

only requirement is that the *transition state* of the addition reaction be ionic in nature. If this is the case, a Marcus-type correlation between rate constants for addition and redox potentials of the sensitizers is expected. The reactions of nitrobenzenes with  $\alpha$ -hydroxyalkyl radicals<sup>13</sup> and with pyrimidin-6-yl radicals (see Tables II and III) seem to fall into this category, as judged from the dependence on radical structure of the rate constants for the addition reaction.

In conclusion, it appears that the ability of nitro compounds to react with reducing radicals by addition<sup>8,10,12-15</sup> may be important in understanding their radiosensitizing action. Binding of nitro compounds to radicals derived from pyrimidine nucleotides<sup>3</sup> and from DNA<sup>7</sup> has in fact been observed.

**Acknowledgment.** We thank Claudia Thom for competent and dedicated technical assistance.

## Conformation of Mono- and Dicarboxylic Acids Adsorbed on Silver Surfaces

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**Abstract:** The geometry and conformation of a number of the ions of monocarboxylic and dicarboxylic acids adsorbed on silver colloid surfaces were deduced from their SERS spectra. Monocarboxylic acids adopt an all-trans conformation on the silver sol surface, as evidenced by the absence of gauche markers in the skeletal C-C stretching region of the spectrum, the presence of the low-frequency "accordion" mode in the C-C-C deformation region, and the alternation of the intensity of the asymmetric CH<sub>3</sub> stretching vibration with the number of carbons in the alkyl chain. We speculate that this conformation is chosen in order to avoid, as much as possible, hydrophobic interactions between the alkyl chain and the aqueous ambient. The carboxylate group is responsible for the surface bond, probably chelating to silver surface sites. The dicarboxylate acids bind through both carboxylate groups. The polymethylene chain is therefore arranged in such a way as best to accomplish this. As a result, trans "markers" are absent suggesting the presence of a large number of gauche or nearly gauche bonds. Succinate ion is shown to have a cis conformation so as to "stand" on the surface on its two carboxylate groups.

Surface-enhanced Raman spectroscopy has been used to investigate a large number of molecules adsorbed on specially prepared metal surfaces<sup>1</sup> among which silver is the most prominent. We have recently shown that molecular orientation upon the metal surface may be deduced from the SERS spectra by applying simple arguments regarding the relative intensities of SERS bands or in some cases the absence of bands.<sup>2,3</sup> Creighton<sup>4</sup> has used similar arguments to deduce the orientation of pyridine on the surface of Ag, Au, and Cu sol particles. In this paper we investigate the surface geometry and conformation of a number of the ions of carboxylic and dicarboxylic acids by analyzing their SERS spectra. An investigation of the conformation of a long-chained thiol adsorbed on silver colloid particles precedes ours.<sup>5</sup>

### Experimental Section

Silver sols were made according to the recipe reported in previous papers.<sup>2,3</sup> Briefly, a sodium borohydride solution (60 mL of  $2 \times 10^{-3}$  M) was mixed with a silver nitrate solution ( $22 \pm$  mL of  $1 \times 10^{-3}$  M).

The adsorbate was introduced to the colloid by dissolving the acids either in pure triply distilled water or in NaOH solution of various pH. A single measured drop of these solutions was added to approximately 1.5 mL of colloid. Concentrations of less than 1 mM resulted thereby. Spectra were recorded with a SPEX 1401 monochromator equipped with photon counting and interfaced to a Textronix 4052 computer. The 514.5-nm line of the Ar<sup>+</sup> laser was used for most of the experiments at a power level of approximately 150 mW. Slits were set to 4 cm<sup>-1</sup> with acquisition times of approximately 0.5 s.

### Results

The SERS spectra of a series of carboxylic acids (valeric to decanoic) and of dicarboxylic acids (oxalic to suberic) adsorbed on aqueous silver sol particles are shown in Figures 1 and 2. The spectra of members of each group (apart from oxalic and valeric acids) show great similarity to one another, yet each differs

markedly from its ordinary solution or liquid Raman counterpart. From the fact that the Raman spectrum of an equivalent number of moles of adsorbate in solution in the absence of silver was undetectable even at a 1000-fold greater sensitivity, we conclude that the SERS spectra of these compounds exhibit considerable enhancement.

The best spectra were obtained with colloid which had aggregated under the influence of the adsorbate. This aggregation process, which is known to produce assemblies of randomly touching sol particles often containing thousands of colloidal particles, was signalled by a change in the colloid's color following addition of adsorbate, from yellow to blue over a period of several hours. The spectra reported were obtained with blue colloids.

No difference was noted between spectra obtained with base added as opposed to base absent except that with suberic acid no SERS spectrum was obtained when base was added. Likewise with sebacic acid we could not obtain a SERS spectrum under any pH conditions. With monocarboxylic acids the SERS spectra became undetectable when chain lengths beyond dodecanoic acid were used.

With all the acids studied the dominant band in the spectrum is near 1400 cm<sup>-1</sup>. This is unequivocally assigned to the symmetric stretching vibration of the carboxylate group, indicating, simultaneously, that the acids bind to the surface as anions and that the COO<sup>-</sup> group is almost certainly on the surface and forms the surface bond. One observed, in addition, intense vibrations in the CH stretching region, C-C stretching C-C-C bending, and COO<sup>-</sup> deformation regions. With some acids one also sees metal-molecule stretching vibrations suggestive of chelating COO<sup>-</sup> groups.

With propionic and butyric acids and newly made colloid one sometimes sees the asymmetric COO<sup>-</sup> stretching vibration at 1000 cm<sup>-1</sup>. At times the intensity of this band even exceeds that of the symmetric COO<sup>-</sup> stretch.

### Discussion

**Monocarboxylic Acids.** The high intensity of the COO<sup>-</sup> symmetric vibration suggests that the series of carboxylic acids are

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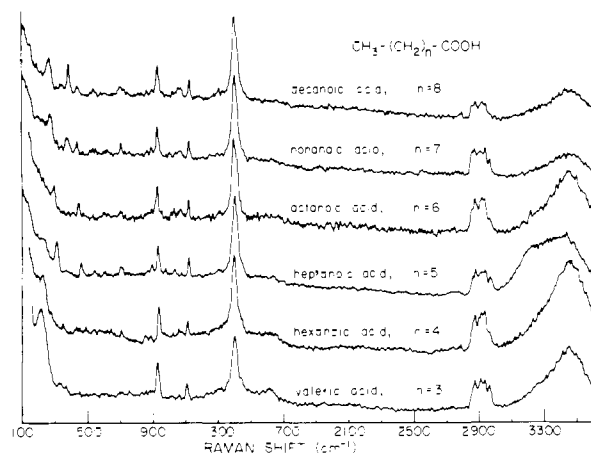


Figure 1. SERS spectra for a series of carboxylates adsorbed on the surface of silver colloid excited with 514.5 nm Ar<sup>+</sup> laser light.

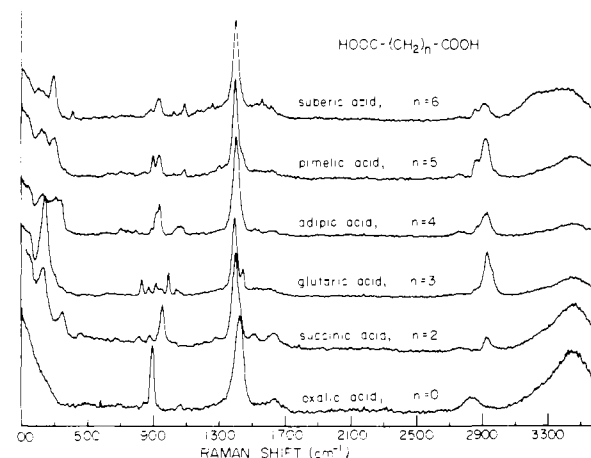


Figure 2. As in Figure 1 but for a series of dicarboxylates.

Table I. Frequency (in cm<sup>-1</sup>) of Bands in Skeletal Region

CH <sub>3</sub> (CH <sub>2</sub> ) <sub>n</sub> COOH					
n = 3	n = 4	n = 5	n = 6	n = 7	n = 8
1109.5	1115, 1064	1118	1120, 1066	1121, 1066	1123, 1062
1106	1112, 1060				

bound to the surface through this groups. In an earlier paper<sup>2</sup> we suggested that it might be chelating. There are three other groups of spectral features which aid us in determining the structure of the molecule and its disposition with respect to the surface. These are the following: the low-frequency C-C-C deformation region, the C-C skeletal stretching region (near 1100 cm<sup>-1</sup>), and the C-H stretching region. Another persistent feature, a band near 930 cm<sup>-1</sup>, is assigned to the C-COO<sup>-</sup> stretch. The skeletal region is particularly informative. It is known, for example,<sup>6</sup> that for long alkanes or alkyl chains, two bands which appear at 1065 and 1123 cm<sup>-1</sup> in the liquid and 1060 and 1130 cm<sup>-1</sup> in the solid are "trans markers". For shorter chains this "trans marker" appears as a single band near 1100 cm<sup>-1</sup>. Likewise a band near 1080 cm<sup>-1</sup> in the liquid and 1096 cm<sup>-1</sup> in the solid is characteristic of gauche bonds. In the SERS spectra of the monocarboxylic acids adsorbed on silver we only see vibrations characteristic of trans conformations and none suggesting gauche (Table I). We suggest, therefore, that the molecule adopts an all-trans conformation on bonding to the surface, as shown in Figure 3. Although the all-trans conformation is not the favored one in the gas phase at room temperature (this conformation is energetically favored, but the entropic effect due to the statistical

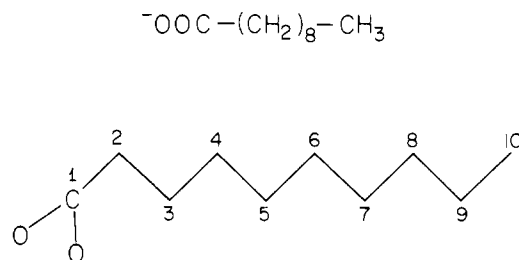


Figure 3. Proposed all-trans surface-bonding conformation for the monocarboxylates adsorbed on silver. The carboxylate group chelates to a silver atom of the surface.

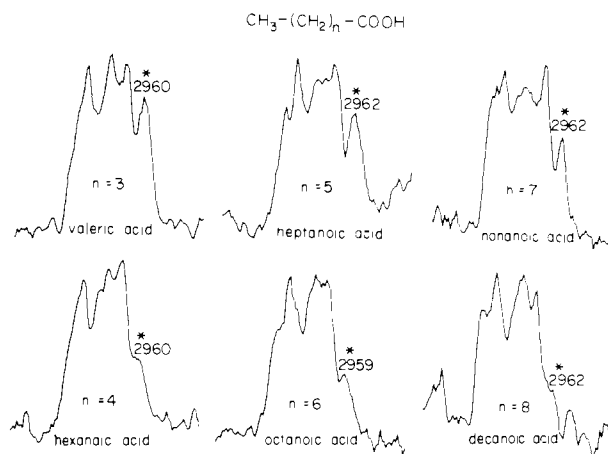


Figure 4. Details of the CH stretching region of the SERS spectra shown in Figure 1. The asterisk indicates the asymmetric stretching frequency of the methyl group.

Table II. Observed Accordion-Mode Frequencies (in cm<sup>-1</sup>)

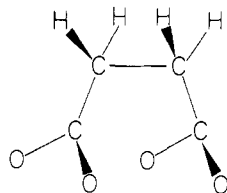
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	367	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> COOH	295
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH	346	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> COOH	271
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> COOH	310	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOH	266

preponderance of gauche forms minimizes the free energy for conformations involving gauche bonds), there is an advantage for its adoption on the surface of a colloidal particle surrounded by water. This is because the hydrophilic group is bound to the surface, and it is the hydrophobic tail that, in this case, is forced to interact with the water. By adopting the all-trans form the molecule may lie close to the surface, thereby avoiding as much interaction with the water as possible. Nevertheless, for long enough chains even this reduced amount of interaction between the hydrophobic group and the water is too great, and the molecule does not adsorb on the surface at all but prefers to form micelles in the aqueous phase, hence our inability to observe SERS with long-chain fatty acids. For acids with shorter chains it is the adsorption energy, of course, which compensates for the unfavorable tail-water repulsions. Our conclusion regarding the molecular structure on the surface is reinforced by other spectral observations. An all-trans polymethylene chain also possesses a characteristic, low-frequency, concerted C-C-C deformation known as the accordion-mode, whose frequency is more or less inversely proportional to the chain length,<sup>7</sup> at least for intermediate length chains. These bands clearly appear in the SERS spectra of the monocarboxylic acids and show the expected chain length dependence (Table II).

Reference to Figure 3 indicates that the proposed, all-trans surface structure places the terminal methyl group near the metal surface for odd-carbon acids and far from the surface for even-carbon acids. The SERS effect is known to be increase in strength as the oscillator approaches the surface, hence one expects to see an alternation in the SERS intensity of bands belonging to the

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**Figure 5.** Proposed surface bonding conformation of succinate. The two carboxylate groups each bind to a silver atom of the surface.

methyl group with chain length. This effect cannot be seen for the symmetric  $\text{CH}_3$  vibration because it is buried within the manifold of CH stretching bands belonging to the methylene groups. The  $\text{CH}_3$  asymmetric stretch, on the other hand, is higher in frequency than any of the methylene vibrations and is consequently clearly resolved. A detailed summary of the CH stretching regions of the six SERS spectra is displayed in figure 4 showing precisely the expected effect: the asymmetric  $\text{CH}_3$  stretching vibration is strong for odd-carbon acids and very weak for even-carbon acids.

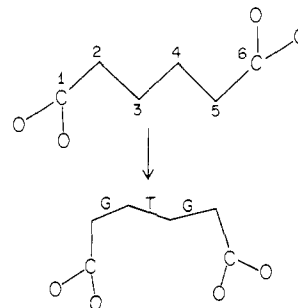
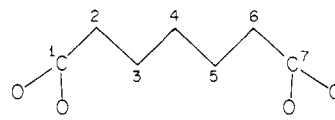
**Dicarboxylic Acids.** As with the monocarboxylic acids SERS spectra were not obtained for acids longer than suberic ( $\text{HOOC}(\text{CH}_2)_6\text{COOH}$ ) presumably for similar reasons.

In attempting to determine the stereochemical properties and mode of bonding of these molecules to the surface, we look for the same spectral clues. In the carbon skeletal region one sees no band in the SERS spectrum of succinic acid while in those of glutamic, adipic, pimelic, and suberic acids one sees bands at 1050, 1057, 1086, and 1090  $\text{cm}^{-1}$ , respectively. The last two frequencies suggest gauche bonds, and while the first two differ somewhat in frequency from the traditional gauche markers, they do indicate that trans bonds are decidedly not dominant features of these molecules. The low-frequency region is likewise devoid of the characteristic "accordion modes" seen in the spectra of the previous set of molecules.

The CH stretching region is also somewhat different for this set. Rather than a group of fairly well resolved vibrational bands one sees a broad feature. This might indicate that unlike the monocarboxylic acids, the SERS spectra of the dicarboxylate are each averages of spectra of several conformers.

Whether these molecules are bonded to the surface through one or both carboxylate groups is difficult to ascertain. We believe that both carboxylate groups are bound to the surface. Our major piece of evidence is the band at 340  $\text{cm}^{-1}$  in the spectrum of adsorbed succinate. This band can only be assigned to the pseudocycle deformation vibration which in solution occurs at 339  $\text{cm}^{-1}$ .<sup>8</sup> Such a band is only possible if the two carboxylate groups eclipse each other as in Figure 5. This particular surface geometry also implies that the C-C stretching vibration should be almost absent since the C-C bond is almost parallel to the surface; and indeed no band is seen in the SERS spectrum of this molecule in the 1000–1150- $\text{cm}^{-1}$  range.

The double-ended bonding scheme also explains the preponderance of gauche or gauche-like bonds. The molecule gains sufficient stability by bonding two carboxylate groups to the surface that it is able to adopt less favorable chain conformation such as gauche or as in the case of succinate even a cis form. For even-carbon dicarboxylic acids, both carboxylate groups cannot bond to the surface in the trans conformation (see Figure 6). In order to do so some bonds must become gauche. In doing so the methylene groups are raised relatively far from the surface. Although in the trans form of odd-carbon dicarboxylic acids both carboxylate groups are properly oriented to bind simultaneously to the surface, some of the methylene hydrogens would be somewhat too close to the surface if it were to do so. To reduce this repulsion, some bonds deform slightly from the trans conformation and may have gauche-like forms. Nevertheless, the deformation required of even-carbon dicarboxylic acids from the



**Figure 6.** Odd-carbon dicarboxylic acids need to modify their structure only slightly to place both  $\text{COO}^-$  groups on the surface. Even-carbon acids must change their conformation radically in order to do so.

trans conformation in order to allow both carboxylate groups to bind to the surface is more dramatic than what is needed in odd-carbon dicarboxylic acids. Consequently, the methylene groups of even-carbon dicarboxylic acids would, on the average, be further from the surface than those of odd-carbon dicarboxylic acids. We can find evidence of this in the CH stretching region. The relative intensity of CH stretching bands in the SERS spectra of odd-carbon dicarboxylic acids is higher than their counterparts in the case of even-carbon dicarboxylic acids (Figure 2). Monocarboxylic acids can, of course, avoid excessive repulsive interactions between the methylene hydrogens and the surface by tilting its unbonded end upward somewhat.

The plurality of conformers for any given molecule is likewise explained by the fact that in the rather disordered Ag surface the molecules may bond to pairs of Ag atoms whose mean distance varies somewhat from site to site, causing the molecule to adopt slightly different conformations in forming the two, chelating  $\text{COO}^-$ -Ag bonds. This constraint does not, of course, apply to the monocarboxylates.

The SERS spectrum of glutaric acid differs somewhat from those of the other acids studied in that it shows a very strong  $\text{COO}^-$ -Ag vibration at 235  $\text{cm}^{-1}$  and several vibrations in the C-C stretching regions. The reason for this is not clear. The other molecules show only one or two bands in this region, at 955, 933, 934 and 932  $\text{cm}^{-1}$  respectively for succinic, adipic, pimelic, and suberic acids. These are ascribed to the C-COO<sup>-</sup> stretching vibration.

The observation that the SERS spectra of propionic and butyric acids included the asymmetric carboxylate CO stretching vibration when fresh colloids were used may arise from the presence of considerable disorder in the structure of the surfaces of those colloid particles. In particular, many more sites would be present in the freshly formed surfaces to which these acids could bind in such a way that the  $\text{C}_2$  axis of the  $\text{COO}^-$  group would be more or less along the average surface boundary. Under those circumstances the asymmetric  $\text{COO}^-$  stretch is expected to be intense. In older colloids the surface has more or less "healed" and most surface sites can only support adsorbate which is bonded with the apex of the  $\text{COO}^-$  group pointing along the average surface normal.

Oxalate is, of course, different from the other acids studied in that it does not possess methylene groups. We have therefore reserved its discussion until the end. Oxalate is a planar ( $D_{2h}$ ) ion. The strongest band in its SERS spectrum at 1420  $\text{cm}^{-1}$  is assigned to the symmetric stretching vibration of the carboxylates. The band at 2835  $\text{cm}^{-1}$  is an overtone of this band. The band observed at 892  $\text{cm}^{-1}$  may at first glance be ascribed to the C-C vibration. In this molecule the frequency of this vibration is depressed to 445  $\text{cm}^{-1}$  in solution<sup>9</sup> due to the electron-withdrawing

(8) Bardet, L.; Maillols, J.; Haillols, H.; Lucas, R. *C. R. Hebd. Seances Acad. Sci., Paris* **1980**, *270*, 158.

effect of the oxygens bonded directly to the two carbons. The absence of this band from the SERS spectrum suggests immediately that the oxalate ion lies down on the silver surface. The band at  $892\text{ cm}^{-1}$  is therefore assigned to the  $\text{COO}^-$  deformation which comes at  $904\text{ cm}^{-1}$  in solution.<sup>9</sup> For the other carboxylate ions this vibration is found near  $670\text{ cm}^{-1}$  in solution. It is not seen in the SERS spectra of the other carboxylates partly because these modes are inherently weak and partly because, unlike the

oxalate ion, the carboxylate groups of the other acids stand up on the surface, at least partially, as in Figure 3.

**Acknowledgment.** We thank NSERC and the donors of the petroleum research fund, administered by the American Chemical Society, for partial support for this work.

**Registry No.** Valeric acid, 109-52-4; hexanoic acid, 1289-40-3; heptanoic acid, 111-14-8; octanoic acid, 124-07-2; nonanoic acid, 112-05-0; decanoic acid, 334-48-5; oxalic acid, 144-62-7; succinic acid, 110-15-6; glutaric acid, 110-94-1; adipic acid, 124-04-9; pimelic acid, 111-16-0; suberic acid, 505-48-6; silver, 7440-22-4.

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## Haptotropic Rearrangements in Polyene- $\text{ML}_n$ Complexes. 3. Polyene- $\text{ML}_2$ Systems

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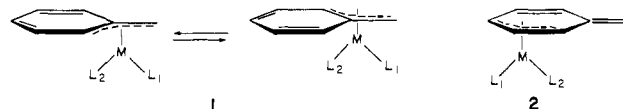
**Abstract:** A general theoretical study has been undertaken for the rearrangement of an  $\text{ML}_2$  group from one coordination site to another in polyene- $\text{ML}_2$  complexes. Extended Hückel calculations have been used to compute the minimum energy reaction pathways in the U, sickle, and W isomers of pentadienyl- $\text{Pt}(\text{PH}_3)_2^+$ , benzyl- $\text{Rh}(\text{PH}_3)_2$ , phenalenium- $\text{Pt}(\text{PH}_3)_2^+$ , quinone- $\text{Pt}(\text{PH}_3)_2$ , fulvene- $\text{Pt}(\text{PH}_3)_2$ , cyclobutadiene- $\text{Ni}(\text{PH}_3)_2$ , benzene- $\text{Ni}(\text{CO})_2$ , and cyclopentadienyl- $\text{Pt}(\text{CO})_2^-$ . A simple, topologically based model is developed to analyze these and other rearrangements. For a  $d^{10}$  complex, it maximizes overlap between the  $\text{ML}_2$   $b_1$  orbital and the LUMO of the polyene along the reaction path. For a  $d^8$  complex, the polyene HOMO is used in an analogous fashion. The method is in good agreement with detailed computations for all systems, except benzene- $\text{Ni}(\text{CO})_2$ . Here superjacent orbital control determines the geometry of the transition state. A qualitative estimate of the activation energy for the rearrangement can be determined by establishing how much overlap between the  $\text{ML}_2$   $b_1$  orbital and requisite polyene  $\pi$  orbital is lost on going from the ground to transition state. Repulsion between the filled  $\text{ML}_2$   $b_2$  and a filled polyene  $\pi$  orbital can also contribute to the barrier. It is shown how perturbation of the electronic properties in the auxiliary ligands at the metal can modify this repulsion and the associated activation energy.

### Introduction

Haptotropic rearrangements, wherein a  $\text{ML}_n$  unit changes its connectivity (hapt number) to some ligand with multicoordination site possibilities, has been extensively studied by experiment<sup>2</sup> and theory<sup>3</sup> for polyene- $\text{ML}_3$  and - $\text{MCp}$  systems. Far less is known<sup>2c</sup> about polyene- $\text{ML}_2$  complexes, although there have been prior theoretical studies of fluxionality in  $\eta^3$ -cyclohexadienyl- $\text{ML}_2$  and  $\eta^2$ -cyclopropenium- $\text{ML}_2^+$  compounds.<sup>4</sup> In this work, we present a general theoretical strategy that can be readily used for analyzing haptotropic rearrangements in polyene- $\text{ML}_2$  complexes. We have also generated potential energy surfaces with the aid of molecular

orbital calculations at the extended Hückel level<sup>5</sup> to check our theoretical model.

Haptotropic rearrangements in 16-electron benzyl- $\text{ML}_2$  complexes nicely illustrate some of our concerns. The compounds undergo a very facile rearrangement shown in 1. While a  $\pi$ - $\sigma$ - $\pi$



route has been commonly proposed for fluxionality in benzyl- $\text{ML}_n$  complexes,<sup>7</sup> this mechanism has been conclusively proven in only

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