

interaction of $[\text{Cr}(\text{ox})_2(\text{phen})]^-$ or $[\text{Cr}(\text{ox})_2(\text{bpy})]^-$ with the cinchona alkaloid cations.

Registry No. $[\text{Cr}(\text{ox})_2(\text{phen})]^-$, 21748-33-4; $[\text{Cr}(\text{ox})_2(\text{bpy})]^-$, 21748-32-3; $[\text{Cr}(\text{ox})(\text{phen})_2]^+$, 32626-76-9; $[\text{Cr}(\text{ox})(\text{bpy})_2]^+$, 32629-19-9; $[\text{Cr}(\text{ox})_2(\text{en})]^-$, 21827-84-9; cinchoninium chloride, 5949-11-1; cinchonidinium chloride, 524-57-2; quinidinium chloride, 1668-99-1; quininium

chloride, 130-89-2; *N*(1)-methylcinchoninium chloride, 93862-43-2; *N*(1)-methylcinchonidinium chloride, 77452-64-3; *N*(1)-methylquinidinium chloride, 93862-44-3; *N*(1)-methylquininium chloride, 64868-38-8; 9-acetoxycinchoninium chloride, 93862-45-4; 9-acetoxycinchonidinium chloride, 93862-46-5; 9-acetoxyquinidinium chloride, 93862-47-6; 9-acetoxyquininium chloride, 93862-48-7; *N*(1)-methyl-9-acetoxyquininium chloride, 93862-49-8.

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Molecular Orbital Study of Heterometallic M_3C_2 Organo-Transition-Metal Clusters: Orientation of the Alkyne Moiety

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EHMO calculations are reported for a series of trimetal-alkyne five-vertex clusters, $\text{M}_3\text{C}_2\text{R}_2$, where $\text{M} = \text{Fe}(\text{CO})_3$, $\text{Co}(\text{CO})_3$, CpFe , CpNi , $\text{CpMo}(\text{CO})_2$. The preferred orientation of the alkyne moiety relative to the trimetallic fragments is rationalized on the basis of the donor and acceptor properties of the R_2C_2 and M_3 fragments, respectively. These predictions correlate very well with the known structures of M_3C_2 clusters. H edge-bridging clusters are also investigated.

In recent years a large number of five-vertex organo-transition-metal clusters have been synthesized and structurally characterized. These clusters, given in Table I, are well typified by the trimetallic systems in which an alkyne moiety furnishes the remaining two vertices.¹⁻¹⁹ These clusters are found in two quite distinct geometries: those possessing seven skeletal electron pairs adopt a square-based-pyramidal geometry while the molecules with only six skeletal electron pairs have the trigonal-bipyramidal structure. In terms of the polyhedral skeletal electron pair (PSEP) theory²⁰ (which, in effect, takes advantage of the isolobal nature of a BH moiety and a variety of organo-transition-metal fragments),²¹ one may classify the former geometry as being derivable from an octahedron with a vacant vertex (as in Figure 1) and as such analogous to the *nido*-borane B_5H_9 . In contrast, the latter molecules closely resemble the *closo*-carboranes $\text{R}_2\text{C}_2\text{B}_3\text{H}_3$.²² These two geometries are distinguished by the orientation of the acetylenic moiety with respect to the metal triangle. The acetylene can be positioned parallel to a metal-metal vector, $\eta^2\text{-}\parallel$,²³ as in the *nido* configuration, or perpendicular, $\eta^2\text{-}\perp$, as in the *closo* arrangement (Figure 1).

A molecular orbital analysis of both *closo* and *nido* $\text{Fe}_3(\text{C}_2\text{O})_2$ will serve as a model for a general introduction to the bonding modes of heterometallic clusters. This model has already been the subject of a detailed study by Schilling and Hoffmann,²⁴ but we think it useful to briefly reiterate the important points. Figure 2 gives an orbital energy level diagram for the two geometries.

Frontier Orbitals of the $\text{Fe}_3(\text{CO})_9$ Fragment (26)

In accordance with the C_3 symmetry of both the *nido* and *closo* complexes, the orbitals are classified as being *s* (symmetric) or *a* (antisymmetric) with respect to the molecular mirror plane. The construction of the $\text{Fe}_3(\text{CO})_9$ entity, 26,²⁴ from three $\text{Fe}(\text{CO})_3$ fragments²⁵ is known and leads to six frontier orbitals; three of these (*1s*, *2s*, *1a*) are donor orbitals while the remaining three (*2a*, *3s*, *4s*) are situated at higher energy and can function as acceptor orbitals (see Figure 2). Of these six orbitals *1s*, *2s*, *1a*, and *4s* are metal-metal bonding while *3s* and *2a* are metal-metal antibonding. For our purposes, the acetylenic ligand will be considered formally as $(\text{C}_2\text{H}_2)^{2-}$ in all the *nido* complexes and as

C_2H_2 in all the *closo* systems studied here.

The *Nido* Case: $[\text{Fe}_3(\text{CO})_9\text{C}_2\text{H}_2]^{2-}$ (27)

The *1s* frontier orbital, which possesses pronounced d_{z^2} character, is only slightly perturbed by complexation with the acetylene. The *2s* orbital, which is principally composed of $d_{x^2-y^2}$ combina-

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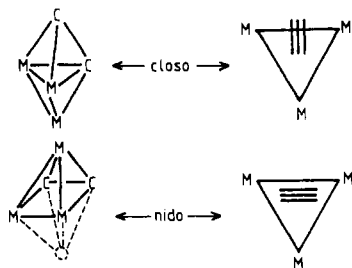


Figure 1. Closo and nido clusters.

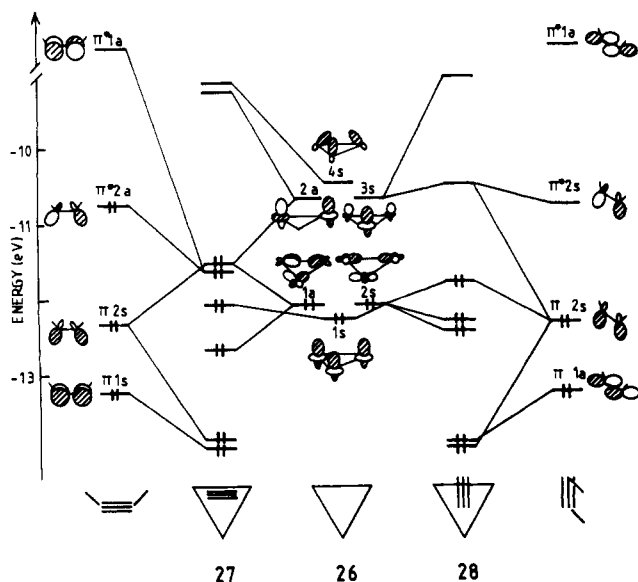
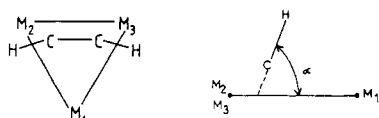
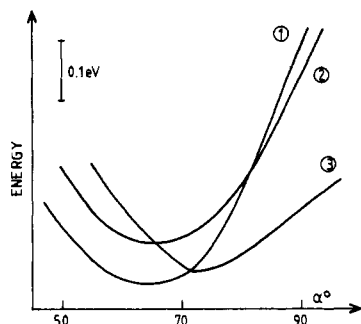
Figure 2. Orbital energy level scheme for *nido*- and *closo*-Fe₃(CO)₉C₂H₂.

Figure 3. Orientation of the alkyne relative to the trimetallic plane.

Figure 4. Variation of electronic energy as a function of angle α : (1) [Fe₃(CO)₉C₂H₂]²⁻; (2) [Fe₃(CO)₃Cp₂C₂H₂]⁴⁻; (3) FeNi₂(CO)₃Cp₂C₂H₂.

tions, is destabilized through interaction with the filled $\pi 2s$ orbital of the acetylene. The third and final filled orbital of the Fe₃(CO)₉ entity is $1a$; this is essentially d_{xy} and is stabilized via interaction with $\pi^* a$ of the acetylene. The two vacant symmetrical orbitals $3s$ and $4s$ (of character d_z^2 for the former, and $s + p_z$ for the latter) strongly stabilize the two occupied πs orbitals. Finally, the $2a$ orbital, which is principally made up of d_{z^2} and d_{xz} on Fe(2) and Fe(3), interacts strongly with the $\pi^* 2a$ orbital of the acetylene. This interaction is particularly favored if the plane containing the acetylenic ligand is not orthogonal to the plane containing the metals but rather is inclined toward it as indicated in Figure 3.

The variation of electronic energy as a function of the angle α (Figure 4) is governed by this interaction. For the model

Table I. Structural Data for Clusters with an M₃C₂ Core

CLOSO CLUSTERS		
1 ²	2 ³	3 ³
NIDO CLUSTERS		
4 ⁴ [α -70.8] (a)	11 ⁶ [α -80.9]	18 ¹⁴ (f)
5 ⁵ [α -79.9] (b)	12 ¹⁰ [α -71.3] (c)	19 ¹⁵ [α -79.8] (g)
6 ⁶ [α -74.5]	13 ⁸ [α -78.7]	20 ¹⁵ [α -70.8] (h)
7 ⁷ (c)	14 ¹¹ [α -78.4] (d)	21 ¹⁶ (i,j)
8 ⁸ [α -75.0]	15 ¹² [α -71.1] (e)	22 ¹⁶ [α -68.0] (i,j)
9 ⁶ [α -74.0]	16 ¹³ [α -72.5]	23 ¹⁷ (i,k)
10 ⁹ [α -81.1]	17 ¹³ [α -70.8] (c)	24 ¹⁸ [α -65.5] (i,l)
OTHER		
25 ¹⁹ [α -71.4] (m)		

^a α is the dihedral angle as defined in the text. ^b Anionic compound. ^c Semibrudging carbonyl. ^d One doubly semibrudging carbonyl. ^e Two semibrudging carbonyls. ^f Edge-bridging methylene. ^g Edge-bridging carbonyl. ^h Face-bridging carbonyl. ⁱ Hydrogen atoms not located by X-ray. ^j Zwitterionic compound. ^k C₂R₂ = C₈H₁₂. ^l C₂R₂ = C₆H₄. ^m Long Pt-Pt distance (3.03 Å).

compound [Fe₃(CO)₉C₂H₂]²⁻ a value for α of 68° is predicted. A similar study of the model [Fe₃(CO)₃Cp₂C₂H₂]⁴⁻ and on the complex Cp₂Ni₂Fe(CO)₃C₂H₂ (9), using the experimental geometry, leads to α values of 69 and 73°, respectively (Figure 4). The experimental value for 9 is 74°. ⁶

These optimized values are in close agreement with those observed on all the known acetylenic trimetallic nido clusters, for which α ranges from 65 to 81° (see Table I). The seven skeletal

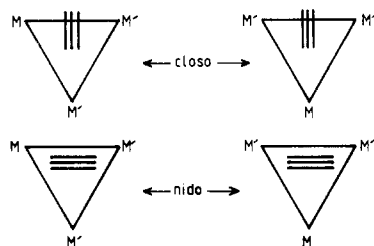


Figure 5. *closo*- and *nido*- M'_2MC_2 clusters.

electron pairs required for the PSEP theory correspond to the six molecular orbitals shown for **27** plus the molecular orbital corresponding to the C–C σ bond, which is not shown in Figure 2.

The Closo Case: $Fe_3(CO)_9C_2H_2$ (**28**)

It is clear that the frontier orbitals of the C_2H_2 moiety are the same for both the *closo* and *nido* complexes. However, these frontier orbitals have different symmetries relative to the molecular mirror plane in the two different geometries, causing them to interact differently with the metal frontier orbitals (Figure 2). Thus, in the *nido* case, $1s$ was scarcely affected, but in the *closo* system, **28**, it is destabilized by the filled π $2s$. $2s$, for its part, is now stabilized by interaction with the vacant π^* $2s$ of the acetylene. This time it is $1a$, which is little affected since π $1a$ and π^* $1a$ of the acetylene are, respectively, at too low and too high an energy to interact significantly. The filled π s acetylenic orbital is seen to be greatly stabilized by the $3s$ and $4s$ orbitals of the metal fragment, and the $2a$ acceptor orbital contributes to the stabilization of the π a occupied orbital. The occupied molecular orbitals in **28** (Figure 2) correspond to five of the six skeletal electron pairs required for a *closo*-carborane; the sixth electron pair corresponds to the C–C σ -bonding orbital not shown in Figure 2. CNDO results recently reported²⁶ are consistent with this MO picture.

The net result of this analysis, which completely agrees with the PSEP theory, reveals that for the seven-skeletal-electron-pair complex the *nido* form is the more stable to the tune of 33 kcal/mol; when the complex has six skeletal electron pairs the *closo* structure is favored by 15 kcal/mol. It follows that the *nido* geometry is preferred with 6.5 skeletal electron pairs (~ 9 kcal/mol), in agreement with the recently published²⁷ structure of $[Fe_3(CO)_9(\mu_3-\eta^2-MeCCO)](PPh_4)_2$.

Heterometallic M_3C_2 Clusters

When the three monometallic fragments are not identical, the PSEP theory would allow several possible isomers, which a priori should be of equal stability. Thus, in a seven-electron-pair cluster possessing two types of metal, two *nido* isomers are possible (Figure 5); similarly, a six-electron-pair cluster could give two *closo* isomers (Figure 5).

In solution, at room temperature fluxionality is commonly observed^{13b,28,29} and several isomers can exist in equilibrium. But, although a fairly large number of heterometallic acetylene complexes have been structurally examined in the solid state, it is noteworthy that only one isomer has been observed for each complex with the sole exception of $(\eta^5-C_5H_5)_2W_2Os(CO)_7(\mu_3-MeC_6H_4C_2C_6H_4Me)$ (**16** and **17**), where crystallographic studies show both rotamers present in the crystal.¹³

In order to understand the factors determining the favored conformation, we undertook a study of the mode of bonding of heterometallic clusters of the type M_3C_2 .

Frontier Orbitals of Heterometallic Fragments

Figure 6 groups together the frontier orbital energy level diagrams of various isoelectronic trimetallic fragments with use of

idealized geometries **26** and **29–40**.

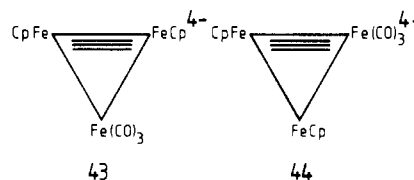
Calculations on **33**, **34**, and **38** were also performed with use of experimental geometries, but they were not significantly different from the results obtained for the idealized geometries. A comparison of these diagrams shows that all the fragments considered have (as does $Fe_3(CO)_9$ (**26**)) a group of three low-lying donor orbitals and three acceptor orbitals at higher energy. The lowering of the symmetry from C_{3v} to C_s or to C_1 results in a splitting of the levels and also some spatial redistribution of the frontier orbitals. Overall, however, these fragments exhibit essentially the same bonding properties. This is not surprising since these trimetallic units are all built up by assembling different but isolobal ML_3 moieties. Nevertheless, there are differences. In particular, the energy level schemes for **26**, **29**, and **30** are practically identical, as are those for **31–35**, or **36–38**, showing that substitution of a Ni atom by Fe^{2+} has but little effect on the bonding properties of a fragment. In contrast, for **26**, **31**, and **36**, it is apparent that the effect of substituting three CO groups by a Cp^- moiety is more important.

Thus, it is reasonable to suppose that changing one metal for another in the same transition series would have a small effect on the bonding properties of a fragment since the greatest influence is attributable to the attached ligands. Consequently, we initially limited ourselves to the study of model *nido* and *closo* complexes constructed from the fragments **26**, **31**, and **36**.

Favored Conformation of Nido Clusters

The acetylene complex formed from fragment **31** can adopt two different geometries, **41** and **42**, whose frontier orbital interaction diagrams are shown in Figure 7.

The symmetrical form **41** leads to an orbital diagram qualitatively identical with that of the $[Fe_3(CO)_9C_2H_2]^{2-}$ complex, **27** (cf. Figure 2), which has the same C_s point group. In the nonsymmetrical form **42** on the other hand, the loss of the plane of symmetry leads to the appearance of further interactions. In this case, the $1s$ and $2s$ frontier orbitals can interact with the π^* molecular orbital of the acetylene, bringing about increased stability in these frontier orbitals; the opposite effect is observed for the $1a$ and $2a$ frontier orbitals because of their destabilizing interaction with the acetylene π orbital. Furthermore, these acetylene π orbitals, in the nonsymmetrical form, are stabilized by all the metal fragment's frontier orbitals. Thus, in the transformation of complex **41** to **42** the energy differential is small. Account must also be taken of the difference in "core" molecular levels, and so the calculated energy gain is only 0.6 kcal/mol in favor of the nonsymmetrical complex **42**. By similar reasoning, for the isomers **43** and **44** derived from fragment **36**, our calculations predict the symmetrical form **43** to be the more stable by 1.4 kcal/mol.



Although the two cases discussed show only small extended-Hückel calculated energy differences between the two isomers, we feel confident that they are indeed significant since they are borne out by the known structures of complexes closely related to those studied here. In particular, we note that **5–7** are all of type **42** while **8–10** are of type **43** (see Table I).

The preference for the nonsymmetrical form in one case and the symmetrical in the other does not seem to be a matter of chance. Indeed, if we compare the charge distributions for the monometallic fragments ($Fe(CO)_3$ or $CpFe$) and for the acetylene in the different model complexes studied (Figure 8), we can extract the following data.

Following our convention of distributing the electrons on the two components of the complex (vide supra), the acetylene behaves toward the trimetallic component as an overall donor of electron density. It follows, therefore, that the ability of the trimetallic

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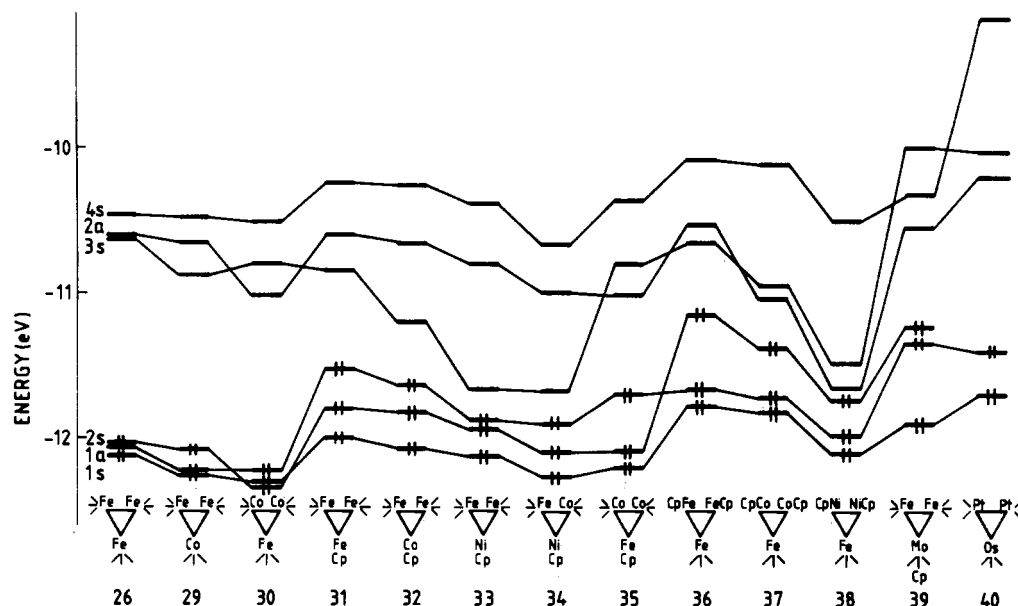


Figure 6. Frontier orbitals of selected trimetallic fragments.

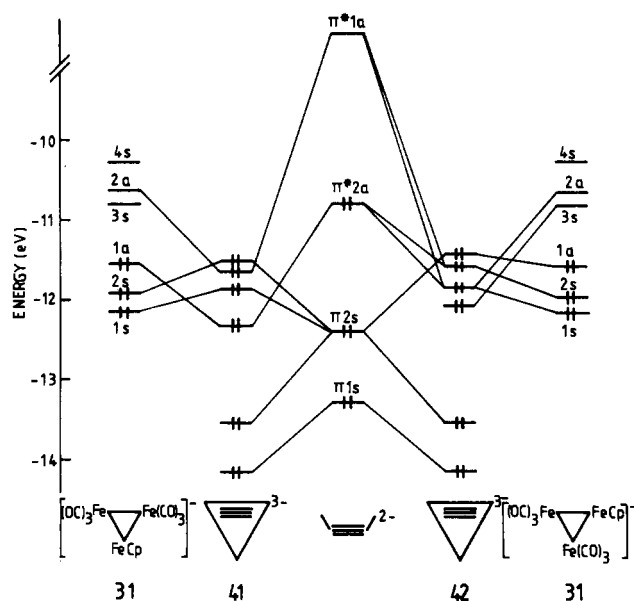


Figure 7. Orbital energy level scheme for the two nido isomers of $[\text{Fe}_3\text{Cp}(\text{CO})_6\text{C}_2\text{H}_2]^{3-}$.

fragment to accept electron density will be the dominant factor. The monometallic fragments corresponding to positions 2 and 3 are always more prone to attract electron density than the fragment corresponding to position 1, which suggests that the fragments in positions 2 and 3 are more strongly bound to the acetylene ligand than is the fragment in position 1. This is confirmed by both the analysis of the overlap populations and the observation of the metal-acetylene distances in the complexes. We see that a CpFe fragment is always more electron attracting than an $\text{Fe}(\text{CO})_3$ fragment. This means that, in order to achieve the maximum bonding between the trimetallic entity and the acetylene ligand, positions 2 and 3, which are those most involved in the bonding, must provide the most favorable interactions, i.e., the most electron-accepting fragments; in this case it is the CpM fragment or fragments. This would explain the favored configurations of isomers 42 and 43 rather than 41 and 44.

The nature of those monometallic fragments which are likely to occupy positions 2 and 3 can be seen by analyzing the diagram showing the frontier orbitals of the trimetallic moieties (Figure 6). Of the three acceptor frontier orbitals, the most destabilized plays a minor role, both for energetic reasons and because of its weaker localization on the metals. The two other acceptor frontier

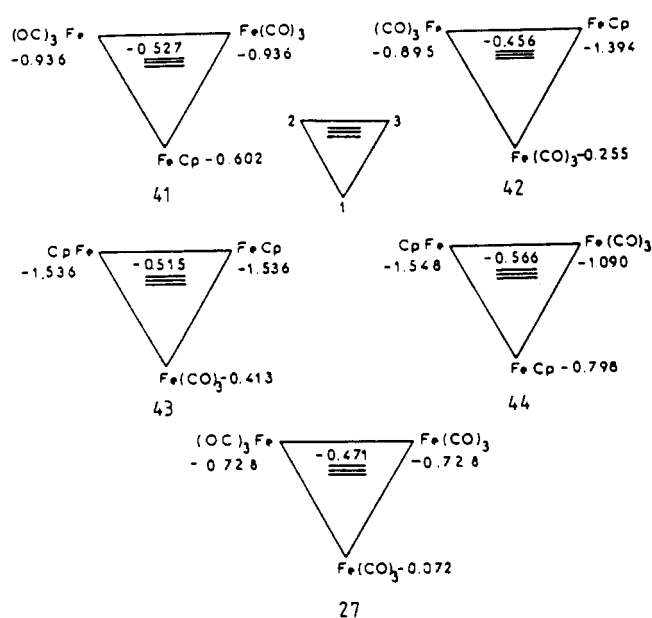


Figure 8. Net charges on the fragments MCp , $\text{M}(\text{CO})_3$, and C_2H_2 .

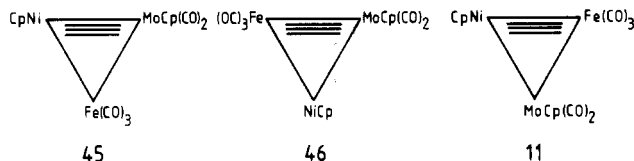
orbitals, which have the more important role, are localized preferentially on the two atoms occupying positions 2 and 3 in the complex. For fragment 31 the overall $3s + 2a$ localization on the iron atom attached to the Cp ligand is 28% vs. 17% for the other iron atoms. For the model 36 the corresponding values are 25% and 11%, respectively.

When the complex possesses two different fragments, $\text{M}(\text{CO})_3$ and $\text{M}'(\text{CO})_3$, the two acceptor frontier orbitals are localized mainly on the more electronegative metal(s). For example, in fragment 30 the overall $3s + 2a$ localization is 23% on each cobalt atom while it is 17% on the iron atom. It follows that the preferred rotamer is the one having the more electronegative atom(s) occupying positions 2 and 3 (see Figure 8) in the complex; these are in fact the metals with the higher atomic numbers and so give the isomer obeying the 18-electron rule. This is confirmed by our calculations on the models $\text{Co}_2\text{Fe}(\text{CO})_9\text{C}_2\text{H}_2$ and $[\text{CoFe}_2(\text{C}(\text{O})_9\text{C}_2\text{H}_2)]^-$. The structural data on $\text{Co}_2\text{Fe}(\text{CO})_9(\text{C}_2\text{Et}_2)$ (4)⁴ and $\text{FeCoNi}(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)(\mu_3\text{-PhC}_2\text{CO}_2\text{-}i\text{-Pr})$ (6)¹⁶ fully bear this out.

If M and M' have similar electronegativities, the real energy difference between rotamers is expected to be very small since the substitution by a phosphine of a carbonyl bonded to cobalt

(which renders the cobalt less electronegative) suffices to stabilize the other isomer, **7**, at least in the crystal.¹⁷

Some of the "M₃C₂" clusters listed in Table I possess as part of their trimetallic entity an ML₄ unit (such as Os(CO)₄ in **15**¹² or Ru(CO)Cp in **14**¹¹) or an ML₅ unit (such as WCp(CO)₂ in **16** and **17**¹³ or MoCp(CO)₂ in **11**⁶). With the sole exception of **17**,¹³ only a single isomer is known from crystallographic data. Typically, the complex FeNiMo(CO)₅(η⁵-C₅H₅)₂(μ₃-PhC₂CO₂-i-Pr)₆ which does not follow the EAN formalism,³⁰ has three possible isomers, **11**, **45**, and **46**. The only complex actually



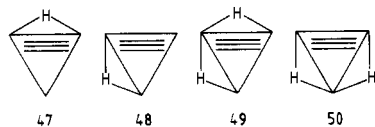
characterized crystallographically adopts structure **11**, through the three isomers coexist in solution.^{6,31}

As d⁵ MCp(CO)₂ is isolobal with d⁹ M(CO)₃,^{21b} this compound is equivalent to the other M₃L₉C₂R₂ nido clusters. Our model for the trimetallic moiety [Fe₂Mo(CO)₈Cp]⁺ (**39**) leads to an FMO pattern similar to those of **26** and **29–38** (see Figure 6). The two vacant orbitals, 3s and 2a, which play the most important role in coordination with the acetylenic group, are localized preferentially on the iron atoms, viz., 27% vs. 8% for the molybdenum atom. Indeed the Mo(CO)₂Cp moiety prefers position 1 (see Figure 8) in the alkyne complexed compound.

The compound **25**¹⁹ may be related to the nido-M₃C₂ complexes. Having a nido geometry but with a long Pt–Pt distance (3.03 Å), this compound possesses only six skeletal electron pairs. Since it is known that a ML₂ unit like Pt(CO)(PPh₃) has one frontier orbital less than a ML₃ fragment,³² it follows that the trimetallic fragment, **40**, has two MO's less than the other M₃L₉ fragments. One of these missing orbitals is an occupied metal–metal-bonding FMO. The other is its antibonding, very high lying counterpart, which is not a FMO. Thus, **40** presents only two occupied metal–metal FMO's below three accepting orbitals (Figure 6). The result is no (or a very weak) Pt–Pt bond, and this leads to six skeletal electron pairs for the corresponding acetylenic cluster, **25**. As in seven-skeletal-electron-pair clusters, the bonding mode of the acetylene ligand is directed by the two lowest vacant FMO's of **40**, which are, as expected, mainly localized on Pt atoms (22% on each platinum vs. 14% on osmium).

Favored Conformation of Edge-Bridging Nido Clusters

A few nido-M₃C₂ transition-metal clusters have bridging ligands, most commonly carbonyls and hydrides^{14–18} (see Table I, **18–24**). The role of these ligands is to bring the number of skeletal electron pairs to seven.²⁰ When the three metallic monomers of the cluster are identical, one (or two) ligand(s), edge-bridging a metal–metal bond, render them nonequivalent. This leads to the possibility of isomers **47** and **48** (or **49** and **50**).



Although edge-bridging hydrides are not accurately located by X-ray diffraction, crystallographic studies predict in each case

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- (31) Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Peng, S.; McGlinchey, M. J.; Marinetti, A.; Saillard, J.-Y.; Ben Naceur, J.; Mentzen, B.; Jaouen, G., submitted for publication. It is noteworthy that in **11** the low-temperature NMR spectrum reveals the presence of two diastereomers in the ratio 6:1. Thus, when there is a noticeable difference between M and M', one rotamer is preferred in solution as well as in the solid state.
- (32) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

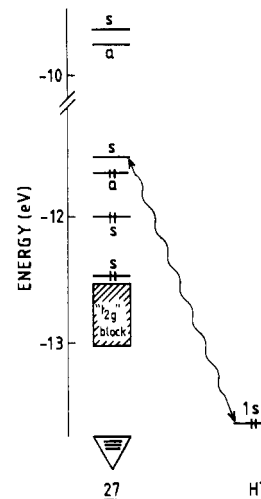
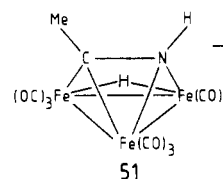


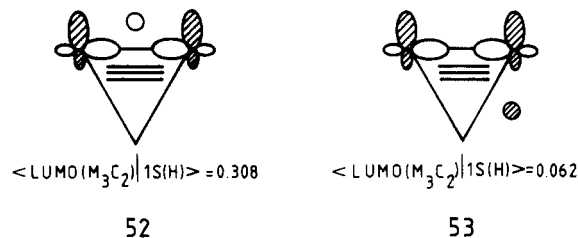
Figure 9. Major interactions between hydrogen and the Fe₃(CO)₉C₂H₂ fragment.

the existence of only one isomer: **47** with one bridging hydride,¹⁶ **49** with two,^{17,18} in total agreement with NMR spectroscopy investigations.³³ Also the low-temperature X-ray crystal structure determination of **51**, a trimetallic cluster³⁴ closely related to our M₃C₂ compounds, shows an edge-bridging hydride located as in **47**.



Calculations on the singly bridged model [HFe₃(CO)₉(C₂H₂)]⁻, where the hydrogen atom is situated in the trimetallic plane, confirm the preference for the symmetrical rotamer **47**. Figure 9 shows the orbitals of the [Fe₃(CO)₉C₂H₂] and H⁻ subunits.

In the symmetrical geometry **47**, the single H 1s orbital interacts mainly in a stabilizing way with the first unoccupied orbital of Fe₃(CO)₉C₂H₂, derived from the 2s orbital of Fe₃(CO)₉ fragment (**26**) (see Figure 2). This orbital is the only symmetrical frontier orbital of the Fe₃(CO)₉ fragment having a significant in-plane metal atomic orbital character. This bonding interaction is shown in **52**. It is obvious from **53** that this interaction is considerably



reduced in the nonsymmetrical geometry **48**. Moreover, there is no other possibility for a good bonding interaction with the orbital derived from the 1a in-plane orbital of the Fe₃(CO)₉ fragment, due to its polarization on only one iron atom. This

- (33) (a) For a review of hydrido-transition-metal clusters, see: Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 146. (b) Deeming, A. J.; Hasso, S.; Underhill, M. J. *Chem. Soc., Dalton Trans.* **1975**, 1614. (c) Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Organomet. Chem.* **1975**, *97*, C16. (d) Jackson, W. G.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Schorpp, K. T. *J. Organomet. Chem.* **1975**, *87*, C27. (e) Castiglioni, M.; Milone, L.; Osella, D.; Vaglio, G. A.; Valle, M. *Inorg. Chem.* **1976**, *15*, 394. (f) Gambino, O.; Sappa, E.; Cetini, G. *J. Organomet. Chem.* **1972**, *44*, 185.
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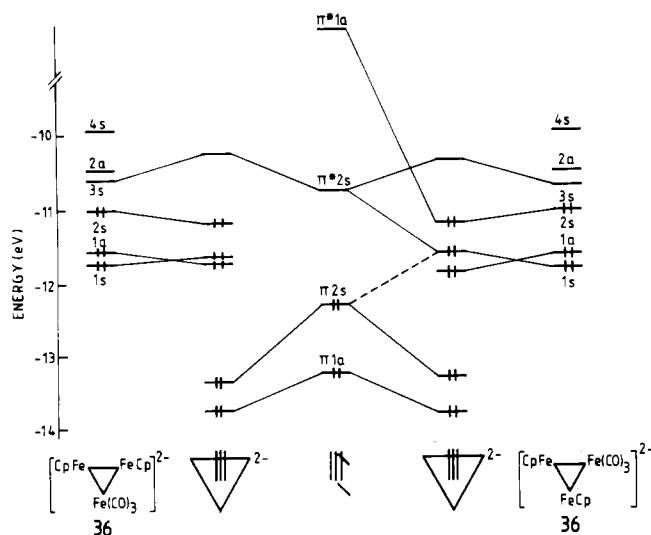
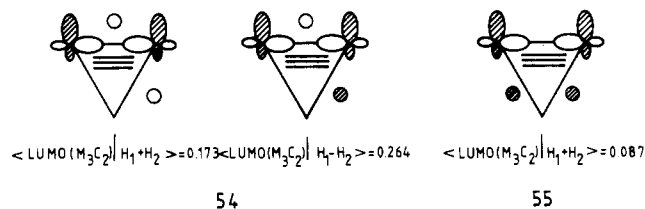


Figure 10. Orbital interactions between $[\text{Cp}_2\text{Fe}_3(\text{CO})_3]^{2-}$ and C_2H_2 for closo isomers.

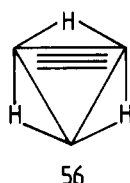
renders the nonsymmetric conformation **48** disfavored.

Also, in agreement with experimental results, our calculation on the doubly edge-bridged model $\text{H}_2\text{Fe}_3(\text{CO})_9(\text{C}_2\text{H}_2)$ gives the nonsymmetrical rotamer **49** as the most preferred. As in the monobridged case, the major bonding role comes from the lower symmetric unoccupied orbital of $\text{Fe}_3(\text{CO})_9(\text{C}_2\text{H}_2)$. This orbital interacts, in a stabilizing fashion, with both in-phase and out-of-phase combinations of the hydrogen orbitals, as shown in **54**.



In the symmetric form **50** only the in-phase hydrogen orbital combination is, to a lesser extent, stabilized (see **55**).

We have also examined the possible existence of a triply edge-bridged cluster using the $[\text{H}_3\text{Fe}_3(\text{CO})_9(\text{C}_2\text{H}_2)]^+$ model (**56**).



The occurrence of triple edge bridging in trimetallic "M₃R" clusters has been reported.³⁵ The model **56** is theoretically stable since our calculations give a HOMO-LUMO gap of about 1.7 eV. As in the two preceding cases, the main bonding interaction comes from the same frontier orbital of $\text{Fe}_3(\text{CO})_9(\text{C}_2\text{H}_2)$, which stabilizes the symmetrical combinations of the hydrogen orbitals.

Favored Conformations of Closo Clusters

The construction of closo acetylene complexes (which have six skeletal electron pairs) from the model fragments **29**, **30**, **31**, and **36** also leads to two isomers for each complex. In every case, the symmetric form yields an orbital diagram qualitatively identical with that of the complex $\text{Fe}_3(\text{CO})_9\text{C}_2\text{H}_2$ of the same C₃ point group (see Figure 10). In the other isomeric form, the absence of symmetry permits a multitude of supplementary interactions

Table II. Extended Hückel Parameters

orbital	H_{ii} , eV	exponents ^a	
		ξ_1	ξ_2
H 1s	-13.6	1.3	
C 2s	-21.4	1.625	
2p	-11.4	1.625	
O 2s	-32.3	2.275	
2p	-14.8	2.275	
Fe 4s	-9.1	1.9	
4p	-5.32	1.9	
3d	-12.60	5.35 (0.5505)	2.0 (0.626)
Co 4s	-9.21	2.0	
4p	-5.29	2.0	
3d	-13.18	5.55 (0.5679)	2.1 (0.6059)
Ni 4s	-10.95	2.1	
4p	-6.27	2.1	
3d	-14.2	5.75 (0.9798)	2.30 (0.5782)
Mo 5s	-8.34	1.96	
5p	-5.24	1.90	
4d	-10.50	4.54 (0.6097)	1.90 (0.6097)
Pt 6s	-9.077	2.554	
6p	-5.475	2.554	
5d	-12.59	6.013 (0.6224)	2.696 (0.5513)
Os ^b 6s	-8.00	2.14	
6p	-4.50	2.10	
5d	-12.50	4.29 (0.59)	1.970 (0.58)

^a Two Slater exponents are listed for the 3d functions. Each is followed in parentheses by the coefficient in the double- ξ expansion. ^b From ref 39.

(stabilizing or destabilizing) between the symmetric and asymmetric frontier orbitals of the acetylene and of the trimetallic fragment. According to our calculations, the nonsymmetrical isomers are expected to be the more stable by 1-4 kcal/mol, with one exception where the symmetric geometry is preferred by 2 kcal/mol. No orbital explanation or simple rule can be found from the MO scheme as was possible for the nido case.

Only three closo compounds of the type studied are structurally known. One is the homotrimetallic cluster $\text{Fe}_3(\text{CO})_9\text{C}_2\text{H}_2$ (**1**).² The others, **2** and **3**,³ which possess ML₃, ML₄, and ML₅ units, are inadequate models for the theoretical analysis, owing to the low symmetry of the trimetallic moiety.

Completion of this study must await the development of synthetic methodology and subsequent structural determinations on heterometallic closo clusters.

Acknowledgment. We thank Dr. A. Marinetti and Professor R. Hoffmann for helpful discussions and the CNRS (France) for financial support.

Appendix

The calculations were carried out via the extended Hückel method,³⁶ with use of the weighted formula of H_{ij} .³⁷ The H_{ii} 's and the orbital parameters, listed in Table II, were taken from ref 38. The idealized experimental structure of $\text{Fe}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)$ (**1**)² serves as the basic geometry for the cluster models. For all first-row transition metals (Fe, Co, Ni) the metal-metal distance was 2.52 Å, M-C(carbonyl) = 1.76 Å, and mean M-C(C₅H₅) = 2.15 Å. The geometry of the nido complexes was obtained from that of the closo complex by displacement of the plane of the acetylene ligand such that one had C_{ac}-C_{ac} parallel to M(2)-M(3) with M(1)-C_{ac} = 2.05 Å and M(2)-C_{ac} = 1.95 Å. The edge-bridging hydrogen(s), lying in the trimetallic plane, was placed 1.75 Å from the iron atoms. In the $[\text{Fe}_2\text{Mo}(\text{CO})_8(\text{C}_5\text{H}_5)]^+$ fragment (**39**) the molybdenum atom was 2.73 Å from the iron atoms. Mo-C(carbonyl) was set at 1.96 Å. The distance from the molybdenum atom to the center of the cyclopentadienyl ring was 2.02 Å. Pt₂Os(CO)₇(C₂H₂) data were taken from the experimental geometry of **25**. The Pt-C(O) and Os-C(O) distances

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were 1.90 Å. In every case $C_{ac}-C_{ac}$ was 1.38 Å, $C-O = 1.16$ Å, and $C-H = 1.09$ Å.

Registry No. 1, 12171-93-6; 2, 85449-66-7; 3, 81368-73-2; 4, 78109-40-7; 5, 76934-00-4; 6, 81141-85-7; 7, 82942-35-6; 8, 76110-38-8;

9, 81141-86-8; 10, 93646-05-0; 11, 81141-84-6; 12, 86288-23-5; 13, 80873-10-5; 14, 79232-24-9; 15, 58023-41-9; 16, 81368-75-4; 17, 81380-32-7; 18, 80004-18-8; 19, 12679-42-4; 20, 93646-06-1; 21, 82740-31-6; 22, 82740-37-2; 23, 57373-22-5; 24, 38979-81-6; 25, 77700-91-5; 27, 93646-07-2; 28, 83802-15-7.

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Bonding and Isomerization in $Fe(CO)_5$

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Molecular orbital calculations in a MINDO type procedure are reported for $Fe(CO)_5$ in a trigonal bipyramid (TB), square pyramid (SP), and points along a Berry pseudorotation path between the two configurations. The metal d orbitals are found to contribute some to intermediate energy level molecular orbitals to shift the relative extent of axial and equatorial bonding in a way that has not been predicted from the usual symmetry orbital overlap picture. This shift is critical to obtaining axial Fe-C bond lengths in agreement with experiment, which ab initio calculations have failed to obtain. The potential energy curve between the TB and SP configurations does not contain a barrier. In the orbital energy curves between the structures, no single orbital or particularly small group of orbitals can be isolated as responsible for the greater stability of the TB over the SP geometry.

Transition-metal carbonyl chemistry is a rich and varied field.^{1,2} Pentacoordinate transition-metal complexes have often been suggested as intermediates in the dissociative reactions of hexacoordinate complexes and in the associative first step in reactions of tetracoordinate compounds. The case of $Fe(CO)_5$ presents a stable pentacoordinate molecule with two geometries very close together in energy. NMR data indicate that the barrier to exchange of axial and equatorial ligands is no more than about 1 kcal/mol.³ The exchange mechanism has most often been ascribed to the Berry pseudorotation mechanism,⁴ with which NMR data for exchange in many pentacoordinate complexes are consistent.⁵ The Berry mechanism consists of a least motion path between the trigonal-bipyramidal (TB) and square-pyramid (SP) geometries. While there have been calculations of the TB and SP structures themselves,⁶⁻¹² there have not previously been calculations of the energy along the Berry path to determine if the SP structure corresponded to a metastable reaction intermediate or to a transition state. If the latter situation prevails, then the activation energy for the axial-equatorial exchange is simply the difference in energy between the TB and SP structures. Otherwise the difference in energy between the TB and SP geometries is not simply related to the activation energy for exchange.

In previous ab initio SCF calculations that have attempted to optimize geometries there has been difficulty with the axial Fe-C bond length being considerably too long.^{6,10} These works stated that they had no explanation for the long axial Fe-C bond. The calculations presented here indicate that the relative axial and equatorial bond strengths are related to the d-orbital interactions even though the total bond strengths are primarily due to iron s and p orbitals.

A variety of roles have been assigned to the d orbitals in transition-metal bonding. Adsorption on metal surfaces has been treated as if the primary bond to the surface was due to d orbitals.^{13,14} In coordination chemistry symmetry orbital and orbital overlap models have been developed that assign most of the d-electron charge to nonbonding or slightly antibonding molecular orbitals that are largely d orbital in character.⁷ This model has been successful in rationalizing many data. Recent semiempirical, $X\alpha$, and ab initio SCF calculations have metal s- and p-orbital interactions being primarily responsible for metal-ligand bonding.¹⁵ In calculations for NiH_2 , the d orbitals have been found to play a major role in the formation of bent metastable states that may be precursors to H_2 dissociation.¹⁶ In this paper the nature of the d-orbital interactions that affect the bonding in $Fe(CO)_5$ are examined.

Computational Procedure

The calculations were done with a semiempirical SCF method that is a modification of MINDO referred to as MINDO/SR. The details of the method as well as its ability to handle a wide variety of compounds including large metal clusters have been reported previously.¹⁶⁻¹⁸ The MINDO/SR procedure explicitly includes electron-electron repulsions and is parametrized to give bond energies and lengths for selected reference compounds in agreement with experimental values.

The computer program used is based on QCPE Program 290 by Rinaldi as modified by Schmidling¹⁹ to incorporate MINDO/3 and vibrational calculations. The Rinaldi program has automatic geometry optimization using analytically calculated gradients. The Schmidling version was modified to incorporate transition metals, symmetry,²⁰ and selective molecular orbital filling.

Atomic parameters for Fe are given in Table I. These parameters are similar to the ones used previously.¹⁷ Adjustments were made in the Fe 4p-orbital exponent, which was lowered from the Clementi and Raimondi²¹ value, in the d-orbital energy, and in a Slater-Condon parameter by de Brouckere.²² These adjustments were made to obtain

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