Mechanistic Features of Metal Cluster Rearrangements

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I. Introduction

For molecules and ions in solution, there exist a plethora of excited vibronic and electronic states that can effect a permutation of nuclear positions in the molecule. This dynamic phenomenon, referred to as stereochemical nonrigidity,[1] or fluxionality,[2] has been well documented in the last 25 years. Some organic molecules, like bullvalene,[3] and many inorganic molecules,[4] such as sulfur tetrafluoride,[5] have been found to undergo fast intramolecular rearrangements. Organometallic molecules, both monometallic and cluster species, have also been shown to be nonrigid structures in solution.[6] Among organometallic cluster compounds, i.e., those compounds containing metal–metal bonds, there has been a special interest in such dynamic processes. This interest is due, at least in part, to the possible role which ligand migration may play in cluster catalysis and to ligand migration as a model for surface mobility of chemisorbed species.[7,8] It is the purpose of this article to analyze the area of cluster rearrangement through the year 1977 not in a comprehensive fashion but with an attempt to categorize and generalize the molecular mechanisms responsible for ligand mobility in clusters. For balance and complementary information, we especially call the reader's attention to recent reviews[9,10] of certain aspects of this subject and to a forthcoming review.[11]

Fluxionality, as it relates to metal clusters, refers to a reversible intramolecular site exchange of ligands bonded to the metal framework of the cluster and also to structural reorganizations within the metal framework. The former process can involve physical movement of the ligands about the cluster. The terms "fluxionality" or stereochemical nonrigidity are commonly applied to those systems where the rearrangement process is fast on the time scale[1] of the method by which it is detected. Almost invariably, the physical technique is based on the nuclear magnetic resonance (NMR) experiment. For the NMR experiment, detection of a dynamic process requires rates in the 10^6 to 10^{-1} s^{-1} range.[12] Instrumental constraints in the NMR experiments limit the maximum temperature range of study from 150 to 200 °C, which then limits the studies to systems with exchange activation energies of less than about 25 kcal/mol. The low-temperature limit for most spectrometers is about −150 °C which sets a lower activation energy limit of ~3–5 kcal/mol. A comprehensive exposition of the theory and practice of dynamic nuclear magnetic resonance spectroscopy has been presented in an edited volume.[13]

Fluxionality, as originally defined by Doering and Roth,[2] refers only to interconversions between *equivalent* molecular configurations, not to isomerizations or tautomerizations; however, the word is now commonly used without such precision. Intramolecular rearrangements that occur in stereochemically nonrigid or fluxional molecules may be placed in two experimentally differentiable classes: mutual exchange and nonmutual exchange processes.[14] In mutual exchange, there is permutation of nuclear (like nuclei) positions without the intermediacy of a second species of appreciable concentration; molecular configuration is maintained. In nonmutual exchange, there is an intermediate of appreciable concentration. A hypothetical example would be a stereochemically nonrigid tetrahedral molecule. One conceivable mutual exchange process would have a square-planar transition state for the permutation of (labeled) ligand nuclear positions while a possible nonmutual exchange process would have a square-planar reaction intermediate of substantial concentration (effectively a tetrahedral ⇌ square-planar isomer equilibrium). The special utility of dynamic NMR studies is that under ideal conditions, either a mutual or a nonmutual exchange process can be fully characterized, whereas most other spectroscopic techniques can unambiguously define only a nonmutual exchange process. In addition, the nuclear magnetic resonance measurement can unambiguously distinguish between intramolecular and intermolecular exchange processes through spin–spin coupling data (magnetic spin of an atom in the ligand coupled with a spin of a cluster metal atom or of another ligand or both). Alternatively, if these necessary spin–spin coupling features are not present in a cluster under study, the molecularity of the exchange can be defined although with less rigor by standard kinetics analyses using the NMR technique.[15] Lineshape analysis of the temperature-dependent NMR spectra (DNMR spectra) can provide activation energies, and these data coupled with permutational analysis often can yield unequivocal mechanistic (permutational) information. This type of analysis, proven to be very effective in the simple case of mononuclear

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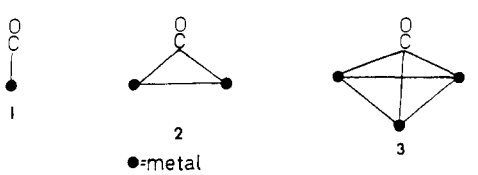
coordination complexes, can be applied to a consideration of intra- and intermolecular exchange.[14] A general discussion of this analysis has been presented by Klemperer.[16]

In terms of time scale, the NMR time window overlaps extensively with the mean lifetimes of large classes of molecules.[1] For these reasons, nuclear magnetic resonance is the most effective single technique for the study of stereochemically nonrigid molecules. Nevertheless, despite the general effectiveness of the technique, it is not a full solution to a delineation of dynamic process in molecular species. Development of alternative and especially complementary techniques is sorely needed. For example, crystallographic data may provide information about the geometric features of low-energy intramolecular rearrangements. Rather convincing analyses have been made in the area of mononuclear coordination complexes to show correlations between the deformation of these molecular complexes by crystal packing forces and plausible physical mechanisms for polytopal rearrangements in the various structural classes.[17,18] Comparable analyses in cluster molecules require a systematic generation of crystallographic data that will allow detailed comparisons of sets of very closely related cluster structures and studies of the structural deformations of a cluster *ion* with variation in the counterion.

When ligand migration in a metal cluster occurs over two or more metal centers, an intermediate bridging interaction is required. In principle, any ligand electronically has a potential for such a bridging interaction. However, the only ligands which to date have been shown to undergo fast migrations in clusters are those of demonstrated capability to bridge bond in the ground-state structure of dinuclear or metal cluster molecules and which have two electron donors in both the terminal and bridge bonding position. If there is a disparity in the extent of electron donation from a ligand in the terminal and bridging positions, facile ligand migration may not occur because there probably will be severe electronic perturbations at the metal centers in the excited or transition state unless there is a synchronous motion of a bridging and of a terminal ligand (or pairs, triads, etc.). Thus an all terminal ligand bonded cluster in this class will tend not to be highly fluxional.

The established class of "migratory" ligands includes carbon monoxide, organic isocyanides, hydride ions, nitric oxide, and in a limited or special context certain organic ligands such as polyenes. Halide ions and alkyl groups are known to bridge bond in clusters but there are no data presently available that establish fast migration processes for these ligands in clusters; it is important to note that halide ions donate two electrons and either four or six electrons in terminal and bridge positions, respectively. Metal clusters with carbon monoxide ligands comprise the largest metal cluster class, and the majority of investigations of metal cluster rearrangements deal with clusters from this class. Accordingly, our discussion largely centers on this class of cluster molecules and ions. The carbon monoxide ligand can bond with metal centers in a cluster in a terminal two-center fashion **1**, edge-bridging three-center mode **2**, and a triangular face-bridging four-center form **3**. In fact, there are cluster molecules, such as $Rh_7(CO)_{16}^{3-}$, in which all three bonding interactions are present in a single cluster.[19] Unsymmetric bridging modes are also established, and these may effectively be considered as linear combinations of **1** with **2** or **3**. Nitric oxide has



been shown to have these very same bonding capabilities and organic isocyanides probably will be similarly characterized. The hydride ligand should prove to be the most "plastic" cluster constructional unit or ligand. To date, terminal, edge-bridging, triangular face-bridging, and five-center square face-bridging interactions have been established. In the larger clusters (six or more atoms), the hydride may reside within the cluster framework. As more neutron diffraction studies of cluster hydrides are completed, this list of bonding interactions should grow. Fortunately, Bau and Churchill and their co-workers are systematically establishing the structures of the cluster hydrides through X-ray and neutron crystallographic studies.

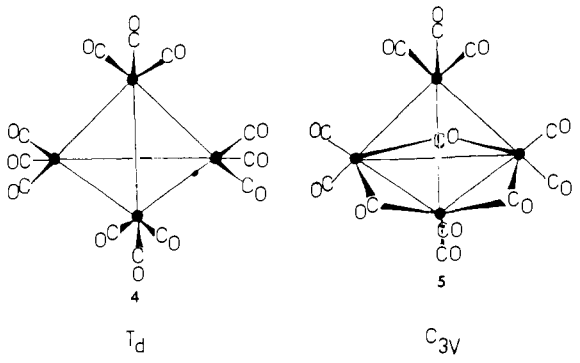
The physical or geometric nature of a cluster rearrangement process is the characterization that the chemist desires. Permutational analysis[16] can eliminate physical processes of incorrect permutational character and thereby limit to some degree the number of acceptable physical processes. Detailed shape (from crystallographic data) analysis of the cluster and closely related ones may provide geometric information about low-energy rearrangement pathways.[17,18] However, in the final analysis, a geometric pathway for a rearrangement is supported on the grounds that it is a chemically and physically reasonable pictorialization. In this last stage of analysis, theoretical analyses may be applied, but the very complexity of metal clusters makes all but the quite qualitative calculations a rather large computational endeavor. This leaves only the relatively unsophisticated but nevertheless important consideration of minimal perturbation of electronic environment and coordination number for each metal atom during the course of the rearrangement. Rearrangements that lead to equivalent but differently labeled configurations from the ground state will tend to be of lowest energy. Metal clusters often have the potential for several different rearrangement mechanisms; however, in highly symmetric cluster molecules, these processes may not be permutationally differentiable, and the process may not be NMR detectable in the absence of observable spin–spin coupling between metal and ligand atoms. Ligand substitutions by similar and by dissimilar ligands can provide lower symmetry cluster derivatives in which the individual processes may be characterized. For some unsymmetrically substituted clusters, the two or three NMR *distinguishable* mechanisms may have the similar *physical* character with the lowest energy process generating equivalent configurations and the other mechanisms generating inequivalent configurations. In addition, ligand substitution in a cluster with ligands that do not readily bridge bond may effectively block an intrinsically low-energy process, and then the exchange may proceed by more localized processes. Ligand substitution with electronically and sterically similar ligands may not substantially alter exchange characteristics, but if the character of the new ligand substituent differs markedly, there may be dramatic effects. Not only may such substitution alter the dynamic features, for example, by raising the activation energy for ligand exchange over multiple metal sites, and, in some cases, by lowering the activation energy for ligand exchange over a more limited area of the cluster, but also may actually alter the ground-state geometry. Effects of this character have actually been observed in metal carbonyl clusters and their isocyanide and phosphine derivatives (vide infra).

Because our principal interest in metal cluster rearrangements is in ligand migration processes, the analysis that follows first addresses multisite exchange problems, then two-center exchanges, cluster framework mobility, and, lastly, single site exchange. Ligand exchange or migration processes are first examined for the carbon monoxide ligand, followed by organic ligands and then hydride ligands. In some cases, different ligand migration processes, for example, carbon monoxide and hydride, appear to be inextricably coupled in the hydrido- and in the organo-metal carbonyl clusters.

II. Classic $M_4(CO)_{12}$ Case—Multicenter Exchange

Two structural forms prevail for both the crystalline and so-

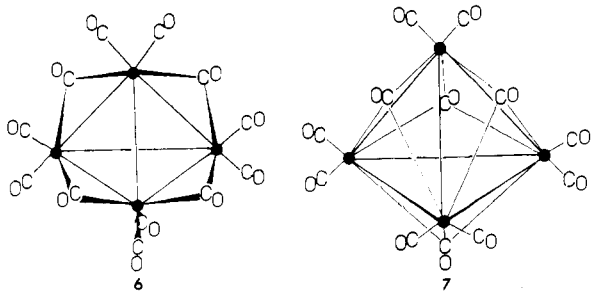
lution ground states of neutral tetranuclear dodecacarbonyl clusters: the T_d form (**4**) with no bridging carbonyl ligands and the C_{3v} form (**5**) with three edge-bridging carbonyls on a common



4 5

T_d C_{3v}

face. A third plausible structure, D_{2d} (**6**), with four edge-bridging carbonyl ligands, has been tentatively proposed as the ground-state solution structure of $Co_4(CO)_{12}$.[21] Another high symmetry form is **7** where all faces of the tetrahedron are triply bridged by a carbonyl ligand.



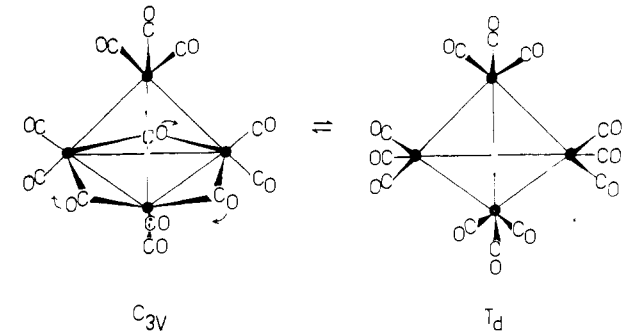
6 7

D_{2d}

Conceptually, there are a large number of physical mechanisms for ligand migration in tetrametal dodecacarbonyls. The simplest of these, and an eminently reasonable physical process, is a more or less synchronous bending of three carbonyl ligands so as to interconvert the C_{3v} and T_d idealized forms (Figure 1). Since both forms are rigorously defined for the solid state (C_{3v} for cobalt[22] and rhodium[23] and T_d for iridium[23]), it is reasonable to presume that the alternative can be an *intermediate* in a rearrangement of the other ground-state form. This basic $T_d \rightleftharpoons C_{3v}$ process was first proposed by Cotton in 1966 for $Co_4(CO)_{12}$ fluxionality.[24] In the C_{3v} form, the carbonyl groups describe an icosahedron and the T_d form, a cube octahedron. Thus, the physical process described for $C_{3v} \rightleftharpoons T_d$ interconversion can also be envisaged as a tumbling of an M_4 tetrahedron inside close-packed carbonyl ligands of interconverting I_h and O_h symmetry arrays.

An alternative multisite exchange mechanism in $M_4(CO)_{12}$ clusters could involve the D_{2d} transition state or intermediate, **6**, which could be attained by a synchronous motion of four terminal carbonyl groups in a ground-state T_d form or by several different physical processes from a C_{3v} ground state. A third alternative multisite exchange process would involve the triply bridged form **7** as a transition state or an intermediate.

In a second category are physical processes that are more localized in character. Thus for the C_{3v} model there could be a synchronous exchange of the three bridging carbonyls with the three carbonyl ligands that are nearly coplanar with bridging ligands, Figure 2. This process alone would equilibrate then only two (a and b) of the four types of carbonyl environments, although a way point in this process is near to the idealized T_d structure, **4**. We intend a literal distinction to be made here between this more localized exchange (no intermediate) and the $C_{3v} \rightleftharpoons T_d$ exchange process with either C_{3v} or T_d an intermediate state. The former exchange will be discussed separately in ligand exchange over three metal sites (section IV). More localized



C_{3v} T_d

Figure 1. The interconversion of the C_{3v} and T_d forms of the tetrametal dodecacarbonyls.

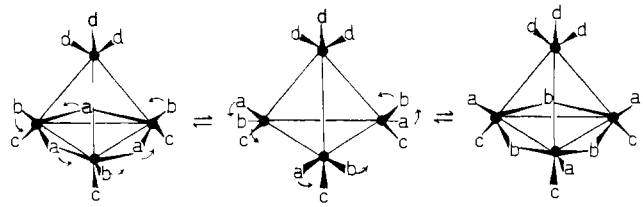


Figure 2. Localized site exchange of three bridging and three terminal carbonyls.

exchange processes involving only two metal centers would seem to generate intermediates or transition states of substantially higher energy than those discussed earlier with the exception of a synchronous bending of two terminally bound carbonyls, each on adjacent metal atoms, to edge-bridging positions and any other two site based exchange that has a pairwise ligand shift.

Experimentally, ligand migration is definitively established for C_{3v} $Rh_4(CO)_{12}$[25-27] and implicated[28] for $Co_4(CO)_{12}$.[21,29] For $Rh_4(CO)_{12}$, the ^{13}C NMR spectrum at −80 °C consists of four multiplets of equal intensity; three are doublets (^{13}C–^{103}Rh spin–spin coupling) representative of three terminal CO environments and one is a triplet (^{13}C coupling with two rhodium atoms) representative of a single, bridging environment.[26] These spectral data are fully consistent with the structure established for this cluster in the solid state.[23] As the temperature is raised, the ^{13}C multiplets broaden, then merge, and then finally yield a binomial quintet. Importantly, $J_{Rh-C}(av) = \frac{1}{4}\Sigma J_{Rh-C}$ (slow exchange limit). The higher temperature multiplet arising from equivalent coupling of all four rhodium nuclei with each carbonyl ligand ^{13}C nucleus unequivocally establishes an *intramolecular* fast migration of carbonyl ligands about the cluster periphery. Mechanistic details, however, remain unresolved; the permutational character of the exchange has not been studied. It is not yet fully established whether one or more mechanisms are operative in the −80 to +60 °C transitional region although there is no visual evidence of site selectivity in the intermediate exchange region. Nevertheless, a facile $C_{3v} \rightleftharpoons T_d$ type of process as envisioned by Cotton would seem to be the most reasonable, low-energy or dominant process. For $Rh_4(CO)_{12}$, the activation energy for the ligand migration process is less than ~14 kcal/mol.

Tetracobalt dodecacarbonyl has the same solid-state structure as does the rhodium analog.[22,23] Consistently, the ^{59}Co NMR spectrum shows two resonances of near 1:3 intensity relationship, as reported by three independent groups of investigators.[21,29] However, the ^{13}C NMR spectrum of the molecule is reported, by two independent groups of investigators, to have three resonances of near-equal intensity, a feature inconsistent with the C_{3v} structure but fully consistent with the D_{2d} structure **6**, and the face-bridged structure **7**.[21,29a] On the other hand, infrared studies of $Co_4(CO)_{12}$ in solution, in matrix-isolated form, and in KBr pellet form, support the thesis that in these physical

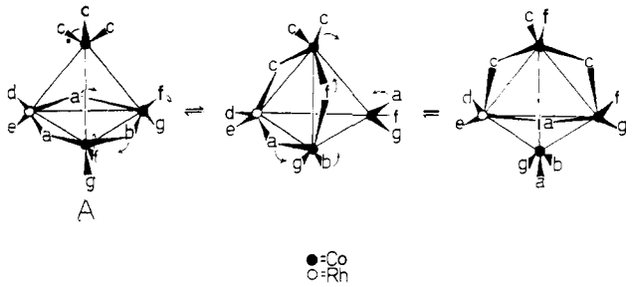


Figure 3. The proposed low-temperature site exchange process for $RhCo_3(CO)_{12}$ which, as shown by the NMR data, does not involve migration of the CO ligands terminally bonded to the rhodium atom.

TABLE I. Qualitative Ordering of Exchange Energetics

cluster	structure[a]	exchange process[b]	collapse temp, °C
$Co_4(CO)_{12}$	?		−20[e]
$Rh_4(CO)_{12}$	II		~−5
$Ir_4(CO)_{12}$	I	not detectible by NMR	
$RhCo_3(CO)_{12}$	II	LT	−45
		HT	30[e]
$Ir_4(CO)_{11}(CNR)$[c]	I	LT	
		HT	
$Ir_4(CO)_{11}(PR_3)$[d]	II	LT	−33
		MT	2
		HT	>31
$Ir_4(CO)_{10}(PR_3)_2$[d]	II	LT	
		HT	
$Ir_4(CO)_9(PR_3)_3$[d]	II	LT	
$Ir_4(CO)_8(PR_3)_4$[d]	II	LT	
$Co_4(CO)_{11}[P(OCH_3)_3]$	II		−5[e]

[a] I = nonbridged form and II = three-edge (common face) bridged form. [b] LT, MT, and HT denote low-, medium-, and high-temperature processes where appropriate. [c] R is *tert*-butyl. [d] $PR_3 = P(C_6H_5)_2CH_3$. [e] Line-broadening effects are not necessarily indicative of a ligand exchange process.

states, there is one pervasive structural form, namely, the C_{3v} form, **5**,[29a] In addition, a derivative of $Co_4(CO)_{12}$, $Co_4(CO)_{11}[P(OCH_3)_3]$, has a ^{13}C spectrum consistent with a derivative of the C_{3v} model; however, there can be no assurance that the basic cluster structure is unaltered by substitution of carbon monoxide by such an electronically different ligand as a phosphite.[29a] The ^{13}C spectrum of $Co_4(CO)_{12}$ should be reexamined at higher fields and with solvents of varying viscosity (to possibly remove "adverse" effects of $^{59}Co-^{13}C$ magnetic interactions), and perhaps the apparent anomaly can be resolved. In any case, the temperature-dependent ^{13}C spectra of $Co_4(CO)_{12}$ suggest facile ligand site exchange although the mechanistic details are unresolved.

A mixed metal dodecacarbonyl, $RhCo_3(CO)_{12}$, appears to have the basic C_{3v} structure of $Rh_4(CO)_{12}$ with the unique ligand-bridged face defined by the rhodium and two of the cobalt atoms.[30,31] The ^{13}C NMR spectrum is essentially consistent with this model with seven of the eight resonances, required for structure A, in Figure 3, observed at −85 °C.[31,32] At elevated temperatures, these resonances broaden and merge. The reported qualitative character of the intermediate exchange region would seem to require at least two different exchange processes. It has been proposed that in the low-energy process, a more or less synchronous bending of two terminal and two bridging carbonyls (Figure 3) equilibrates the three $RhCo_2$ faces and renders all but the two terminal carbonyl groups attached to rhodium equivalent to each other and concomitantly equilibrates the set of two rhodium terminal bonded carbonyl ligands.[31] In the higher energy exchange process in $RhCo_3(CO)_{12}$, all carbonyl ligands become equivalent on the NMR time scale

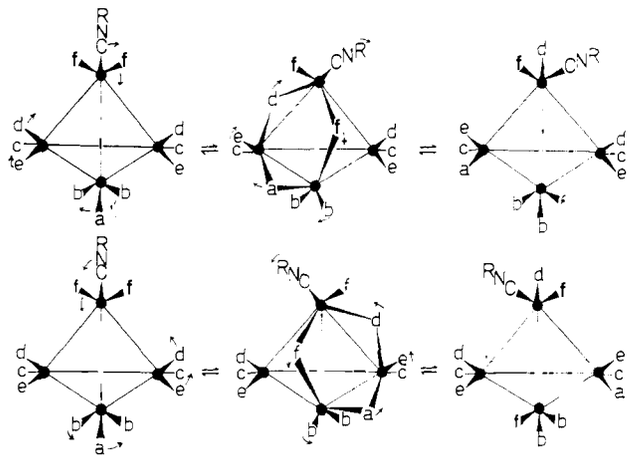


Figure 4. Proposed "T_d" ⇌ "C_{3v}" ligand migration process in $Ir_4(CO)_{11}[CNC(CH_3)_3]$ involving movement of $CNC(CH_3)_3$ and carbonyl "a". Note that the trans relationship of "a" to the isocyanide moiety is maintained, despite the site exchange. Ligand migration about the remaining two tetrahedral faces does not alter this stereochemical relationship, and hence, carbonyl "a" remains magnetically distinct in this process.

through a process that cannot be defined by the NMR spectral features. Alternatively, the two-step process for ligand migration in this cluster could comprise a rearrangement to the face-bridged intermediate, structure **7**, with a return only to an equivalent "C_{3v}" structure with rhodium in the unique edge-bridged face for the low-energy process and with the population of "C_{3v}" stereoisomers with rhodium at the unique vertex for the higher energy process.

Ligand migration over metal centers in T_d $Ir_4(CO)_{12}$ cannot be studied because (1) all carbonyl groups are equivalent and (2) there is no suitable naturally occurring iridium isotope to monitor $Ir-^{13}C$ spin–spin coupling phenomena. However, derivatives of $Ir_4(CO)_{12}$ have provided keen insight to the general question of exchange mechanisms in $M_4(CO)_{12}$ clusters (Table I). Substitution by electronically comparable ligands like isocyanides does not substantially perturb the basic structure. $Ir_4(CO)_{11}[CNC(CH_3)_3]$ has the same nonbridged structure of the parent dodecacarbonyl and has fluxional properties.[33] Rearrangement in this cluster occurs through at least two distinct processes whereby all carbonyl ligand environments are rendered equivalent. The lower energy process yields two sets of carbonyl environments of relative intensities ten and one. This phenomenon can be neatly described by an idealized "T_d" ⇌ "C_{3v}" process that avoids an isocyanide bridged intermediate or transition state and by which carbonyl "a" remains magnetically distinct as shown in Figure 4.[33] (Obviously none of the forms for $Ir_4(CO)_{11}[CNC(CH_3)_3]$ can have C_{3v} or T_d symmetry; the qualifying term idealized or the notation "T_d" and "C_{3v}" is used for simplicity in referring to derivatives of the parent $M_4(CO)_{12}$ cluster in nonbridged (T_d) or bridged (C_{3v}) forms.) The higher energy exchange process in $Ir_4(CO)_{11}[CNC(CH_3)_3]$ which equilibrates all carbonyl ligands could be described by an analogous traverse but one in which a bridging isocyanide state is allowed—and by other physical processes.

Substitution of one carbonyl ligand in $Ir_4(CO)_{12}$ by an electronically quite different ligand, a phosphine like $P(C_6H_5)_2CH_3$, illustrates two crucial points. Most importantly, the substitution of one carbonyl ligand by a phosphine shifts the ground-state structure to the idealized "C_{3v}" form with three edge-bridging carbonyl groups on a common face and with the unique phosphine ligand at an axial position in the unique carbonyl bridged face, Figure 5-A.[34] The ^{13}C NMR spectrum is fully consistent with this structural form at −88 °C (see Figure 5), and ligand exchange in this cluster occurs above −88 °C in three discrete steps.[34] Secondly, the important dynamic point is that for the two lowest energy processes, the idealized "C_{3v}" ⇌ "T_d" re-

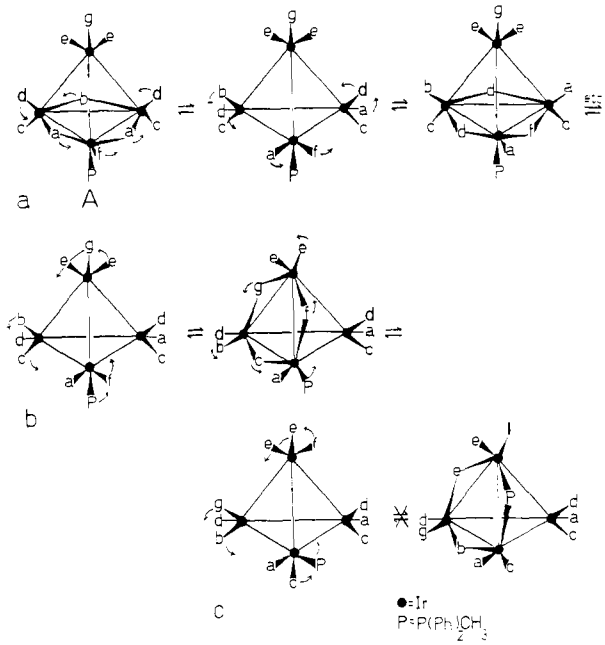
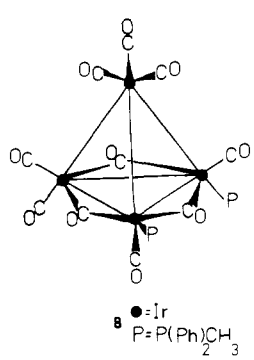


Figure 5. (a) Proposed low-temperature "C_{3v}" $\rightleftharpoons$ "T_d" site exchange process for $Ir_4(CO)_{11}[P(C_6H_5)_2CH_3]$. In the process, the phosphine ligand remains axial with respect to the bridged face. (b) Site exchange scheme at ~2 °C. The phosphine ligand assumes an equatorial position with respect to the bridged face. (c) An unfavorable site exchange scheme involving a bridging phosphine.

arrangement suffices to explain the observed equilibration of carbonyl environments. At −33 °C conversion of the "C_{3v}" ground-state form to the "T_d" excited state in which all carbonyl ligands are terminal followed by return to an equivalent (to the ground state) configuration retaining an axial phosphine ligand can represent the low-energy process whereby carbonyl environments a, b, d, and f are equilibrated (Figure 5a). In the intermediate exchange process, which occurs at 2 °C, carbonyl environments c and e are equilibrated with the a, b, d, and f set, and could be described by a return from the nonbridged intermediate to a nonequivalent configuration (new intermediate) in which the phosphine ligand is in a radial site, as shown in Figure 5b. The third and highest energy observable process through which all carbonyl ligands become equivalent occurs at ~30 °C and requires a process distinct from the generalized "C_{3v}" $\rightleftharpoons$ "T_d" mechanism (assuming that a "C_{3v}" $\rightleftharpoons$ "T_d" type of multistep process with a bridging phosphine ligand at some step as in Figure 5c will be a relatively unfavorable process). A simple pseudo-threefold twist mechanism about the apical iridium (metal site with all terminal ligands) in concert with the previous mechanisms would suffice to equilibrate all carbonyl environment.

More highly substituted phosphine derivatives of $Ir_4(CO)_{12}$ also have "C_{3v}" edge-bridged ground-state structures. The disubstituted derivative has both phosphine ligands at separate iridium atoms in the unique face, and one is radial and one is axial, **8**.[34]



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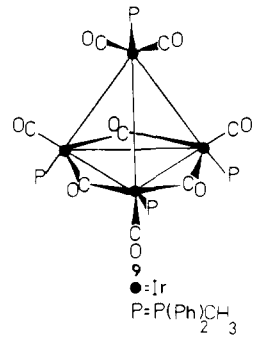
The trisubstituted derivative is analogous with two radial and one axial phosphine ligand substituted at individual iridium sites in the unique face.[34] These derivatives exhibit ligand-exchange processes, although of higher activation energy than for exchange in $Ir_4(CO)_{11}PR_3$, but the NMR data provide no definitive mechanistic information. A similar situation applies to $Ir_4(CO)_8(PR_3)_4$ in which all four iridium atoms have a phosphine substituent, **9**.[34,35] It should be evident by inspection of Figure



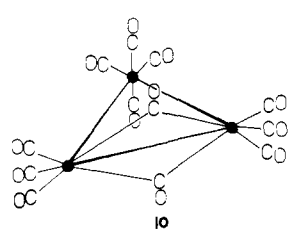
9

5 that these multisubstituted derivatives do not have the possibility of ligand migration through a traverse of *equivalent* "C_{3v}" configurations analogous to the lowest energy process postulated for $Ir_4(CO)_{11}PR_3$ because all these derivatives have radial phosphine substituents. All three of these multisubstituted derivatives ultimately exhibit only one ^{13}C NMR signal at high temperatures which requires one or more processes distinct from the idealized "C_{3v}" $\rightleftharpoons$ "T_d" process.[34]

All available data clearly indicate that the idealized T_d or nonbridged M_4L_{12} structural form is close in energy to the C_{3v} or edge-bridged form in the carbonyl ligand system and that a dominant low energy ligand exchange process involves a C_{3v} $\rightleftharpoons$ T_d reaction path. There are, however, other less definitive data that implicate D_{2d} or near D_{2d} forms (four edge-bridging ligands) and possibly the face-bridged form **4** that are of comparable energy to the idealized T_d (nonbridged) and C_{3v} (common face-bridged) forms. Other rearrangement traverses, although not rigorously excluded on the basis of available data and the mechanistic analyses, appear to be generally higher energy traverses than the C_{3v} $\rightleftharpoons$ T_d rearrangement unless ligand substitutional effects substantially raise the energy of this latter rearrangement. Ligand substitution can raise the activation energy for carbonyl group migration in a localized region of the cluster. Application of a highly favorable process such as the "T_d" $\rightleftharpoons$ "C_{3v}" traverse can generate either equivalent or inequivalent configurations in the return from the excited state for a derivative of $M_4(CO)_{12}$. If the latter is required for effective ligand migration, then the activation energy for this generation of an inequivalent configuration (intermediate) probably will be larger than that for the parent $M_4(CO)_{12}$ *molecule*. Ligand substitution also can lower the activation energy for ligand migration *in a localized region of the cluster* with respect to that for ligand migration in the parent cluster as will be described in the discussions of two-center and one-center processes.

III. Trimetal Dodecacarbonyls

The $M_3(CO)_{12}$ clusters, known for iron, ruthenium, and osmium, have either the carbonyl-bridged C_{2v} structure (**10**) as



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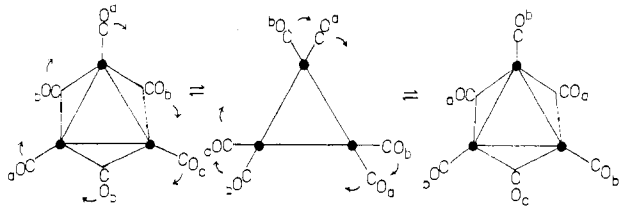
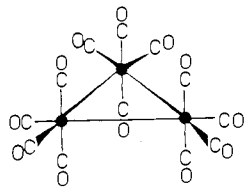


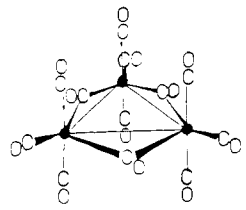
Figure 6. The merry-go-round process. The six participating ligands are approximately coplanar with the M_3 face.

found for iron[36] (only C_2 symmetry because the carbonyl bridges are unsymmetric) or the nonbridged D_{3h} structure (**11**) as found



11 ●=Ru, Os

for ruthenium[37] and osmium.[38] The plausible triply edge-bridged D_{3h} alternative (**12**) is known for $Ru_3(CO)_{10}(C_4H_4N_2)$[20] and for



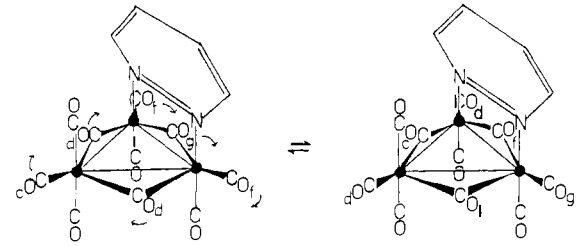
12

$Pt_3[P(C_6H_5)_3]_3(CNR)_3$.[39] Nothing is known about the energy relationships among these three forms, and ligand migration processes are uncharted for the $M_3(CO)_{12}$ clusters. The iron[40] and ruthenium[41] clusters have single ^{13}C resonances to below −100 °C and are obviously fluxional. However, the osmium cluster is rigid on the NMR time scale at 25 °C.[41,42] Exchange collapse was observed at 80 °C and a single sharp resonance at 150 °C, but the ^{13}C NMR spectra do not provide enough permutational information to distinguish between one-, two-, and three-center processes in this osmium cluster. Although the iron cluster exchange process is readily envisaged as involving the nonbridged D_{3h} form as a transition state or intermediate, delineation of ligand migration about these clusters cannot be rigorously achieved. As noted in the following section, derivatives of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ appear to undergo a three-metal center based exchange through a transition state or intermediate analogous to the triply bridged form **12**. There is also evidence discussed in the two-center exchange section that rearrangements based on interconversion of forms **10** and **11** operate in some trimetal cluster molecules.

IV. Ligand Exchange over Three-Metal Sites

A. Introduction

The relatively large area of carbonyl ligand exchange processes that involve three-metal sites is applicable to three-atom and to larger cluster molecules. Hence this area cannot be concisely summarized in structural terms as was done for the tetrahedral tetrametal dodecacarbonyls and their derivatives simply because of the diversity of structural and stereochemical forms in trinuclear clusters. Nevertheless, there is a relatively common three-metal site exchange process that has a domino-like physical character wherein six ligands approximately defining a common plane move synchronously about the metal triangle as depicted in Figure 6. This process also appears in tetranuclear metal clusters and a related process seems to occur



●=Ru

Figure 7. A modified merry-go-round process advanced for $Ru_3(CO)_{10}(C_4H_4N_2)$.

in larger clusters where the ligand migration occurs about three metal atoms that lie more or less in a common plane. Accordingly, this general (not limited to three-metal sites) process is discussed in this section. For a graphic and concise description of this process, we will refer to it as the merry-go-round process. Notably, this process is related to the apparently common "T_d" ⇌ "C_{3v}" ligand migration process found for tetrametal dodecacarbonyls and their derivatives; they might be distinguished by the character of the potential energy surface: the latter has a "C_{3v}" or "T_d" intermediate whereas the "merry-go-round" process may or may not involve an intermediate.

There also appears to be a three-dimensional form of the merry-go-round process wherein the carbonyl ligands that undergo facile interchange of positions share a common conical surface above a cluster polyhedral face, and this ligand migration mechanism may be especially important for the larger cluster polyhedra. These conical surfaces may vary widely in angle, and the two-dimensional merry-go-round process is really the limiting case where the angle is 180°.

No process has yet been clearly identified where a merry-go-round process operates in a common *cylindrical* surface above a cluster polyhedral face; this would involve the so-called axial ligands of a D_{3h} $M_3(CO)_{12}$ cluster or a derivative of it.

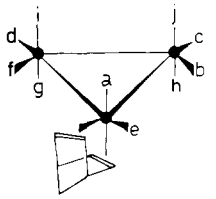
B. Planar Merry-Go-Round Process

The merry-go-round process may be operative in a derivative of $Ru_3(CO)_{12}$ in which two cis axial carbonyls have been replaced by a bidentate diazene ligand.[20] At low temperatures, the ^{13}C spectrum consists of a seven-line pattern that is consistent with the solid-state structure (Figure 7). A three-step exchange occurs to eventually render all carbonyl ligands magnetically equivalent.[20] The first or lowest temperature process, −156 to −90 °C, operates to equilibrate the equatorial carbonyl ligand environments (c, d, f, and g). For this process, the simplest physical mechanism, as depicted in Figure 7, is the concerted motion of all six coplanar equatorial carbonyl ligands about the triangular Ru_3 plane. Exchange mechanisms operating in the two higher energy processes cannot be uniquely defined from the available data, although carbonyl ligand axial ⇌ equatorial interchange localized at individual metal sites (see later discussion of single site exchange) coupled with the merry-go-round process would suffice to *rationalize* the observations.

Studies by Shapley and co-workers[43,44] with phosphine, chelating phosphine, and nitrile derivatives of $Os_3(CO)_{12}$ strongly indicates that the merry-go-round process is a common three-center process provided that ligands which do not easily bridge bond are not in equatorial sites and thereby "block" the merry-go-round process. For example, in $Os_3(CO)_{10}(NCCH_3)_2$ with both acetonitrile ligands bound to different osmium atoms at axial sites in a trans relationship, the merry-go-round process accounts nicely for the observed low-temperature migration process which is facile even at −88 °C.[44] This may be contrasted with the behavior of the bisphosphine (dimethylphenyl) derivative of $Os_3(CO)_{12}$ in which the two phosphine ligands are

bonded to the same osmium atom and both are at equatorial sites. Here the merry-go-round process is "blocked" and all the observed dynamic ligand processes appear to be based on two-center (metal) site exchange which occurs about −5 °C, and single-center (metal) site exchange processes which are evident above 40 °C.[43] A similar phenomenon is observed for the bidentate phosphine complexes of $Os_3(CO)_{10}$ where the two phosphorus atoms are attached at vicinal equatorial sites of two osmium atoms and the mono- and bis(triethylphosphine) derivatives (vide infra).[45]

In $Os_3(CO)_{10}$(norbornadiene), the diene bridges (chelates) an equatorial and an axial site on one osmium atom.[46] In this array, the merry-go-round process is also blocked, but to a limited extent. At temperatures above −100 °C where the ^{13}C spectrum is a ten-line pattern fully consistent with the structure **13**, there



13

●=Os

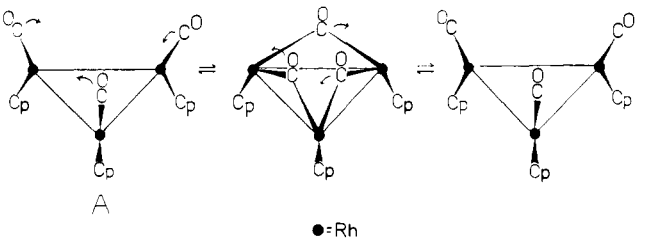
is a limited exchange such that four axial ^{13}C resonances i, j, g, and h (associated with the unsubstituted osmium atoms) are converted to two averaged axial resonances, and four equatorial resonances, b, d, e, and f, are averaged into two equatorial resonances. This observed process is fully explained if a planar merry-go-round process is involved, but with an oscillatory constraint because of the diene substituent.[46] In a formally analogous derivative, the 1,3-cyclohexadiene derivative, there is a stereochemical and basic structural identity.[47] However, there is no evidence of the merry-go-round process as the low temperature process. In this cluster derivative, because of steric and electronic diene factors (conjugated vs. nonconjugated in norbornadiene), single metal site processes appear to dominate the lower temperature exchange processes (see section on single site exchange mechanisms), and the planar merry-go-round exchange may become significant only at a relatively elevated temperature.[47] That a multisite process analogous to that found at low temperatures for the norbornadiene complex, **13**, is not detected suggests a rather profound steric and electronic perturbation of the potential rearrangement surface occurs in the substitution of the nonconjugated diene by the conjugated diene.

The "$T_d \rightleftharpoons C_{3v}$" process that seems to commonly operate in $M_4(CO)_{12}$ clusters and specifically in $Rh_4(CO)_{12}$ is readily formulated as the merry-go-round process as may be seen by the similarity between Figures 2 and 6. Each tetrahedral face has nine carbonyl ligands associated with it, six of which are approximately coplanar with that face and participate in the merry-go-round process, while three carbonyl ligands are axial with respect to that M_3 face and are spectators to the ligand migration. The distinction is between processes that traverse the T_d form as a transition state and as an intermediate.

In heteronuclear clusters like $H_2FeRuOs_2(CO)_{13}$ and $H_2FeRu_3(CO)_{13}$, the planar merry-go-round process has been postulated to account for some of the exchange phenomena observed in the ^{13}C DNMR spectra.[48,49]

C. Modified Merry-Go-Round Process—The Conical Surface

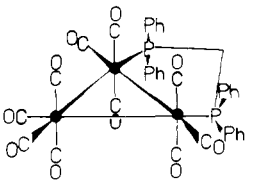
In the C_{3v} isomer of $(\eta^5\text{-}C_5H_5RhCO)_3$, structure A, Figure 8, the carbonyl ligands form an all-cis array on one side of the Rh_3 triangle and reside at bridging positions.[50] In the low-temperature spectrum, the ^{13}C spectrum is a triplet which broadens and then



●=Rh

Figure 8. The ligand site exchange scheme for C_{3v} $[\eta^5\text{-}C_5H_5RhCO]_3$ where the participating carbonyl ligands sweep out a near-conical surface in the rearrangement sequence.

emerges as a quartet at 26 °C.[51] These data which define a facile migration of carbonyl ligands about the triangular cluster are consistent with a concerted motion of the bridging ligands to an intermediate or transitional array of terminal ligands. This motion, as shown in Figure 8, would define a conical rather than planar reaction surface with a conical angle of approximately 56°. The conical surface merry-go-round process should be relatively common in the larger metal clusters that have triangular faces. In the same sense that the planar surface represents one extreme of the conical surface, a cylindrical array of ligands is representative of the other extreme. Concerted motion of axial ligands in metal clusters, a motion of ligands that are approximately *normal* to a cluster face, has been postulated for only one cluster, $Ru_3(CO)_{10}[(C_6H_5)_2PCH_2P(C_6H_5)_2]$, **14**. The low-tem-



14

●=Ru

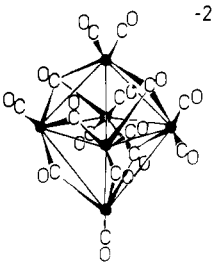
perature process operative in **14** (which is fast at −40 °C), is consistent with a pairwise bridge exchange mechanism (vide infra) based on two metal sites about that edge which is phosphine substituted (see Figure 16).[52] The position of attachment of the chelate in these positions does not interfere with motion of the six coplanar carbonyl ligands. However, at a temperature in excess of 111 °C, the axial ligands are proposed to migrate about either face of the Ru_3 cluster, in a manner similar to that depicted in Figure 8. Decomposition problems above 111 °C prevented the observation of a well-defined fast-exchange spectrum. The mechanistic proposal is valid only if there is no equatorial–axial interconversion of the $(C_6H_5)_2PCH_2P(C_6H_5)_2$ ligand. Motion of the $(C_6H_5)_2PCH_2P(C_6H_5)_2$ ligand, which is a reasonable possibility at elevated temperatures, renders the coplanar two- and three-center processes viable mechanistic possibilities.

Distinctive in range of size and structure are the rhodium clusters. This series of clusters, as the full data are reported, should serve as a critical test of theories, or generalizations for metal clusters—and any purported general understanding of ligand migration. A summary of the available structural and dynamic characteristics of the rhodium cluster series is given in Table II. For the smallest of these clusters, $[(\eta^5\text{-}C_5H_5)RhCO]_3$, and $Rh_4(CO)_{12}$, the conical merry-go-round and planar merry-go-round processes, respectively, appear to be operative. For $Rh_6(CO)_{15}^{2-}$ (**15**), the ^{13}C NMR spectrum is a binomial septet to −70 °C, and all carbonyl groups must be rapidly migrating over the cluster periphery at this relatively low temperature.[53] By analogy with the corresponding cobalt derivative which is crystallographically defined and which has an IR spectrum similar to that of the rhodium cluster ion,[54] there are three cluster faces each with triply (face) bridging carbonyl ligands, and there is also a cluster face with three edge-bridging and three terminal car-

TABLE II. Solution Dynamics of the Rhodium Carbonyl Clusters

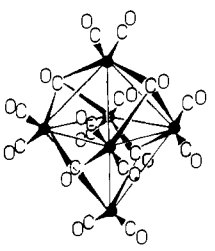
cluster	structure[a]	solution dynamics
$((\eta^5\text{-}C_5H_5)RhCO)_3$	Figure 8	fluxional[b] at 26 °C
$Rh_4(CO)_{12}$	**5**	fluxional at 60 °C
$Rh_6(CO)_{15}^{2-}$	**15**	fluxional at −70 °C
$Rh_6(CO)_{16}$	**16**	rigid[c] at 70 °C
$Rh_6(CO)_{15}C^{2-}$	**17**	rigid at 25 °C
$Rh_7(CO)_{16}^{3-}$	**18**	three edge-bridging and three terminal carbonyls equilibrated at 25 °C
$Rh_{12}(CO)_{30}^{2-}$	**19**	rigid at 72 °C
$Rh_{13}(CO)_{24}H_2^{3-}$	Figure 9	nine edge-bridging and twelve terminal carbonyls exchanging at −80 °C
$Rh_{17}S_2(CO)_{32}^{3-}$	**20**	one set of eight bridging and one set of eight terminal carbonyls exchange above 160 °C

[a] Structures are referred to by the numbering scheme in the text. [b] The term "fluxional" is used here to indicate that all carbonyl environments are equilibrated on the NMR time scale. [c] The term "rigid" is used here to indicate that there are no ligand site exchanges occurring at a rate which is detectable on the NMR time scale.

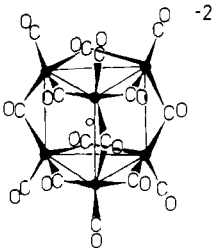


15
●=Co, Rh

bonyl ligands displaced outward from that face so as to define a shallow cone. Clearly, several distinct processes must be operative in this highly fluxional cluster, but at least one of these may be based on the seemingly common process of a synchronous motion of six ligands in a conical array. In the closely related cluster $Rh_6(CO)_{16}$ (**16**), there is neither an edge-bridged



16
●=Rh



17
●=Rh
○=C

face nor an open face not already encumbered by a face-bridging CO ligand.[55] Explicably, no carbonyl ligand migration has been detected in this symmetrical cluster up to 70 °C.[53] The trigonal prismatic $Rh_6(CO)_{15}C^{2-}$ (**17**) does have edge-bridged faces, but the crystal structure shows that the terminal carbonyls do not sweep out a common conical surface with the edge-bridging carbonyls.[56] The ^{13}C NMR spectra from −70 to 25 °C are fully consistent with the solid-state structure.[57] For $Rh_7(CO)_{16}^{3-}$ (**18**), the ^{13}C NMR spectrum at −70 °C is fully consistent with the solid-state structure.[53,58] At 25 °C, the spectrum shows rapid exchange between a set of three bridging and a set of three terminal carbonyl ligands. There are two such sets common to one cluster face with all carbonyl ligands in both sets sharing a conical surface above the common face. Presumably these are the sets involved in the exchange. Among the larger rhodium

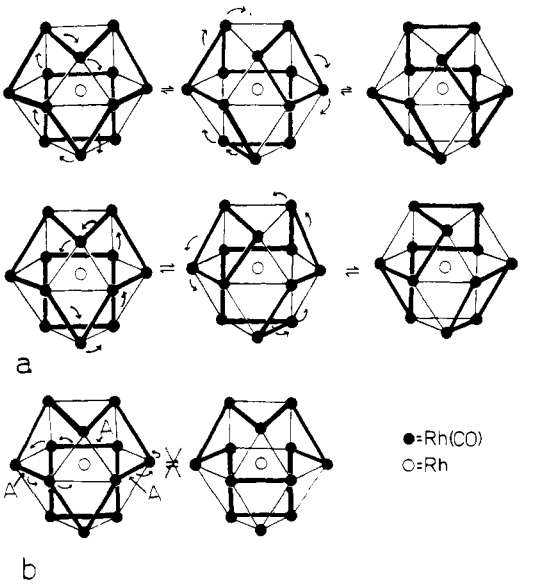
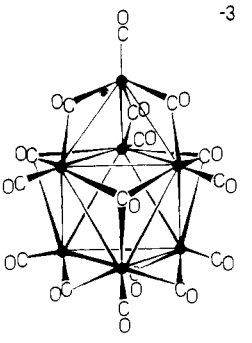
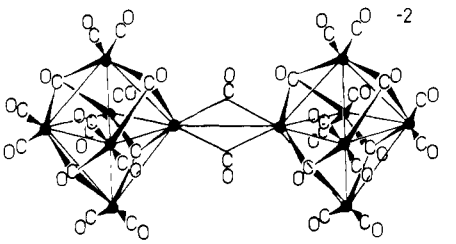


Figure 9. (a) Postulated six-center ligand migration processes for $Rh_{13}(CO)_{24}H_2^{3-}$ in which 21 carbonyl environments are equilibrated. The broader lines between rhodium centers represent edge-bridging carbonyls, and each rhodium center of the framework has a single terminal carbonyl attached which is not depicted, but which participates in the fluxional processes. The proposed mechanism entails the synchronous motion of three bridging carbonyls to terminal positions and three terminal carbonyls to edge-bridging positions about a hexagonal belt of the cluster. This occurs in three distinct fashions so as to generate an equivalent configuration in each instance. The third of these exchange processes is accessible only after operation of either of the first two routes. The operation of route one followed by route three is depicted on the first line of the figure, and the operation of the second route followed by route three is shown on the second line of the figure. (b) Ligand migration involving bridging carbonyls "A" would generate a nonequivalent configuration. This process is not observed in the DNMR spectra.



18
●=Rh

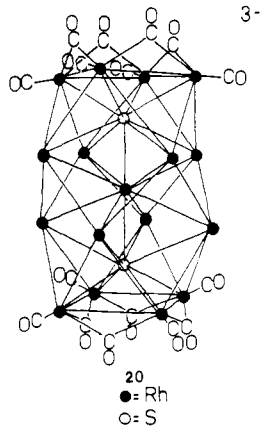
clusters is the dodecanuclear $Rh_{12}(CO)_{30}^{2-}$ (**19**) in which two Rh_6 octahedra are joined by carbonyl ligand bridges. This linked octahedral cluster also shows no evidence of intramolecular CO migration up to 52 °C[60] as does the parent $Rh_6(CO)_{16}$ cluster.



19
●=Rh

A process formally related to the merry-go-round but based on six metal atoms would appear to operate in $Rh_{13}(CO)_{24}H_2^{3-}$. This cluster, representative of a hexagonal close-packed metal

cluster,[61] undergoes a ligand migration process below room temperature that equilibrates 21 of 24 ligand environments.[62] The mechanism proposed for this exchange, depicted in Figure 9a, is a synchronous process involving six terminal and three bridging carbonyl ligands about hexagonal belts of the polyhedron. Bridging carbonyls "A" cannot participate in this process without generating a nonequivalent configuration (Figure 9b).[62] Another unusual large cluster, $Rh_{17}S_2(CO)_{32}^{3-}$, which is based on stacked square antiprisms, **20**,[63a,c] is rigid on the NMR time



scale to temperatures above 100 °C. At 160 °C, one set of eight terminal and one set of eight bridging carbonyl ^{13}C resonances are equilibrated.[63b] The exchange could involve the two outer square faces and comprise a merry-go-round process operating on a square rather than a triangular face. The high temperature required for the ligand migration to become ^{13}C NMR detectable is in accord with the crystallographic evidence that the bridging carbonyls do not form a common plane or cone with the terminally bonded carbonyls.[63a]

D. Ligand Migration in Four-Metal Atom Butterfly-Type Structures

A potentially common ligand migration process for M_4 butterfly structures which may be regarded either as a four-metal center exchange, or a two-center exchange in which there is a mono-bridged intermediate, has been postulated for the observed carbonyl migration in $Co_4(CO)_{10}(C_6H_5C{\equiv}CC_6H_5)$. This mechanism is depicted in Figure 10 and comprises in essence the breaking and re-forming of unsymmetric carbonyl bridge bonds across opposite edges of the Co_4 framework. The ligand migration defines two intersecting planes which are nearly coincident with the two Co_3 planes in the Co_4C_2 framework.[64]

E. Ligand Exchange Involving a Face-Bridging Ligand

Any ligand exchange process that involves a ligand bridging a triangular face is by structural definition a three-metal center process. Ligand migration processes involving either a face-bridged ligand ground state, excited state, or transition state would seem at first glance to be an eminently reasonable process. In fact, a plausible physical process of this type was described in the tetrametal dodecacarbonyl section for the **4** ⇌ **7** conversion in $M_4(CO)_{12}$ clusters. Generally speaking, such processes seem feasible for metal clusters which have four or more polyhedral faces where concerted processes operating on several faces can preserve electronic balance in excited or transition states. Operation of such a process in a three-metal cluster or only at one face of a larger cluster does present problems in maintaining an electronic balance at each metal atom. Relatively little is known about ligand migration processes based on a face-bridged ligand. Notably some classic structures like $Rh_6(CO)_{16}$ (**16**) which have face-bridging ligands show no

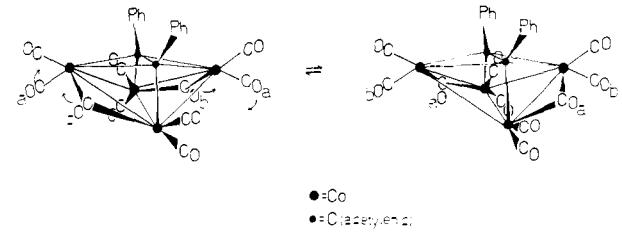
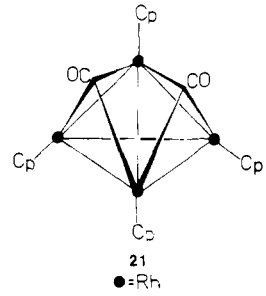
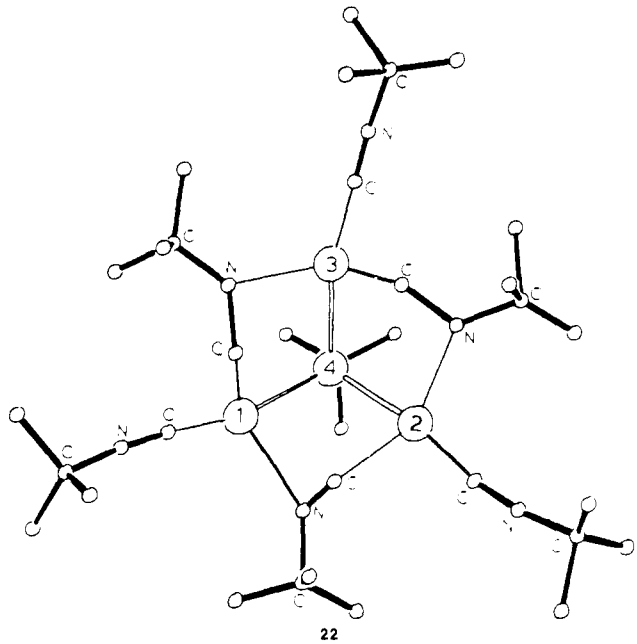


Figure 10. Proposed ligand migration scheme for butterfly type clusters like $Co_4(CO)_{10}C_2(C_6H_5)_2$.

evidence of ligand migration at 20 °C or slightly above. Such systems should be examined at higher temperatures. On the other hand, $(\eta^5\text{-}C_5H_5)_4Rh_4(CO)_2$ (**21**) and $Rh_6(CO)_{15}^{2-}$ (**15**), both



of which have face-bridging carbonyl ligands, exhibit equilibration of carbonyl ligands below 20 °C, but the dominant exchange mechanisms in these clusters have not been defined.[53,65] Another somewhat unusual example is that of $Ni_4[CNC(CH_3)_3]_7$ (**22**)



where the C_{3v} metal framework is postulated to "breathe" so as to create an averaged T_d metal environment. The three bridging isocyanide ligands are postulated to scramble about the four equivalent faces of this time-averaged structure which then equilibrates the *terminal* basal and apical isocyanide environments.[66]

A face-bridging mechanism has been defined by Shapley and co-workers[67] for the C_s isomer of $[(\eta^5\text{-}C_5H_5)RhCO]_3$ (Figure 11-A), which is edge-bridged in the crystalline form.[68,69] It had been expected[65] that, since the carbonyls are not all cis and do not form a common planar or conical array, the high-temperature ^{13}C NMR spectrum would consist of two quartets (due to ^{103}Rh–^{13}C coupling) in 1:2 intensity ratio. This was observed at −120 °C, but the spectrum collapsed to a single quartet at 25 °C without any evidence of isomerization to the all-cis C_{3v}

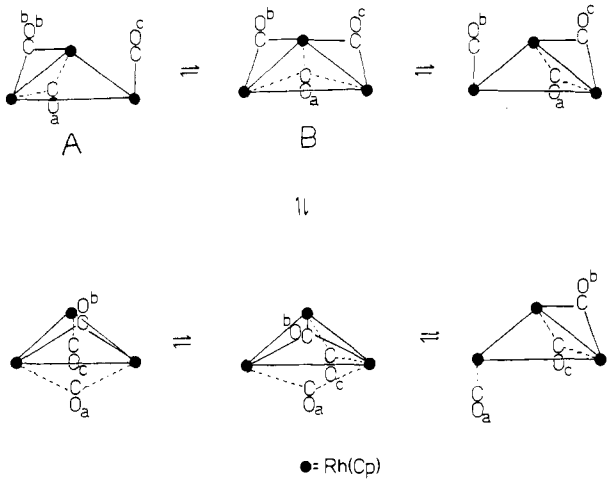


Figure 11. The proposed site exchange scheme for C_s $[RhCO(C_5H_5)]_3$.

isomer. These observations led to the mechanistic proposal outlined in Figure 11 which entails simultaneous motion about a face and an edge and which leads to averaging of the carbonyl environments without $C_s \rightleftharpoons C_{3v}$ interconversion.[67] The observation of the proposed intermediate (Figure 11-B) as the ground-state structure for $[C_5H_5Co(CO)]_3$[70] lends credibility to the proposed pathway.

V. Two Metal-Centered Ligand Exchange Processes

A. Introduction

Analysis of the available data for intramolecular ligand exchange in metal clusters clearly reveals the existence of exchange processes that involve the migration of ligands over two adjacent metal sites. However, because the large clusters often exhibit several different exchange processes, some of which are energetically distinguished by only a few kilocalories/mole, it often is not possible to unequivocally define the two-center processes. On the other hand, the dinuclear metal complexes which are not clusters (they may be considered as cluster prototypes) are potentially better models for study to define the full details of two-center site exchange processes. For this reason, the relatively definitive studies of two-center exchange based on dinuclear complexes are described in this section. The important established or implicated types of two-center exchange processes discussed in this section are organized on the basis of mechanism. These are (1) the pairwise exchange which was proposed and intensively investigated by Adams and Cotton[71-73] and (2) the one-for-one exchange presently implicated for Rh_2 complexes.[74,75] There is a formal similarity between the pairwise exchange process (two-center) and the merry-go-round process described above for triangular faces, wherein there is a pairwise character to the exchange. Each of these processes operates essentially in a plane that includes the two or three metal atoms.

B. Two-Center Pairwise Exchange Mechanism

Interchange of ligands about two metal centers in dinuclear complexes has been found to most commonly involve the pairwise mechanism illustrated in Figure 12. In this process, ligand bridges are opened and closed pairwise in a trans, coplanar, and concerted fashion.[71] In bridged dinuclear clusters this results in a nonbridged intermediate of sufficient lifetime that there may be rotation about the metal–metal bond prior to bridge reclosure which then may effect a cis $\rightleftharpoons$ trans isomerization. The latter occurs, once again, in a trans, concerted manner. It is important to recognize that when the bridged cluster is the

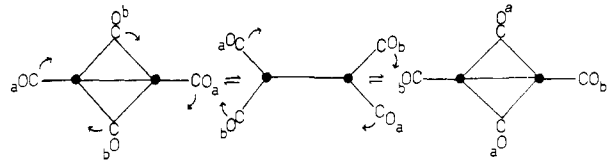
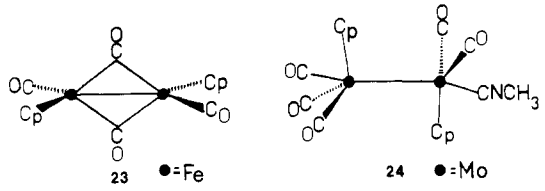


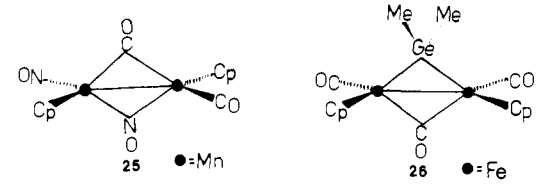
Figure 12. The pairwise, two-center exchange mechanism. Participating ligands are approximately coplanar and exchange in a synchronous fashion. Either structure may be the ground-state form.

ground-state structure, the time which the molecule spends as a nonbridged intermediate is negligible compared to the average time which it spends in the bridged form. Therefore, this intermediate is not commonly detectable by the NMR technique, nor methods such as infrared spectroscopy since, at any given instant, the population of the nonbridged excited state is very small. Rather, the presence of the intermediate is inferred as part of a mechanistically reasonable explanation of the permutational data. The isolation and characterization of closely related bridged, unsymmetrically bridged and nonbridged dinuclear clusters representative of various points along the theorized molecular pathway lend additional credence to the mechanistic proposal. This mechanism has been characterized for both bridged and nonbridged ground-state structures; *trans*-$[\eta^5$-$C_5H_5Fe(CO)_2]_2$ (**23**) is an example of the former,[71,76,77] and $(\eta^5$-$C_5H_5)_2Mo_2(CO)_5(CNCH_3)$ (**24**) is representative of the latter.[78,79] The observation of two cyclopentadienyl resonances



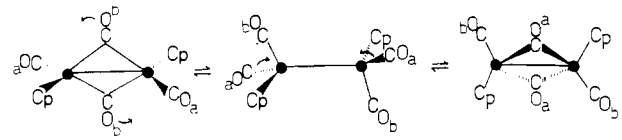
at −60 °C and only one C_5H_5 resonance in the ^1H NMR spectrum of **24** at 62 °C demonstrates that the isocyanide participates in the internuclear scrambling and, consequently, that pairwise exchange need not involve identical ligands.[79] Similarly, pairwise exchange of carbonyl and nitrosyl ligands is reported for **25**.[80]

A rather unusual pairwise exchange involving a $Ge(CH_3)_2$ group and a carbonyl ligand is proposed to account for the cis $\rightleftharpoons$ trans isomerization of $(\eta^5$-$C_5H_5)_2Fe_2(CO)_3(Ge(CH_3)_2)$ (**26**).[81]



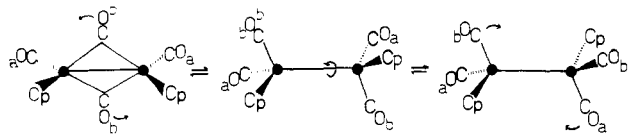
The $Ge(CH_3)_2$ group is not normally found in a terminal bonding position, implying that pairwise bridge opening would be a process with a substantially higher activation energy. In agreement, $\Delta G^{\ddagger}_{298}$ has been calculated to be 21.1 ± 0.9 kcal/mol, corresponding to about 50 rearrangements per second at 160 °C. This is just enough to coalesce the ^1H methyl resonances of the cis and trans isomers which are separated by only 10 Hz. However, the bridging and terminal ^{13}C carbonyl signals are separated by about 1600 Hz and require an exchange rate of about 3500 s^{-1} to reach coalescence. As a result, the carbonyl resonances are only slightly affected by the rather slow bridge $\rightleftharpoons$ terminal exchange process.[81]

In those instances where there are detectable quantities of both bridged and nonbridged forms of the cluster molecule, it may usually be inferred that the barrier to site exchange is low. This has been found for solutions of $Co_2(CO)_8$ (**27**) for which an equilibrium mixture of bridged and nonbridged has been established from infrared studies.[82] Explicably, $Co_2(CO)_8$ is fluxional



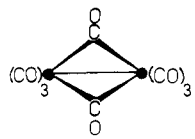
●=Fe

Figure 13. Pairwise ligand exchange process implicated for *trans*-$[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$.



●=Fe

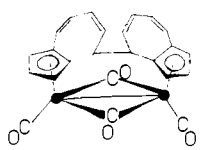
Figure 14. Ligand site exchange scheme proposed for *cis*-$Fe_2(CO)_4[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. Rotation of the nonbridged form is required for ligand interchange to occur in a trans, concerted manner.



27 ●=Co

on the NMR time scale below −90 °C, but the rearrangement mechanism is not established for this molecule.[64,83] A similar exchange may also occur in $Co_2(CNC_7H_9)_8$ for which the ^1H NMR resonances of the xylyl groups suggest that the isocyanides are rearranging rapidly on the NMR time scale below − 90 °C.[84]

Those dinuclear complexes whose dynamic behavior has been found to conform to the pairwise exchange mechanism, as formulated by Adams and Cotton, are subject to its mechanistic constraints, namely, that all bridge opening and closing occur pairwise in a trans, nearly planar oriintation. In this context, when intermetal ligand scrambling requires internal rotation of the nonbridged intermediate, the barrier to rotation contributes to the observed activation energy. Thus, in *trans*-$[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ (**23**), CO_a and CO_b may interchange directly through a nonbridged intermediate as shown in Figure 13, but in *cis*-$[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ an internal rotation (and concomitant cis to trans interconversion) of the nonbridged form is required for bridge terminal exchange to occur (Figure 14). Consistently, the trans form is fluxional[85] at −59 °C and the cis form is fully fluxional only at 53 °C.[71,76,77] Restricting rotation of the nonbridged intermediate impedes the operation of the pairwise exchange, so that in $\eta^{10}\text{-}C_{10}H_8\text{-}C_{10}H_8Fe_2(CO)_4$ (**28**), where the



28 ●=Fe

C_5H_5 rings are closely tied together, fast internuclear CO exchange occurs only above 80 °C.[86] Substitution of a phosphite for a terminal CO in **28** completely blocks bridge-terminal exchange by the pairwise exchange mechanism;[86] as depicted in Figure 15, the organic ligand makes the anti-rotamer, A, of the nonbridged intermediate unfavorable, so that to re-form the bridges in a trans fashion using carbonyl "a" would require an unlikely bridging phosphite isomer, B. As expected, there is no fast interchange of carbonyls "a" and "b" in phosphite derivatives up to 100 °C.[86] In like manner, one may explain the dynamic behavior of dinuclear clusters in terms of the pairwise exchange mechanism, and trends in rearrangement rates can be predicted where this mechanism is geometrically feasible.

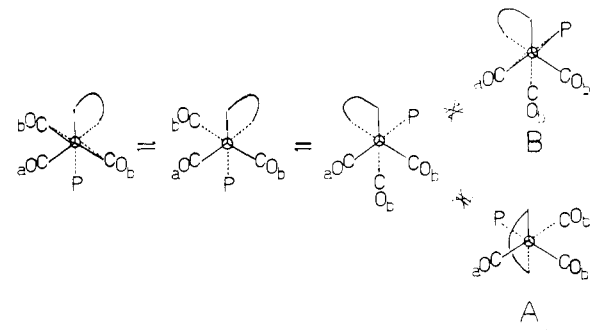


Figure 15. The blocking of pairwise ligand exchange in $(\eta^{10}\text{-}C_{10}H_8\text{-}C_{10}H_8)Fe_2(CO)_3P$ by the bidentate organic ligand. The molecule is represented as a projection down the Fe–Fe axis. Dotted lines represent bonds to the "hidden" iron center.

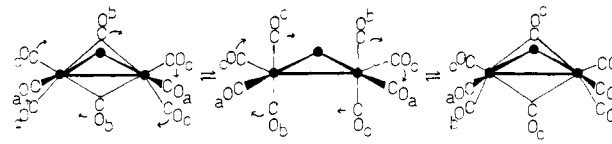
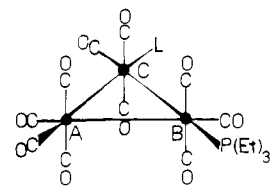


Figure 16. Pairwise ligand exchange over two metal sites in trimetallic clusters. The six participating ligands are approximately coplanar.

A process closely related to pairwise exchange has been well documented for trimetallic clusters which are either nonbridged or bridged (in the plane of the three metal atoms). This mechanism, depicted in Figure 16, entails the synchronous movement of six ligands in a circular fashion about two metal centers where once again ligand bridges are formed and broken in a pairwise fashion. Repetition of this process about the same two metal centers will lead to the equilibration of ligands b and c in Figure 16, while repetition about different pairs of metals will lead to multicenter ligand mobility. For triangular metal clusters undergoing ligand scrambling via this route, the exchange process requires the approximate coplanar arrangement of the six participating carbonyls. Those two sites "trans" to M_1 (CO_a in Figure 16) are roughly perpendicular to the near plane formed by the other six carbonyl ligands and do not participate in this exchange. Indeed, X-ray analyses indicate that in analogous bridged and unbridged structures these sites occupy almost identical positions.[45] The activation energy for this type of exchange appears to be lowered about an M–M edge where a phosphine has been substituted for a "trans" carbonyl ligand (CO_a in Figure 16).

Pairwise exchange about two metal sites in a trimetallic cluster is well defined from studies of phosphine derivatives of $Os_3(CO)_{12}$ where individual carbonyl ligands can be more incisively delineated in the ^{13}C spectrum of the derivative cluster. The parent cluster $Os_3(CO)_{12}$ exhibits the structurally expected inequivalence of axial and equatorial carbonyl ligands in its ^{13}C NMR spectrum at 25–100 °C; exchange occurs above 100 °C, but the mechanism, be it centered on one, two, or three metal sites, cannot be defined from the NMR data.[41,42] Phosphine substitution may neatly block the common type of three-center exchange. Nevertheless, the phosphine substituent(s) promotes exchange at two-center sites which include the metal atom with the phosphine substituent. Thus in $Os_3(CO)_{11}P(C_2H_5)_3$ (**29**), a



29 ●=Os
L=CO
30 L=P(Et)$_3$

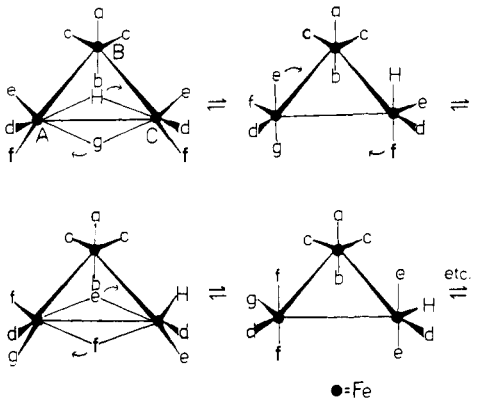


Figure 17. Possible pairwise exchange in $HFe_3(CO)_{11}^-$ in which a nonequivalent configuration is generated.

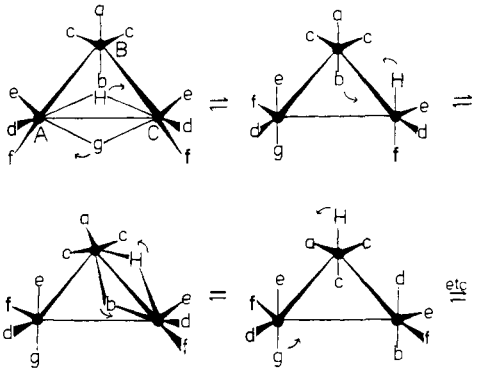


Figure 18. Possible pairwise exchange in $HFe_3(CO)_{11}^-$ in which an equivalent configuration is generated.

rapid exchange of six carbonyl ligands is evident in the ^{13}C NMR spectrum at 25 °C, and is consistent with the exchange process depicted in Figure 16 operating about the Os_A–Os_B edge. Note here that the edge with no phosphine substituent does not have a pairwise exchange mechanism operating at 25 °C over these two unsubstituted metal atoms. The phosphine substitution promotes two-center axial–equatorial exchange about that edge which has a phosphine in a "trans" position, and at a much lower temperature than that required for axial–equatorial interchange in the parent cluster. With the substitution of another equatorial carbonyl ligand by triethylphosphine, $Os_3(CO)_{10}[P(C_2H_5)_3]_2$ (**30**), a fluxional structure is generated, and in this case, the pairwise exchange occurs at 5 °C, and the ^{13}C DNMR data indicate that this pairwise exchange operates only about the Os_A–Os_B edge.[45] Note that a similar pairwise exchange about the Os_A–Os_C or Os_B–Os_C edge would require the phosphine substituent to assume an axial position, a feasible process but one that should be of higher energy than that for the Os_A–Os_B centers where only equivalent configurations (with differently "labeled" ligand sites) are generated.

Triiron dodecacarbonyl exhibits a single ^{13}C resonance down to −100 °C.[40] Here the apparent ligand exchange process cannot be studied, but it has been commonly presumed that this exchange occurs through a rapid interconversion of the bridged C_2 form, **10**, and the nonbridged D_{3h} form, **11**, as discussed in the preceding section on the $M_3(CO)_{12}$ clusters. (This carbonyl cluster does not have C_{2v} symmetry because the bridging carbonyl ligands are unsymmetric.) The proposed $C_2 \rightleftharpoons D_{3h}$ or idealized $C_{2v} \rightleftharpoons D_{3h}$ process allows for migration of all carbonyl ligands about the cluster if the D_{3h} excited state is an intermediate. If there is no intermediate state, the process is the two-center pairwise exchange. Thus for a trimetallic cluster, there may be multicenter exchange over three sites, localized exchange over two metal sites, or in a multistep two-site process effective ligand exchange over three metal centers. The character of exchange in trimetallic clusters where the two-center

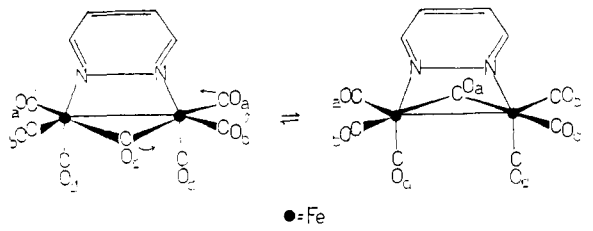


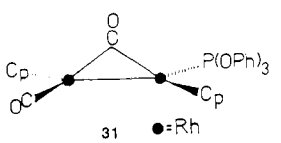
Figure 19. Proposed ligand migration mechanism for $Fe_2(CO)_7(C_4H_4N_2)$. The migrating carbonyls are approximately coplanar.

pairwise and the multicenter exchange mechanisms are feasible will depend upon the relative energies of the molecular configuration that can be generated by this pairwise exchange. This point is rather nicely illustrated in the NMR spectra for $HFe_3(CO)_{11}^-$ (Figure 17-A).[42,87] Scrambling of carbonyls labeled e, f, and g by a two-center process as in Figure 17 leads via a nonbridged excited state to intermediate bridged structures with the hydride in nonbridged equatorial and axial positions. Since the resulting structure is hydride bridged, these configurations clearly would be of higher energy. In contrast, multicenter exchange (Figure 18) would lead directly from a nonbridged excited state to an equivalent, hydride bridged configuration. The experimental observation is that in the low-temperature (i.e., less activated) process, the environments of carbonyls g and b are averaged, and, a, c, d, e, and f are averaged but not with g and b. All this is consistent with a multicenter ligand migration. It is interesting to note that the first report on the dynamic behavior of $HFe_3(CO)_{11}^-$ proposed that the lowest temperature process consisted of pairwise exchange between Fe_B and Fe_C, and between Fe_B and Fe_A, with the hydrogen and carbon monoxide bridging ligand pair between Fe_A and Fe_C remaining stationary.[42] The presence of a stationary pair of diaxially bridging ligands on an adjacent edge would make pairwise exchange about the other two edges of the metal triangle a process stereochemically distinct from the mechanism of Figure 16. Such a process has not yet been delineated for any cluster systems.

Dinuclear systems which possess only one bridging CO in the solid-state structure cannot be expected to operate by pairwise bridge opening and closure. However, the pseudo-planar arrangement of participating ligands is maintained in clusters where the bridging CO and one or more terminal carbonyls are approximately coplanar. Such a process may be operative in $Fe_2(CO)_7(C_4H_4N_2)$, which is monobridged in the ground state.[88] In the low-temperature process only carbonyls a, b, and c, which are approximately coplanar, were observed to exchange (^{13}C NMR study) in a "synchronous" fashion (Figure 19). The same process probably operates in $Fe_2(CO)_5[(C_6H_5)_2PCH_2P(C_6H_5)_2]$.[89] This mechanism may be viewed as a prototype for the two-center exchange process found in many M_3 clusters (Figure 16). A similar process is believed to operate in $Fe_2(CO)_7[\mu\text{-}SnCH_3(C_6H_5)]_2$, where bridge-terminal exchange may be coordinated with a flapping motion of the tin group bridges as depicted in Figure 20, and could account for the character of the ^{13}C and ^1H NMR data.[90]

C. One-for-One Two-Center Ligand Exchange

A possible two-center exchange process which does not involve coplanar ligands is the concerted one-for-one ligand exchange mechanism. This type of mechanism has been postulated from DNMR studies for *trans*-$(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$,[74] shown in Figure 21, and for the phosphite derivative $(\eta^5\text{-}C_5H_5)_2$-



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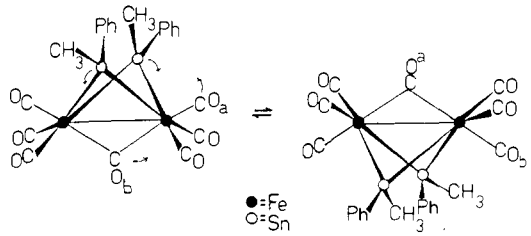


Figure 20. Proposed "bridge flapping" in conjunction with bridge ⇌ terminal CO exchange for $Fe_2(CO)_7[\mu\text{-}SnCH_3(C_6H_5)]_2$.

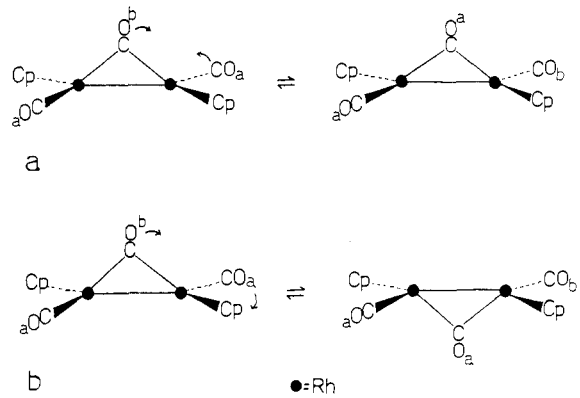
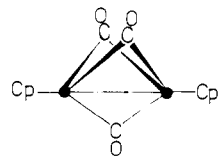


Figure 21. Two possible pathways for the one-for-one exchange in $Rh_2(\eta^5\text{-}C_5H_5)_2(CO)_3$. In a, the carbonyls exchange through a "cis" oriented pathway. In b, the carbonyls exchange through a "trans" oriented pathway. This latter mode of exchange would generate the optical enantiomer of the molecule.

$Rh_2(CO)_2P(OC_6H_5)_3$ (**31**).[75] Since trans → cis isomerization was not observed, the lifetime of any nonbridged form of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ is presumed to be short with respect to the time required for trans ⇌ cis isomerization to occur via rotation about the Rh–Rh bond.[1] However, this interpretation is not definitive because the cis form has not yet been isolated, and its energy relative to the trans form is unknown; if the equilibrium constant is small, the cis isomer might escape detection in the NMR experiment.

The crystal structure of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ established that the bridge and terminal carbonyls are not coplanar in the solid state of this complex.[91] It is possible that carbonyl interchange in this dinuclear complex occurs by cii pairwise exchange through a triply bridged intermediate (**32**). However, the variable-temperature ^{31}P NMR data for **31** unequivocally show that the phosphite remains associated with only one rhodium center so that pairwise carbonyl and phosphite exchange cannot be occurring through a triply bridging excited state.[75]



32

In nonbridged dinuclear clusters such as $(C_9H_8)Fe_2(CO)_4L$ (L = CO, $P(C_2H_5)_3$) (Figure 22-A), internuclear CO exchange has been detected and is proposed to involve CO transfer from Fe_1 to Fe_2 with concomitant redistribution of the π electrons of the 7-H indene ligand so as to maintain electroneutrality at the individual iron centers (Figure 22).[92] This represents another distinct two-center pathway. Interestingly, in the phosphine derivative, only one carbonyl of the $Fe(CO)_2P(C_2H_5)_3$ unit participates in this process.

D. Two-Center Exchange. Conclusions

The critical and common feature of the two-center mechanisms of Figures 12, 16, and 19 is the coplanar or nearly coplanar arrangement of the migrating ligands. As such it would appear that these mechanisms would only be applicable to those clusters that have an area both "above and below" the metal–metal bond accessible to ligands, i.e., "flat" metal clusters. This constraint eliminates these mechanisms from operating in metal clusters which form polyhedra, typically clusters with four or more metal atoms, and to date, coplanar two-center pathways have not been delineated for any clusters with more than three metal atoms. Indeed, there has been, as yet, no unambiguous delineation of any two-center processes for metal cluster polyhedra. However, two-center processes such as the one-for-one exchange depicted in Figure 21 or hypothetical cis, pairwise bridge exchange outlined in Figure 23, would not, a priori, seem unreasonable,[93,94] and such mechanisms may be established in future investigations.

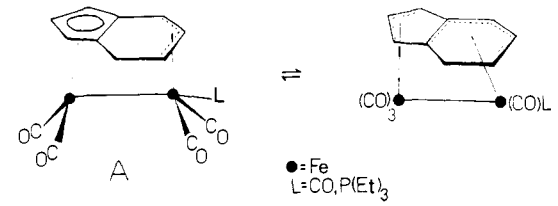


Figure 22. Carbonyl migration scheme proposed for $C_9H_8Fe_2(CO)_4L$.

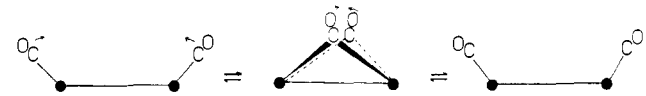


Figure 23. Hypothetical cis-pairwise ligand exchange mechanism between two metal centers.

VI. "Defect" Structures

Another interpretation of fluxional behavior has been proposed in which ligand migration is predicted for "defect" structure clusters.[7] A "defect" in a cluster structure may be viewed as a departure from the molecular symmetry of the cluster by one metal center, edge, or face. Thus, $Rh_4(\eta^5\text{-}C_5H_5)_4(CO)_2$ (**21**) possesses two open or "defect" faces and is fluxional at room temperature.[65] Similarly, $Rh_6(CO)_{15}^{2-}$ (**15**) is the "defect" analog of $Rh_6(CO)_{16}$ (**16**) in which one face-bridging CO has been replaced by three edge bridges; the former is fluxional at −70 °C while the latter is rigid at +70 °C.[53] The defect argument may even be extended to $Os_3(CO)_{11}P(C_2H_5)_3$ (**29**), the defect analog of $Os_3(CO)_{12}$ (**11**). In this instance one CO has been replaced by a phosphine and the "defect" phosphine derivative is fluxional approximately 100 °C below **11**.[45]

VII. Effect of Charge on Carbonyl Ligand Migration in Clusters

Increased negative charge on the cluster appears to lower the barrier to carbonyl ligand migration. Thus, $[Rh_{13}(CO)_{24}H_2]^{3-}$ (**25**) is stereochemically nonrigid at −80 °C, whereas the isostructural $[Rh_{13}(CO)_{24}H_3]^{2-}$ is "fluxional" only above 25 °C.[62] Analogous behavior is reported for $[Rh_4(CO)_{11}]^{2-}$ and $[Rh_4(CO)_{11}(COOCH_3)]^{-}$.[95] The genesis of this rate enhancement has been ascribed to increased electron density on the cluster skeleton which then makes intermediate carbonyl-bridged structures more favorable.[95] A bridging carbonyl group is more effective than a terminal group in removing electron density from the metal and increase in electron density often shifts even the ground-state structure from an all terminal ligand array, e.g., $Ir_4(CO)_{12}$, to a bridged array, as in $Ir_4(CO)_{12-x}(PR_3)_x$. A quantitative analysis of ligand migration is complicated by the structural changes which often accompany a change in electron density

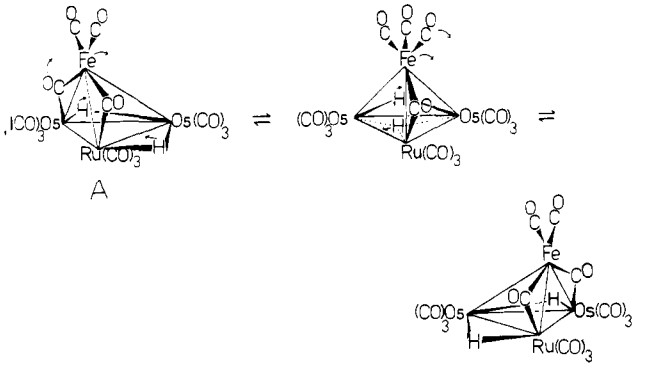


Figure 24. Proposed metal framework deformation in concert with hydride and carbonyl migration for $H_2FeRuOs_2(CO)_{13}$.

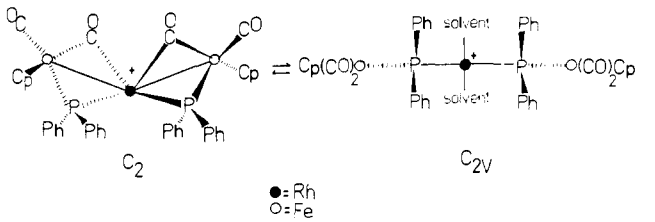
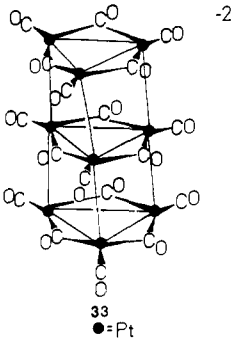


Figure 25. Proposed equilibration of carbonyl environments via metal–metal bond breaking in $[Rh\{Fe(PAr_2)(CO)_2(\eta^5\text{-}C_5H_5)\}_2]^+$. Solvent coordination is proposed to aid formation of a C_{2v} intermediate which effects racemization. There are alternative mechanisms.

on the metal atom. An interesting experimental test of this plausible hypothesis would be the investigation of CO mobility in the isostructural series $[Pt_3(CO)_6]_n^{2-}$ (n = 1–6) (**33**).[95a] In this family of clusters, the electron density on the metal atoms is proportionately decreased by the addition of more $[Pt_3(CO)_6]$ units to the cluster helix, and, on this basis it might be expected that CO scrambling would become less facile as the cluster size is increased.



33

VIII. Metal Framework Reorganization in Metal Clusters

Just as ligand atom positions in clusters may be substantially affected by low energy bending and stretching modes, so should the relative metal atom positions in clusters be affected. Because of the intrinsic multicenter bonding in cluster polyhedra, facile metal atom migrations about cluster site positions, analogous to the ligand migrations, is not probable, but reorganization of the cluster framework, e.g., conversion of a compressed C_{3v} tetrahedral array to a regular tetrahedral array, may be an integral element in some processes that lead to equilibration of ligand environments. Interestingly, metal surfaces show some plastic behavior. Some of the less densely packed faces in close-packed metals, e.g., the 110 face in close-packed metals, undergo surface structure reorganization in chemisorption processes. Generally, metal atom migration on close-packed surfaces has a relatively high activation energy (40–80 kcal/mol) as judged from field emission spectroscopy studies of metal crystal faces on which a second metal has been introduced.

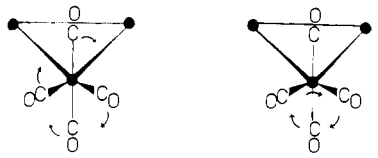
Participation of the metal framework in the fluxional process, as postulated for $Ni_4[CNC(CH_3)_3]_7$,[66] has been reported only infrequently; in most systems investigated, the metal cluster itself is considered to serve as a static "surface" about which ligand scrambling occurs. However, stereochemical nonrigidity of the cluster framework has been proposed for several metal clusters. In $H_2FeRuOs_2(CO)_{13}$ (Figure 24-A) there is believed to be a stretching of the Fe–Os and Fe–Ru skeletal bonds concurrent with motion of both a bridging carbonyl and a bridging hydride which generates the molecular enantiomer of the cluster.[49] This is depicted in Figure 24.

Actual metal–metal bond breaking is postulated to occur in the chiral complex $[Rh\{Fe[P(C_6H_5)_2](CO)_2(\eta^5\text{-}C_5H_5)\}_2]^+$.[96] As shown in Figure 25, the Rh–Fe interactions are broken with solvent assistance and with the simultaneous breaking of the Rh–CO bridge bonds. This generates a C_{2v} intermediate which, possessing two mirror planes, serves to equilibrate all four carbonyls in one step and racemize the complex. Skeletal mobility is even more pronounced in $Pt_9(CO)_{18}^{2-}$ (**33**).[95,97] Analysis of the coupling patterns in the ^{195}Pt NMR spectrum has led to the conclusion that the outer Pt_3 triangles are rapidly rotating with respect to the inner Pt_3 unit, even at −85 °C. Thus in a localized sense there is a rapid breaking and remaking of Pt–Pt bonds, so that the metal framework may hardly be considered to be conformationally rigid. Similar behavior is reported for $[Rh_2Pt(CO)_x]_2^{2-}$.[98] A dramatic *intermolecular* exchange involving the cluster framework is reported to occur between $Pt_9(CO)_{18}^{2-}$ and $Pt_{12}(CO)_{24}^{2-}$. At room temperature, the two clusters are reported to exchange $Pt_3(CO)_6$ units at a rate which is fast on the Pt NMR time scale.[95,97]

The potential for dynamic behavior of the cluster framework is the essence of an alternative explanation of the fluxionality of $Fe_3(CO)_{12}$ advanced by Johnson.[99] In this proposal, which places an emphasis on ligand–ligand van der Waals interactions rather than ligand–metal bonding interactions, the 12 carbonyl ligands which form a static icosahedral array are proposed to rotate with respect to the Fe_3 unit. Such a process would be concerted in the sense that all 12 carbonyl ligands are simultaneously involved in any bond-making and bond-breaking processes. However, this model has been criticized[20] on the grounds that it is inconsistent with the data from other M_3 clusters in which one or more carbonyls have been replaced by other ligands. Recently, Johnson's approach has been extended to larger clusters by Evans.[10]

Although participation of the cluster framework in fluxional processes has only recently been documented, stereochemical nonrigidity of the metal skeleton should not be unexpected since clusters easily undergo skeletal transformations upon changes in oxidation state or the numbers of ligands. Furthermore, both thermochemical data[100] and molecular orbital calculations[101] for carbonyl metal clusters indicate that *on average* the metal–metal bonds are slightly weaker than the metal–carbonyl bonds (however, in some clusters the lowest energy dissociative process is loss of a ligand, not scission of a metal–metal bond especially for clusters based on second and third row metals).

Deformations of a cluster framework must occur to some extent in many cluster–ligand rearrangements. For example, the C_s ground-state structure of $HFe_3(CO)_{11}^-$ (Figure 17-A) possesses bridged and unbridged Fe–Fe edges of 2.577 and 2.690 Å (esd of 0.003 Å), respectively.[102] Mobility of carbonyl and hydride ligands is presumed to take place via the all terminal intermediate in Figure 17, which re-forms bridges about a previously nonbridged edge so as to generate an equivalent configuration. This requires an Fe–Fe bond length reorganization of 0.113 Å during ligand migration.[87]



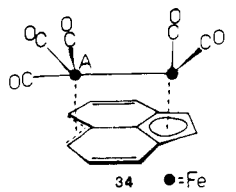
a b

Figure 26. (a) Pseudo-fourfold rotation of four carbonyl ligands at a single metal center of a trimetallic cluster. (b) Pseudo-threefold rotation of two equatorial and one axial carbonyl at a single metal center of a trimetallic cluster.

IX. Ligand Exchange about a Single Metal Center

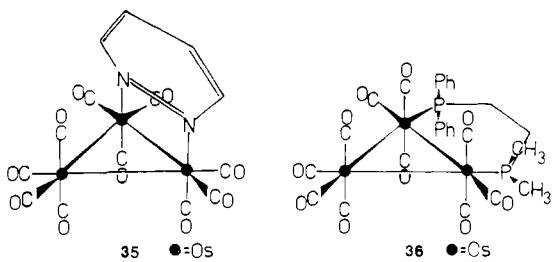
Ligand exchange about one metal center is a commonly detected process in metal clusters, and it is a process well documented for mononuclear coordination complexes. Two general mechanisms have been found in dinuclear and cluster complexes: simple scrambling of terminal ligands about one metal center, and the breaking of an unsymmetrically bridging ligand–metal bond at the longer metal to bridging ligand bond side, followed by ligand scrambling at the metal which formed the shorter metal to bridging ligand bond.

Ligand exchange at a single metal site is nicely illustrated by the temperature-dependent ^{13}C NMR spectra of $Fe_2(CO)_5$(acenaphthalene) (**34**), which show a "scrambling" of the carbonyl



34 ●=Fe

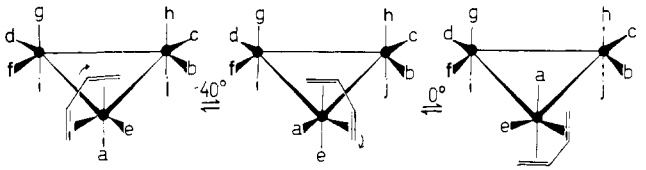
ligands about Fe_A at 75 °C, but no evidence of internuclear CO migration at that temperature.[103] The detailed nature of carbonyl motion about one metal center has been investigated for M_3 clusters. The studies have addressed the issue of whether CO scrambling on an $M(CO)_4$ unit occurs by a pseudo-fourfold (pairwise) or pseudo-threefold (nonpairwise) rotation process (Figure 26a, b). Extensive ^{13}C NMR investigations for $(C_4H_4N_2)Os_3(CO)_{10}$ (**35**)[104] and $Os_3(CO)_{10}((CH_3)_2PCH_2CH_2(C_6H_5)_2)$ (**36**)[43] have shown that, at least for these systems,



35 ●=Os **36** ●=Os

the pseudo-threefold or nonpairwise rotation process occurs on the unique $M(CO)_4$ unit and is the prevailing low-temperature exchange process. The dynamic behavior of $Os_3(CO)_{10}$(1,3-cyclohexadiene) is different.[105] The low-temperature process, at −40 °C, is consistent with a pseudo-fourfold 90° rocking motion (Figure 27) about the diene-substituted osmium, which then is proposed to progress to a 360° rotation at 0 °C.[105]

The second type of mechanism may operate in systems with an unsymmetrically bridging carbonyl group such as $(C_6H_5)_4C_4Fe_2(CO)_5L$ (**37**, L = CO, $P(C_6H_5)_3$),[106] and $(C_6H_8O_2)Fe_2(CO)_6$ (**38**),[107] where carbonyl scrambling about one metal center has generally been found to occur first on the metal atom with the *shorter* bridging bond, and to include the unsymmetrically bridging CO. Specifically, the bridge bond is broken on the longer and presumably weaker side, and rotation of carbonyl ligand units



●=Os_5

Figure 27. Pseudo-fourfold rotation proposed in $Os_3(CO)_{10}$(1,3-cyclohexadiene).

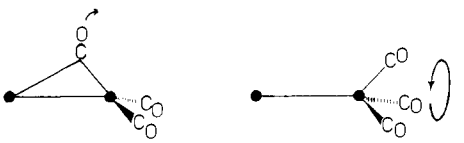
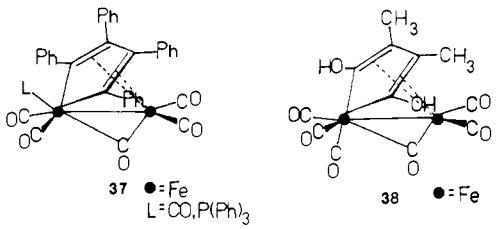
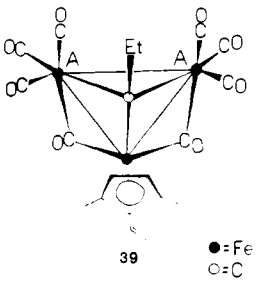


Figure 28. Representation of the scission of an unsymmetrically bridging carbonyl bond on the long side followed by carbonyl ligand scrambling.



37 ●=Fe L=CO,$P(Ph)_3$ **38** ●=Fe

follows. This is depicted in Figure 28. There is one reported complex, $Fe_3[C(C_2H_5)][\eta^5\text{-}C_5H_2Me_2(C_2H_3)](CO)_8$ (**39**), for which

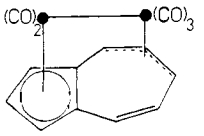


39 ●=Fe ○=C

the ^{13}C DNMR data show that the terminal carbonyl ligands scramble while the bridging carbonyls remain magnetically distinct.[108] The NMR spectra do not establish whether the carbonyl interchange is about the individual iron centers or if it entails *inter*metal carbonyl exchange through a bridging intermediate. However, the observed ligand mobility in **39** does not exclude the possibility that the process occurs by first breaking the bridging CO bond to Fe_A followed by carbonyl scrambling about Fe_A and then subsequent reclosure of the bridge bond by the *same* carbonyl to Fe_A. Thus, for this mechanistic possibility, breaking the unsymmetrically bridging CO–metal bond on the longer side would still be a prerequisite to scrambling of the terminally bound ligands.

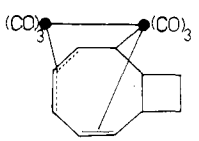
When it is not energetically feasible for a ligand to bridge between metal centers then intermetallic ligand exchange is ruled out. It would seem reasonable, then, that as the metal–metal bond distance increases a bridging interaction should become less accessible, and the energetic barrier to intermetal ligand exchange should also increase. To a first approximation, it appears that the M–M bond length might be utilized as a gauge for the ease of internuclear ligand migration. Indeed, it is generally observed that bridged ground-state structures are less common for the 4d and 5d transition elements where the M–M bond distances are generally longer than for analogous clusters of the 3d elements. Such is the case with $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$; only the iron cluster is bridged in the crystalline form. However, in $RhCo_3(CO)_{12}$ a $RhCo_2$ face and not the smaller Co_3 face has three edge-bridging carbonyl ligands. Further, it

is typically found, although not without some exceptions,[109,110] that for analogous clusters of a transition metal group, ligand migration becomes less facile within the group in proceeding from the 3d to the 4d and from the 4d to 5d elements. Thus, $Fe_2(CO)_5$(azulene) (**40**) undergoes internuclear exchange at 85

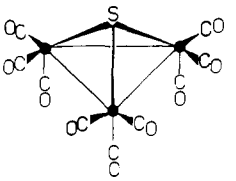


40 ●=Fe,Ru

°C whereas the corresponding process in $Ru_2(CO)_5$(azulene) occurs in excess of 105 °C[111] and $Ru_3(CO)_{12}$ is fluxional at low temperatures, whereas the isostructural osmium cluster does not rapidly rearrange until temperatures of 60 °C are reached. However, it appears that electronic differences between the 3d, 4d, and 5d metals are of equal or greater importance than the M–M bond distance criterion. The same order in fluxionality of 3d > 4d > 5d occurs both in mononuclear complexes where there is no M–M bond to consider, and in heterometallic clusters where fluxionality is observed about *individual* metal centers. Examples of the latter class include $H_2FeOs_3(CO)_{13}$ and $H_2FeRu_3(CO)_{13}$, where the low-temperature process consists of CO scrambling about the lone iron centers in each cluster.[48,49] Additionally, in closely related clusters where the ligand scrambling is about the *individual* metal centers, such as $Fe_2(CO)_6(\eta^6\text{-}C_{10}H_{12})$[112] and $Ru_2(CO)_6(\eta^6\text{-}C_{10}H_{12})$ (**41**),[113] there



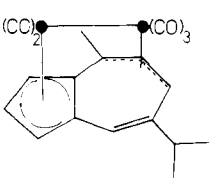
41 ●=Fe,Ru



42 ●=Ru,Os

is usually a smaller activation energy in the cluster with the lighter metal centers; the $Fe(CO)_3$ and $Ru(CO)_3$ units of **41** are fluxional at −50 and +60°C, respectively. An analogous trend has been reported for $H_2M_3(CO)_9S$ clusters with M = Ru or Os, **42**.[114] In $RhCo_3(CO)_{12}$, the two terminal carbonyl ligands bonded to rhodium are the "last" to exchange with the remaining set (at this point averaged set) of carbonyl ligands.

A more valid test of the metal–metal bond length criterion would be to compare the ease of intermetal ligand scrambling in structurally related clusters of a specific metal. Such a comparison has been made for at least one family of cluster molecules, $Fe_2(CO)_5$(cycloolefin), where the cycloolefin is azulene (**40**), guaiazulene (**43**), 7-*H*-indene (Figure 22-A), and ace-

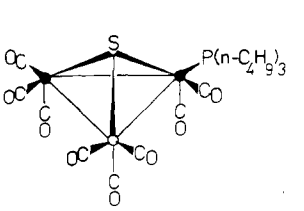


43 ●=Fe

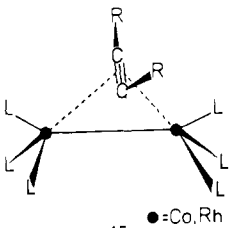
naphthalene (**34**).[92] The wide variations in the barrier to internuclear CO scrambling cannot be reconciled with the Fe–Fe bond lengths which are all about 2.8 Å in this isostructural series. Therefore, for this family of clusters, electronic and steric properties of the polyene are dominant contributors to the activation barrier for intermetal ligand migration. Analogous data for cluster series where the metal–metal bond length is *not* constant, are quite limited and are from structurally diverse sets.

Substitution of a carbonyl ligand by a phosphine or phosphite ligand appears to lower the activation barrier to localized CO scrambling at an adjacent metal center. This has been noted for $C_{10}H_{12}Fe_2(CO)_5L$ (**41**, L = CO, $P(CH_2CH_3)_3$), where the coalescence temperature for CO scrambling about Fe_B is 45 °C lower in the phosphine derivative than in the unsubstituted dinuclear complex.[112] Similarly, in the cluster $SFeCo_2(CO)_8[P(OC_6H_5)_3]$ (**44**), CO scrambling is more facile at the $Co(CO)_3$ unit than at the phosphine-substituted Co center.[115]

In order to rationalize this effect for **44** relative to the parent nonacarbonyl, it has been noted that electron density donation by a phosphite should weaken the metal–metal bonds of the cluster because the LUMO is antibonding with respect to the cluster framework.[116] The weakened metal–metal bonds facilitate the rotation of the $M(CO)_3$ unit as a *whole* with respect



44 ●=Co ○=Fe



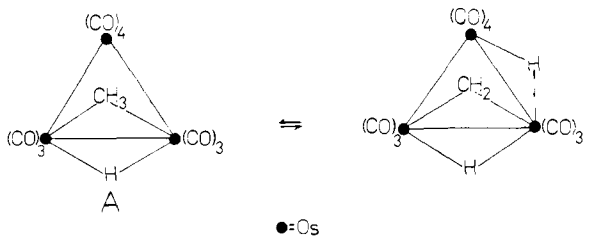
45 ●=Co,Rh L=CO,PF_3

to the rest of the cluster.[115] This interpretation of ligand scrambling at a single metal center is conceptually distinct from the pseudo-threefold rotation of three carbonyl ligands envisioned for **36**[43] and has also been considered in NMR investigations of "sawhorse" complexes of the types $Co_2(CO)_6(RC_2R')$ and $Rh_2(PF_3)_6RC_2R'$ (**45**, R, R′ = alkyl, aryl).[117,118] These studies have shown that as the electronegativity of the acetylene substituents increases, the activation energy for ligand migration about a single metal center also increases. This is ascribed to the increasing strength of the metal acetylene bond as the electron-accepting ability of the acetylene increases.[117,118] Thus, for these systems it is more appropriate to consider ligand mobility based on rotation of the ML_x unit rather than a polytopal rearrangement about the individual metal center.

X. Organic Ligand Rearrangement Processes in Clusters

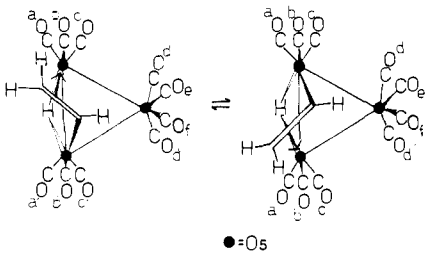
The mobility of organic ligands in metal clusters cannot be easily classified in a mechanistic context with those of the relatively simple donor ligands H, CO, NO, and RNC because of the common multicenter bonding of these organic ligands and the π- and σ-bonding versatility of many organic ligands. There have been few reports of intracluster mobility of simple alkyl groups. This is probably due to the special instability problems often encountered with transition metal alkyl compounds which has limited their investigation. Internuclear alkyl group exchange is well documented for the group 3 metal trialkyl dimers (for which there are no metal–metal bonds), and so it is reasonable to anticipate that similar processes will be delineated for transition metal clusters in the near future. One extremely intriguing alkylmetal cluster system not only shows a methyl bridging ligand but also a facile interconversion with a hydridometal complex with a bridging methylene ligand. In $HOs_3(CO)_{10}CH_3$ the methyl group unsymmetrically bridges one edge of the cluster (Figure 29-A), and this complex is in equilibrium with a second hydride cluster complex $H_2Os_3(CO)_{10}CH_2$, wherein the methylene group symmetrically bridges a cluster edge.[119]

Olefinic systems have been shown to undergo migration over the cluster surface, although the olefinic ligand retains its basic position in the cluster. The cluster prototype, $Fe_2(CO)_5(C_8H_8)$ (**46**), shows this type of behavior; the barrier to rotation of the cyclooctatetraene ring is only about 2 kcal/mol as determined from a solid-state NMR investigation.[120] Similarly, for $Ni_3(CO)_3(C_8H_8)(CF_3C_2CF_3)$ (**47**), in which the Ni framework de-



●=Os

Figure 29. Representation of the proton tautomerism established for $HOs_3(CO)_{10}CH_3$. There is evidence that the methyl group unsymmetrically bridges between the osmium centers with an Os–C–H–Os type of binding.



●=Os

Figure 30. The $\sigma \rightleftharpoons \pi$ interconversion proposed for $HOs_3(CO)_{10}CHCH_2$.

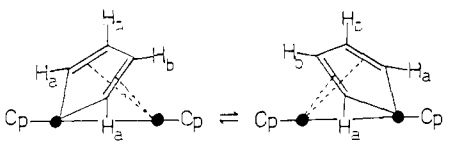
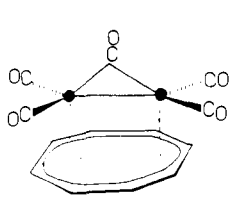
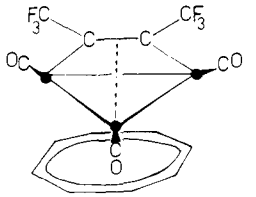


Figure 31. The proposed $\sigma \rightleftharpoons \pi$ ferrole ring interconversion where hydrogen atoms "a" and "b" remain magnetically distinct.

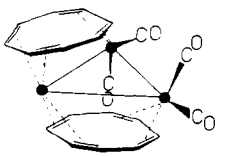


46 ●=Fe



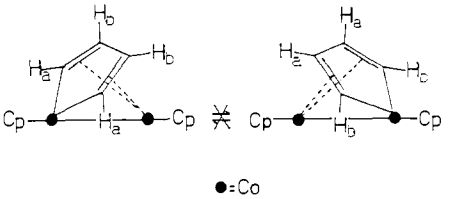
47 ●=Ni

scribes an isosceles triangle, only one ^1H NMR signal is observed for the cyclooctatetraene protons at −90 °C indicating rapid ring motion and perhaps a "breathing mode" of the Ni triangle.[121] The trinuclear cluster $(\eta^8\text{-}C_8H_8)_2Ru_3(CO)_4$ (**48**) has two cy-



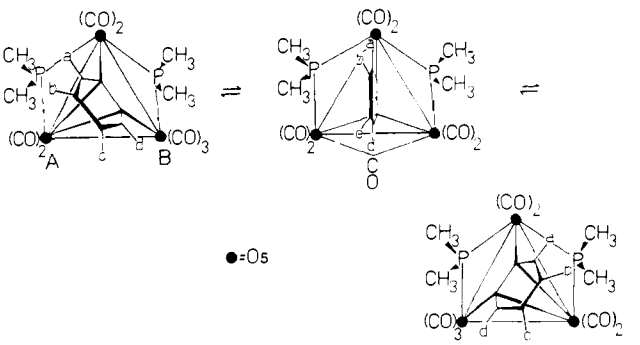
48 ●=Ru

clooctatetraene rings oriented so that the molecule is dissymmetric, possessing approximate C_2 symmetry.[122] At 25 °C, the ^1H NMR of **48** shows only one sharp resonance for the cyclooctatetraene protons, indicating that both rings are undergoing some rapid dynamic process.[123] A correlated motion of the two cycloolefins about the Ru_3 unit may be occurring here although the mechanism is undefined. Another form of a fluxional process occurs in $HOs_3(CO)_{10}CHCH_2$, where the vinyl group appears to oscillate between two osmium centers to which the vinyl group conceptually interacts in a π and σ fashion (Figure 30).[124] In this postulated process, the rapid motion of the olefin serves to account for the observed equilibration (^{13}C NMR) of carbonyl environments a, b, c, and d with a′, b′, c′, and d′, respectively. Since the olefin remains on one side of the metal triangle, carbonyls e and f remain unique. A mechanistically similar pathway is proposed for $HOs_3(CO)_9(P(CH_2CH_3)_2CCH_2)$ (**49**).[125]



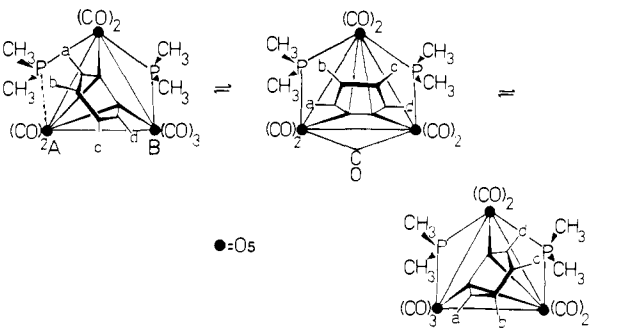
●=Co

Figure 32. A $\sigma \rightleftharpoons \pi$ ring interconversion in which hydrogen atoms "a" and "b" are equilibrated.



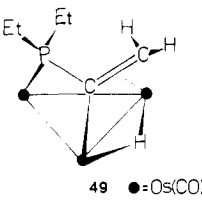
●=Os

Figure 33. The proposed low-temperature ligand exchange process in $Os_3(C_6H_4)[P(CH_3)_2]_2(CO)_7$. The four benzyne protons remain magnetically distinct.



●=Os

Figure 34. The proposed high-temperature ligand exchange process in $Os_3(C_6H_4)[P(CH_3)_2]_2(CO)_7$. The benzyne protons are coalesced to yield an AA′BB′ ^1H NMR spectrum.



49 ●=$Os(CO)_3$

Ferrole-type structures such as $(\eta^5\text{-}C_5H_5)_2Co_2(C_4H_4)$ appear to undergo σ–π interconversions involving two σ-bond and two π-bond interactions (Figure 31), as evidenced by the DNMR data.[126] At 160 °C the cyclopentadienyl ring proton resonances coalesce, but the individual resonances due to H_a and H_b of the C_4H_4 group remain sharp. An alternative but unlikely mechanistic rationale is exchange of the C_5H_5 rings between the two cobalt centers. The mechanism depicted in Figure 32 which would coalesce the H_a and H_b signals[126] is not operative on the NMR time scale. The observed activation energy for the ferrole fluxional processes is typically about 25 kcal/mol which places this process at the upper end of those fluxional processes which are NMR detectable. A more complicated $\sigma \rightleftharpoons \pi$ interconversion seems to occur in $Os_3(C_6H_4)[P(CH_3)_2]_2(CO)_7$.[127] As shown in Figures 33 and 34, the proposed mechanism involves interchange of two σ bonds and one π bond over the Os triangle by motion of the benzyne ring in two distinct fashions corresponding to "low" and "high" temperature processes. In the low-temperature process (Figure 33), the motion of the benzyne ring renders the $P(CH_3)_2$ groups equivalent, but the four benzyne

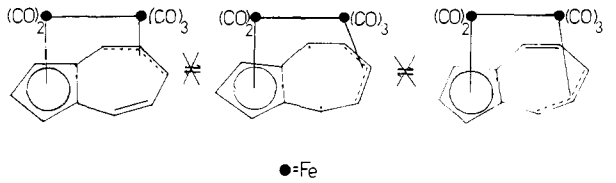


Figure 35. Representation of biradical generation in a 1,2 shift of the metal–olefin bond for $(C_{10}H_8)Fe_2(CO)_5$.

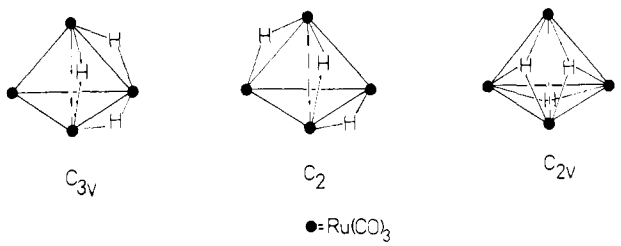


Figure 36. Postulated isomers of $[Ru_4H_3(CO)_{12}]^-$ in which all CO ligands are terminally bonded. An equilibrium mixture composed of the C_{3v} and C_{2v} or C_2 isomers may exist.

protons remain respectively unique and yield an ABXY ^1H NMR spectrum in the phenyl region. At higher temperatures (Figure 34) motion of the benzyne ring generates a mirror plane perpendicular to the benzyne ring and this coalesces the phenyl proton resonances into an AA′BB′ pattern. In order to maintain electroneutrality, it is postulated that carbonyl ligand exchange between Os_A and Os_B occurs in concert with both these processes. Note that the phosphido groups remain in bridging positions throughout the transformations.[127]

The rearrangements which occur in olefin derivatives of clusters appear to be subject to constraints on the nature of the metal–olefin bond shift. Specifically, a (1,2) shift is preferred to a (1,3) (1,4), or random-bond shift.[128] Similar behavior is observed for monometallic olefin complexes. In systems where a (1,2) shift is not feasible, the activation barrier to rearrangement is high. Thus, $(C_{10}H_8)Fe_2(CO)_5$ (**40**), which cannot execute a (1,2) shift without generating a diradical (Figure 35) is rigid on the NMR time scale at room temperature; a (1,3) shift which would lead directly to an equivalent configuration is not observed.[129,130] Movement of the cycloolefin ligand with respect to the cluster framework requires reorganization of the π-electron system. In clusters where the olefin ring is significantly buckled (as ascertained from the X-ray structure), this motion necessitates large conformation changes in the carbon skeleton which may substantially contribute to the activation energy. The extent of ring buckling has been correlated with the barrier to fluxionality for closely related $Fe_2(CO)_6$(cycloolefin) complexes.[112]

XI. Migration of Hydride Ligands in Metal Clusters

As expected and found for metal surfaces, the mobility of a hydrogen atom (or hydride ligand) on or in the cluster should be a process that encounters very small activation barriers. Available NMR data for cluster hydrides clearly indicate this is the case for clusters and that the activation energies may be as low as, or even lower than, 3–5 kcal/mol. For example, the trinuclear cluster $\{HRh[P(OCH_3)_3]_2\}_3$ (**50**) has a hydride resonance that consists of a septet (spin–spin coupling with all six phosphorus atoms) of quartets (coupling with all three rhodium atoms) that is invariant down to ~−90 °C, a temperature limit imposed by the nature of effective solvents for the cluster. The quartet splitting demonstrates that migration of the hydrides about the Rh_3 triangle is fast even at −90 °C.[131]

The series of clusters $H_4Ru_4(CO)_{12-x}(P(OCH_3)_3)_x$ (x = 1–4) show only one hydride proton resonance from +25 to −100 °C regardless of the degree of substitution.[132] Thus, there is a rapid

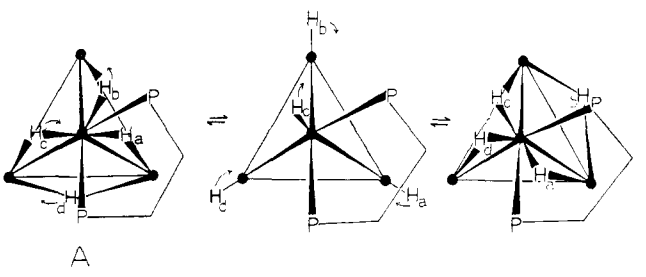
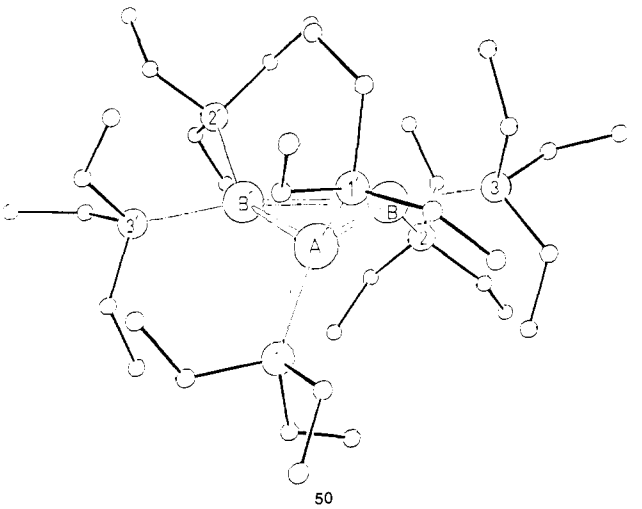
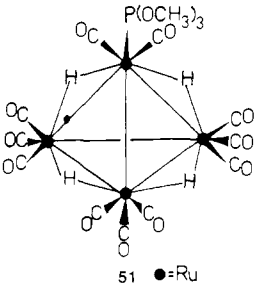
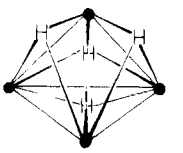


Figure 37. Hydride exchange scheme for $H_4Ru_4(CO)_{10}[(C_6H_5)_2PCH_2CH_2P(C_6H_3)_2]$. The synchronous motion of all four hydrides renders H_b and H_d magnetically equivalent.

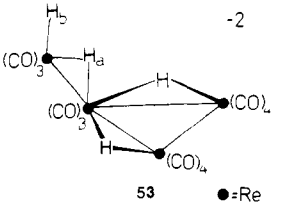


intramolecular motion of the hydrides in an, as yet, undefined manner. The low-temperature limit was reached for $H_4Ru_4(CO)_{11}P(OCH_3)_3$ (**51**) at −124 °C;[132] however, it is not clear whether the hydride hydrogen atoms migrate along cluster edges or, by analogy to the face-bridged ground-state structure of $H_4Re_4(CO)_{12}$[133] (**52**), along cluster faces. NMR studies of





$[Ru_4H_3(CO)_{12}]^-$ have led to the postulation of an equilibrium distribution of C_{3v} and C_{2v} or C_2 isomers (Figure 36) which are rapidly interconverting at 54 °C, but once again the spectral evidence is not definitive.[134] ^{13}C NMR data indicate that the single hydride atom in the octahedral $HOs_6(CO)_{18}^-$ resides above an octahedral face. In this octahedral ion, the hydride migration which occurs rapidly at temperatures above −112 °C is most simply described by a hydride atom motion between cluster faces.[135] A one-for-one exchange mechanism similar to that proposed for $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2L$ (L = CO, $P(OCH_2CH_3)_3$) has



been postulated for hydrides a and b in $H_4Re_4(CO)_{13}^{2-}$ (**53**).[136]

The mechanism of hydride mobility has been clearly delineated[137] in the chiral molecule $H_4Ru_4(CO)_{10}[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$, shown in Figure 37-A. The low-temperature process, shown in Figure 37, must involve the synchronous motion of all four hydride ligands to generate the enantiomeric isomer. In so doing, the motion makes hydrides b and d equivalent and renders the cis and trans relationship of the phosphorus atoms to hydride c equivalent on the NMR time scale.

In the remarkable cluster ion $Rh_{13}(CO)_{24}H_3^{2-}$, discovered by Chini and co-workers, the hydrogens reside inside the cluster polyhedron and are associated with internal faces of the square polyhedral faces.[138] Proton NMR studies reported by Chini show that hydrogen atoms do migrate *within* the cluster, suggesting that possibly hydrogen atom migration on metal surfaces may at least partially occur through a path just below the metal surface.[62] Many other examples of hydride mobility are known (a comprehensive review of cluster hydrides will be published soon), but there are few mechanistically defined hydride migrations in metal clusters and these have been cited above. Structurally, the hydride ligand is the most stereochemically adaptable ligand in cluster chemistry. Bonding modes established by X-ray and neutron crystallographic studies include terminal, edge-bridging, triangular, and square face-bridging, and the hydride ligand may be within or on the periphery of the metal cluster framework. Interestingly, the most common form is edge-bridging and rare is terminal bonding as judged by the presently available structural data.

XII. Clusters and Surfaces

A critical comparison of these ligand migration mechanisms in metal clusters with those of chemisorbed species on metal surfaces will be presented in a following review of clusters and surfaces.[139] Clearly, many of the cluster multisite exchange mechanisms which involve a coplanar array of ligands and metal atoms cannot be operative on dense, flat metal surfaces.

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