by back-bonding with a com-

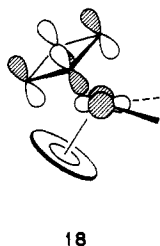
bination of cyclobutadiene highest π orbitals, b_1 , 16. In



the D_{4d} geometry both xy and $x^2 - y^2$ are stabilized each by interaction with one ring, 17. If both xy and $x^2 - y^2$ were filled, i.e., d^4 or d^6 , a typical "busy orbital" situation is created.¹³ This should favor the staggered conformation. So it does, by a little, 0.8 kcal/mol. Pitzer, Goddard, and Schaefer calculate a rotational barrier of 1.3 kcal/mol for Cb_2Ni , favoring the eclipsed form, however.¹²

For two d electrons the situation is quite different. Maximum back-bonding is attained in the eclipsed conformation, and the preference expressed is substantial.

The barrier remains almost the same as the Cb rings are bent back, to an angle between the normals as small as 120° . This is because the $x^2 - y^2$ evolves into a "y²" orbital $1a_1$ (Figure 5). There is again a preferential orientation for interaction, 18.



Next we add two hydrides, to form $Cb_2MoH_2^{2-}$. The two ligands interact mainly with $2a_1$ and b_2 of Cb_2Mo , leaving $1a_1$ approximately unaffected. The barrier to Cb rotation should not be changed much. It is calculated as 0.34 eV at Cb-Mo-Cb 140° .

In $Cb_2Mo(CO)_2$,²² we calculate a much smaller barrier favoring the staggered geometry, 0.04 eV. It appears that the diminution of the barrier is primarily due to the delocalization of $1a_1$, heavily involved in π bonding with the carbonyls. There are also some small contributions in a_2 and b_2 orbitals favoring the eclipsed conformer.

For the $CbCpMoS_2CNMe_2$ system,²⁵ the computed energy barrier is 0.26 eV, considerably larger than for $Cb_2Mo(CO)_2$ and comparable to $Cb_2MoH_2^{2-}$. Our calculation indicates that the difference in $1a_1$ orbital energy can account for the barrier. However, the y^2 character in $1a_1$ is only 40%—it is substantially delocalized. An additional factor contributing to the difference in energy between the extreme orientations in this orbital comes from repulsive interaction between Cb and two S atoms. Our partially optimized geometry has S-Mo-S 80° , S-C-S plane bent 20° from the equatorial plane toward the Cp ring, and a Cb center-Mo-Cp center angle of 125° .

Our calculations on $CbCpV(CO)_2$, $CbCpMo(Cl)(CO)$, $CbCpNb(C_2H_5)(CO)$, and $CbMo(CO)Cl$, all show that the staggered conformer is more stable. The rotation barrier for the first system is only 0.03 eV, similar to that for $Cb_2Mo(CO)_2$. The barriers for the other molecules are 0.26, 0.16, and 0.15 eV, respectively. The last system is a model for the dimeric $[CbMo(CO)_2Br]_2$ with two bridged Br atoms.^{29b} The observed solid-state conformations of the last two complexes indeed show the Cb ring staggered with

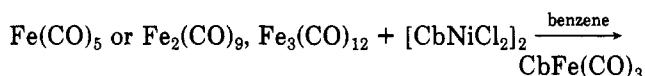
respect to the ML_n fragment.^{26,29b}

The general feature that emerges from these calculations is that the rotational barrier is dominated by the $1a_1$ orbital. The electronic contribution from this orbital invariably favors the staggered form. However, the barrier is modified to some extent by steric interaction between the Cb ring and the ML_n fragment.

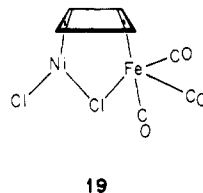
π -Ligand Transfer Reactions

The reaction referred to is one in which an organic π ligand is transferred from one metal center to another.³⁰ The type of reaction appears to be quite general, occurring with various π ligands such as allyl, Cb, Cp, and arene. However, this synthetic technique is of special importance and most often used for the cyclobutadiene-metal complexes, large numbers of which can be obtained only by this novel route. We would like to examine some possible reaction mechanisms for this process.

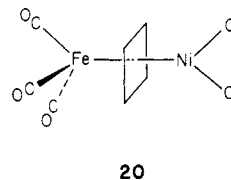
A typical reaction is that between an iron carbonyl and $CbNiCl_2$ dimer in benzene solvent.³¹



One would expect $Fe(CO)_4$ fragments to be available early in the reaction sequence, whatever the iron carbonyl reagent. In the mechanism proposed by Efraty,^{30b} the loss of carbonyl from $Fe(CO)_4$ is driven by halogen bridge formation in the binuclear complex intermediate 19 which eventually forms the product $CbFe(CO)_3$.



In this section we will examine a possible alternative mechanism, based on our previous study of the electronic structure of inverse sandwiches.³² In particular an intermediate structure 20 will be suggested. The choice



between 19 and 20 is reminiscent of the choice between triangular and linear H_3 geometries in the hydrogen exchange reaction of $H + H_2$.

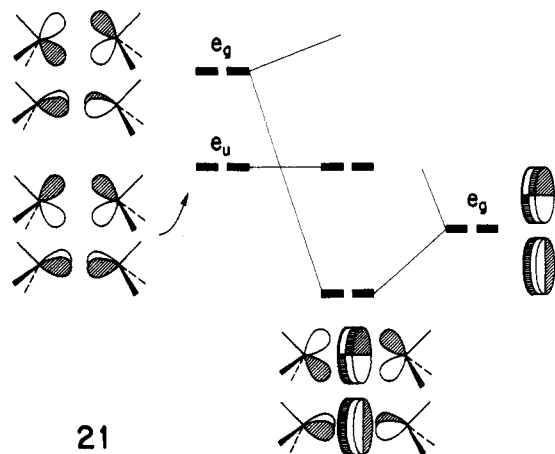
Let us first review the electronic structure of the inverse sandwiches.³² Suppose each ML_n fragment in these carries an e_1 set of frontier orbitals. The plus and minus combination of the two fragment orbitals are then e_u and e_g , 21. The e_g set interacts with the centered ligand orbitals and is stabilized. The bonding electrons here can be thought of as coming from the π ligand. The e_u set can accommodate up to four metal nonbonding electrons. These do not overlap with any ligand π electrons. An interesting electronic flexibility arises from the inverse sandwich structure—namely, that electrons can be brought near a

(29) (a) P. Maitlis and M. L. Games, *Chem. Ind. (London)*, 1624 (1963); (b) M. Mathew and G. J. Palenik, *J. Organomet. Chem.*, **30**, 185 (1973).

(30) For reviews, see (a) P. M. Maitlis, *Adv. Organomet. Chem.*, **4**, 95 (1966); (b) A. Efraty, *J. Organomet. Chem.*, **57**, 1 (1973); (c) A. Z. Rubezhov and S. P. Gubin, *Adv. Organomet. Chem.*, **10**, 347 (1972).

(31) R. Bruce, K. Moseley, and P. M. Maitlis, *Can. J. Chem.*, **45**, 2011 (1969).

(32) J. W. Lauher, M. Elian, R. H. Summerville, and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 3219 (1976).

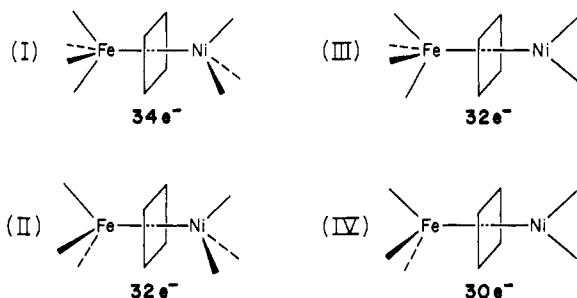


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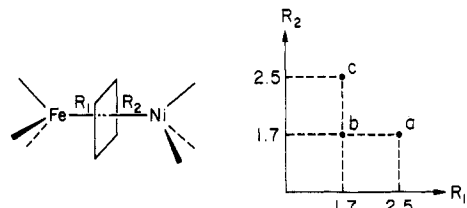
filled π system without suffering destabilizing repulsive interactions.

The key feature of the inverse sandwich structures is that electronically stable structures for electron counts up to 34 for the two centers together are allowed. This electron count allows $\text{Fe}(\text{CO})_4$ (16 electrons) to approach an 18-electron CbML_n complex from the backside of the Cb ring without an appreciable energy barrier.

In our calculation, we would like to consider the incoming group as either $\text{Fe}(\text{CO})_4$ or $\text{Fe}(\text{CO})_3$. The latter fragment may be present in the late stages of the reaction. Then we may have either 34-electron or 32-electron intermediates. We would like also to consider two alternatives for the attacked Cb complex, a dimer or a monomer. The class of Cb complexes of the type $[\text{CbMX}_2]_2$ $X = \text{Ni}, \text{Pt}$ is relatively unstable.³³ In our calculations dimer dissociation into monomers is exothermic by 0.8 eV for Ni and 0.3 eV for Pt. In the computations we take as a monomer CbNiX_2 , and model a dimer by CbNiX_3^- . Four possible inverse sandwiches will be considered, I-IV. A



complete potential energy surface would vary independently the metal to ring distances R_1 and R_2 , 22, generating



22

23

a complete (R_1, R_2) surface, 23. We have found it sufficient to consider just three points on that surface $(R_1, R_2) = (2.5 \text{ \AA}, 1.7 \text{ \AA}), (1.7 \text{ \AA}, 1.7 \text{ \AA}), (1.7 \text{ \AA}, 2.5 \text{ \AA})$ to be called a, b, and c, respectively. They correspond obviously to the two asymmetrical extremes and one symmetrical waypoint.

The computed curves are shown in Figure 8. Let us note the following interesting features:

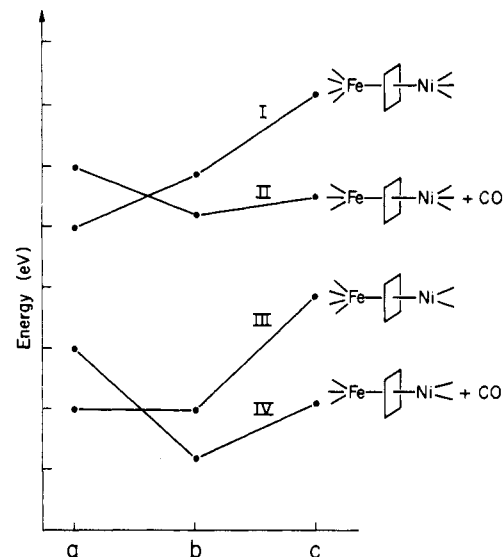


Figure 8. Potential curves of the four systems, I-IV, in the π -ligand transfer process. The points a, b, and c along the potential curves are defined in 23.

(a) Focusing on the energy difference between a and b we see that formation of a 34-electron inverse sandwich (I) is more repulsive than a 32-electron system (II, III), and the 30-electron case (IV) is quite attractive.

(b) I and III move to high energy at point c since they approach there the 20-electron $\text{CbFe}(\text{CO})_4$. Dissociation of a CO from there is calculated to be ~ 1.8 -eV exothermic.³⁴

Based on these surfaces we may distinguish two types of pathways which are differentiated only on the nature of the attacking group, $\text{Fe}(\text{CO})_3$ or $\text{Fe}(\text{CO})_4$.

(1) If the approaching metal fragment is $\text{Fe}(\text{CO})_3$ the reaction path is along curve II or IV, depending on whether the Cb complex attacked is dimeric or monomeric. There is no qualitative difference between these—no energy barrier to reaching the inverse sandwich waypoint. If the leaving group NiCl_2 or NiCl_3^- is stabilized by solvent, point c will be lowered in energy compared to its position in Figure 8.

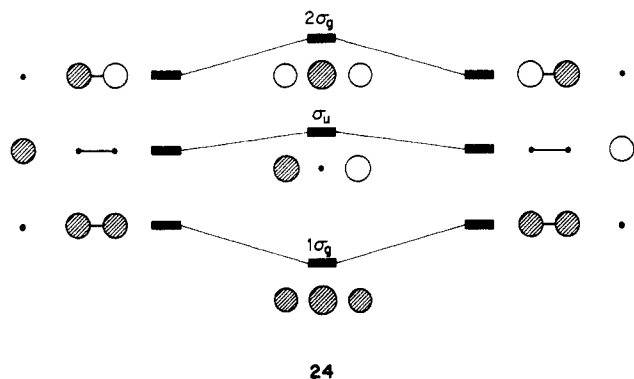
(2) If the attacking group is $\text{Fe}(\text{CO})_4$ the system will be trapped in front of the repulsive wall on curve I or III. The Cb monomer model, curve III, allows $\text{Fe}(\text{CO})_4$ to come somewhat closer to the Cb ring. By losing a carbonyl, the reacting system can make its way to curve II or IV, respectively, and then complete the reaction.

To summarize: First, the ligand transfer reaction through an inverse sandwich is easier for $\text{Fe}(\text{CO})_3$ than $\text{Fe}(\text{CO})_4$. Second the reaction is nearly independent of the dimeric or monomeric form of CbNiCl_2 . We are encouraged to suggest this mechanism by some trial calculations on the alternative halogen-bridged structure 19, for which a substantially higher energy is computed. However, a full examination of alternative reaction mechanisms was not attempted.

The inverse sandwich mechanism bears some resemblance to the SN_2 reaction or the prototype radical abstraction $\text{D} + \text{H}_2 \rightarrow \text{DH} + \text{H}$. The orbitals for this simple system are drawn in 24. In the course of the reaction the σ_g bonding orbital spreads to three centers, while the nonbonding σ_u delocalizes to the termini. In the reaction

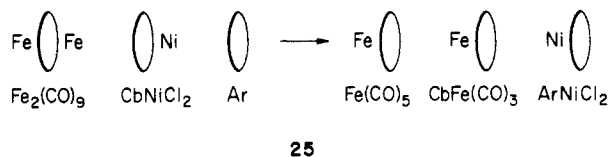
(34) The energies on curves I and III at point C, involving $\text{CbFe}(\text{CO})_4$, are not obtained directly from the calculation, since they go to the corresponding ionic configurations $\text{CbFe}(\text{CO})_4^{2+} + \text{NiCl}_2^{2-}$ and $\text{CbFe}(\text{CO})_4^{3+} + \text{NiCl}_3^-$, respectively. The reported energies are obtained by readjusting the occupation numbers to give neutral fragments.

(33) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, 1, 519 (1962).



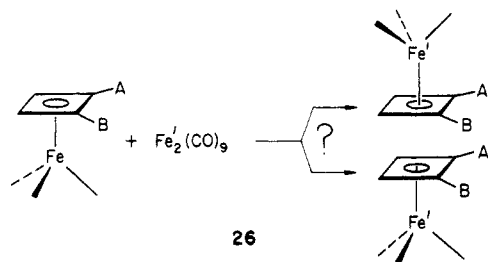
there is a flow of bonding electrons from right to left and nonbonding ones to the right. The $1\sigma_g$ and σ_u orbitals correspond to the e_g bonding and e_u nonbonding orbitals of the inverse sandwich. The important feature of both systems is that the central participant (H or Cb) can maintain constant and maximal bonding throughout the reaction. We feel that this is a necessity for safe transfer of a fragile ligand such as cyclobutadiene.

An interesting perspective on the overall process of ligand transfer between $\text{Fe}_2(\text{CO})_9$, the CbML_2 complex, and benzene solvent is obtained if one recalls that $\text{Fe}_2(\text{CO})_9$ itself can be thought of as an inverse sandwich.³² The symbolic equation 25 summarizes the idea. The rings are



symbols for three CO's, Cb, or arene. The overall process starts with two metals bound to one ring, another metal to a second ring, and a free ring. It ends up with three rings each bound to one metal. No concert is implied for the reaction, yet it is interesting that what one has in the process is just a rearrangement of rings with their bonding partners.

An interesting probe of the inverse sandwich mechanism would be the reaction of an optically active $\text{CbFe}(\text{CO})_3$ derivative with $\text{Fe}_2(\text{CO})_9$, 26. Inversion of configuration should be the consequence of the inverse sandwich mechanism.



It should be noted that the inverse sandwich mechanism proposed here is less likely for Cp or arene transfer than for Cb transfer. The Cp or arene complexes do not have such high-lying occupied orbitals to stimulate electrophilic type attack on the complexed ring, a feature that a referee has pointed out is typical of Cb complexes.

Inner and Peripheral Electrons

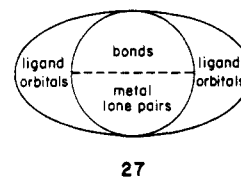
Twice in the preceding discussion there has emerged a division of the electrons of a complex into some deeply involved in bonding, some localized on the metal, and some others primarily localized on the external ligands. Thus in Cb_2M we had the high-lying e_{1u} set, primarily cyclobutadienoid in character. In the hypothetical inverse

TABLE III: Parameters Used in EH Calculation

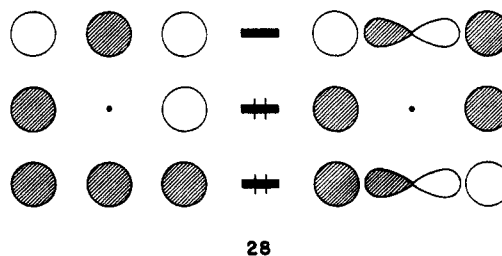
orbital	H_{ii} , eV	ζ_1	ζ_2	C_1^a	C_2^a
Ti 3d	-11.10	4.55	1.40	0.4206	0.7839
4s	-8.90	1.08			
4p	-6.48				
V 3d	-11.00	4.75	1.70	0.4755	0.7052
4s	-8.81	1.30			
4p	-5.52				
Cr 3d	-11.20	4.95	1.80	0.5058	0.6747
4s	-8.66	1.70			
4p	-5.24	1.70			
Mn 3d	-11.59	5.15	1.90	0.5311	0.6479
4s	-8.63	1.80			
4p	-5.06	1.80			
Fe 3d	-12.63	5.35	2.00	0.5505	0.6260
4s	-9.91	1.90			
4p	-5.07	1.90			
Ni 3d	-12.99	5.75	2.00	0.5683	0.6292
4s	-8.86	2.10			
4p	-4.90	2.10			
Nb 4d	-12.10	4.08	1.64	0.6401	0.5516
5s	-10.10	1.89			
5p	-6.86	1.85			
Mo 4d	-10.50	4.54	1.90	0.5899	0.5899
5s	-8.34	1.96			
5p	-5.24	1.92			
Cl 3s	-30.00	2.03			
3p	-15.00	2.03			
S 3s	-20.00	1.82			
3p	-13.30	1.82			
C 2s	-21.40	1.625			
2p	-11.40	1.625			
H 1s	-13.60	1.30			

^a Coefficients in double ζ expansion.

sandwich transition state for Cb exchange, $L_n\text{M}^{\leftrightarrow}\text{Cb}^{\leftrightarrow}\text{ML}_n$, a similar set, came up now localized on the ML_n extremes. A most schematic representation of the electron distribution, excluding core electrons on the metal and ligands, is given in 27.



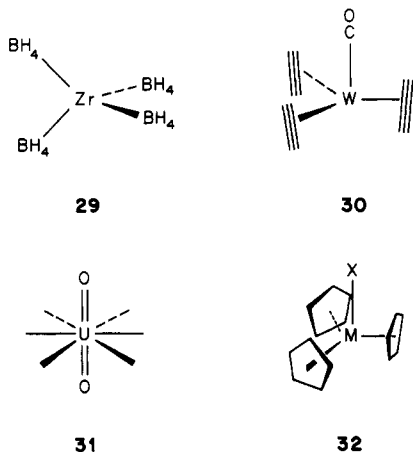
This kind of electron partitioning is not restricted to Cb complexes. It arises in main group chemistry in electron-rich three-center bonding, be it $\text{H}^- + \text{H}_2$, hydrogen bonding, the SN_2 transition state, or the thiothiophenes.³⁵ The three-center bonding scheme, whether it uses a central s or p orbital 28, puts the top two



(35) See R. Gleiter and R. Gygas, *Top. Current Chem.*, **63**, 49 (1976), and references therein.

electrons at the periphery of the molecule. Similarly, in "octet-expanded" structures of the SR_4 , PR_5 , SR_6 type there arise high-lying orbitals localized on the ligands.³⁶

In transition-metal complexes one common class of 18-electron rule "exceptions" illustrates the same phenomenon. In some geometries a symmetry-adapted linear combination of ligand orbitals does not find a match in the central atom d orbitals (though it might do so in f orbitals—how much that interaction is worth is problematical). See for instance 29–32.³⁷



(36) (a) B. M. Gimarc, J. F. Liebman, and M. Kohn, *J. Am. Chem. Soc.* **100**, 2334 (1978); (b) B. M. Gimarc and S. A. Khan, *ibid.*, **100**, 2340 (1978); (c) B. M. Gimarc, *ibid.*, **100**, 2346 (1978).

(37) (a) $(BH_4)_4Zr$: P. H. Bird and M. R. Churchill, *Chem. Comm.*, 403 (1967). (b) $W(RC\equiv CR)_3CO$: D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Ross, and J. G. Grasselli, *J. Am. Chem. Soc.*, **86**, 3261 (1964); R. B. King, *Inorg. Chem.*, **7**, 1044 (1968). (c) Cp_3M and Cp_3MR : G. Perego, M. Cesari, F. Farina, and G. Lugli, *Acta Crystallogr., Sect. B*, **32**, 3034 (1976); B. Kanellakopoulos and K. W. Bagnall, *MTP Int. Rev. Sci., Inorg. Chem., Ser. 1*, **7**, 299–322 (1972). See also J. Leong, K. O. Hodgson, and K. N. Raymond, *Inorg. Chem.*, **12**, 1329 (1973); J. L. Atwood, C. F. Hains, Jr., M. Tsutsui, and A. E. Begala, *Chem. Commun.*, 452 (1973); G. W. Halstead, E. C. Baker, and K. N. Raymond, *J. Am. Chem. Soc.*, **97**, 3049 (1975); T. J. Marks, A. M. Seyam, and J. R. Kolb, *ibid.*, **95**, 5529 (1973); E. O. Fischer and H. Fisher, *J. Organomet. Chem.*, **6**, 141 (1966). (d) UO_2L_2 : M. E. Dyatkina and Yu. N. Mikhailov, *Zh. Strukt. Khim.*, **3**, 724 (1962); L. Cattalina, U. Croatto, S. Degetto, and E. Tondello, *Inorg. Chim. Acta Rev.*, **5**, 19 (1971). (e) $(Cp)_4U$: J. H. Burns, *J. Am. Chem. Soc.*, **95**, 3815 (1973).

We feel that these systems with external or peripheral electrons are not just an oddity but possibly an important clue to a general feature of reactivity in saturated systems. In the course of a reaction, it is difficult, if not impossible, to keep any molecular system at a level of uniform or constant bonding. Electron repulsions naturally occur. The existence of ligand nonbonding orbitals add valuable flexibility, without much cost in energy, to systems with a variable number of electrons. Thus it enables the system to cope with a situation of electron supersaturation in the transition state by storing the excess electrons in a peripheral region. The excess electrons can be relieved later when the intermediate breaks apart. The low cost in energy in this center to periphery electron shuttling situation allows the molecular system to explore the potential energy surface near a crowded conformation on the way to a productive reaction channel.

Acknowledgment. The Cb_2ML_n problem was suggested to us by Dr. A. Efraty, and early calculations on it were done by Dr. J. Dill. We thank K. Tatsumi for his assistance with the calculations. The permanent address of S. Chu is Department of Chemistry, National Tsing-Hua University, Hsinchu, Taiwan. We thank the National Science Council, Taiwan, Republic of China, for support which made his stay at Cornell possible. S. Chu also thanks Roald Hoffmann for his kind hospitality during his stay at Cornell.

Appendix

Our calculations were of the extended Hückel type,³⁸ with "weighted" H_{ij} 's.³⁹ The parameters taken from previous calculations⁴⁰ are listed in Table III.

(38) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179 (1962); **37**, 2872 (1962).

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

(40) R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 7240 (1976); B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *ibid.*, **101**, 585 (1979); T. A. Albright, R. Hoffmann, Y. Tse, and T. D'Ottavio, *ibid.*, **101**, 3812 (1979).

Anion-Induced Triplet Quenching of Aromatic Ketones by Nanosecond Laser Photolysis

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Triplet quenching of some aromatic ketones by anions has been studied by nanosecond laser photolysis in $H_2O:CH_3CN$ (4:1) mixtures. A linear relationship between $\log {}^3k_q$ (the quenching rate constant) and ΔG (the free-energy change for electron transfer) was obtained, indicating that the triplet quenching is caused by electron transfer from the donor anion ${}^1X^-$ to the acceptor (the triplet state of aromatic ketones ${}^3A^*$). Electron transfer (or charge transfer) from ${}^1X^-$ to ${}^3A^*$ is a key step in the quenching. There was no appreciable difference in the quenching efficiency between the ${}^3(\pi, \pi)^*$ and ${}^3(n, \pi)^*$ states. Estimations of 3k_q values, using ΔG^* (the potential barrier for electron transfer) calculated by the Marcus, Rehm–Weller, Scandola–Balzani, and Polanyi equations, were carried out. The Polanyi equation was found to fit the experimental data fairly well.

Introduction

It is well-known that quenching of electronically excited states by ground-state species results from electron transfer, energy transfer, heavy-atom effects, or complex formation. Of these, electron-transfer (or charge-transfer) reaction in the excited state is one of the most important

processes. In a study on quenching of the electron donor and acceptor system (EDA) of aromatic compounds, Rehm and Weller¹ have shown a correlation between the

(1) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, **8**, 259. *Ber. Bunsenges. Phys. Chem.* **1969**, **73**, 834.