quate precautionary measures should be taken.) After cooling to 20 °C, the tube was opened, the solution concentrated to dryness and dissolved in 50 % aqueous acetic acid (5 ml). After 1 h at room temperature, the solution was concentrated to dryness, the product reduced with aqueous sodium borodeuteride and worked up as usual. Part of the product was acetylated and investigated by GLC-MS, another part (from *2, 3* and *4*) was permethylated [11] and analysed by GLC-MS.

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Dependence of Equilibrium Geometry and Rearrangement Modes on Electron Count in One Class of Trinuclear Complexes of Acetylene

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The reaction of ethylene with $M_3(CO)_{12}$, M = Ru, Os leads to two types of complexes in both of which two hydrogens have been stripped from the ethylene.[1] One has a vinylidene ligand, while the other is acetylenic. Another acetylene complex is observed when $Fe_2(CO)_9$ is treated with diphenylacetylene.[2] In both compounds the acetylene is sitting above a triangular base of metals and their associated carbonyls. However, the orientation of the organic π system differs in the two clusters. In $Fe_3(CO)_9C_2Ph_2$ the acetylene is perpendicular to a metal − metal bond, *1*, whereas $H_2Os_3(CO)_9C_2H_2$ has the acetylene parallel to a metal − metal bond, *2*, as do several isoelectronic molecules.[3] We show that this is a consequence of the different electron counts in the two systems (the Os complex has two more electrons than the Fe, if we consider the H's as protonic.), and we calculate a potential energy surface for the intricate relative motion of the acetylene and the metal frame.

1

2
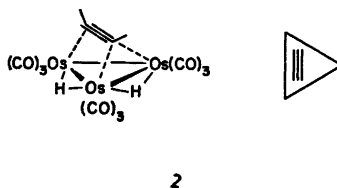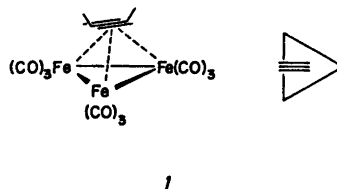
The preference for the perpendicular conformation in the iron system is a consequence of the symmetry properties of the acetylene π orbitals and the cluster fragment levels.[4] In conformation *2* of the neutral iron system there is a low-lying empty orbital which is approximately 90 kJ/mol lower than its counterpart *1*. Occupation of that level causes the reversal of the conformational preference, with

2 the preferred structure for the electron-rich system. The observed geometries may also be explained in terms of the polyhedral skeletal electron pair theory.[5]

The calculated optimum location of the acetylene is somewhat displaced from a position above the center of the metal triangle. In $Fe_3(CO)_9C_2H_2$ the acetylene is moved towards an $M-M$ bond, in accordance with the structure known.[2] This produces three minima, as shown schematically in 3.

3   *4*
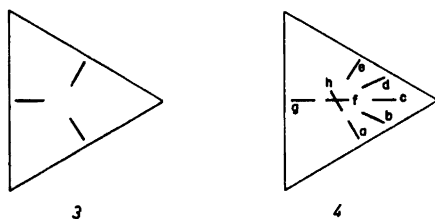
How should the molecule move between these three positions? We calculate transition states at *b* in *4* and its five symmetry-related sites. The equivalent minima may be interconverted by a "120° scan", $a{\to}b{\to}c{\to}d{\to}e$ $(\equiv a)$ or by a "60° scan", $a{\to}b{\to}c$, followed by a "slide", $c{\to}f{\to}$ $g(\equiv a)$. The first path climbs the same transition state twice $(b\equiv d)$, whereas the second does it only once, $b{\to}c{\to}f{\to}g$ being all downhill in energy. The "slide-centered rotation-slide" path $a{\to}h{\to}f{\to}g$ encounters a higher barrier in the rotation $h{\to}f$. The two lower energy paths have different consequences on maintaining the "in-out" labeling of the two ends of a complexed acetylene.

In the electron-richer system there are three equivalent minima, shown in *5*, in which the

5   *6*   *7*
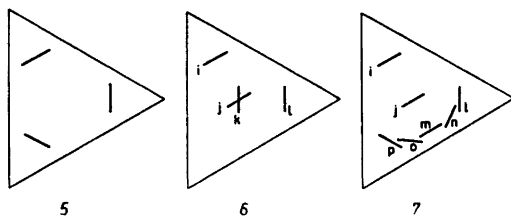
parallel acetylene is slightly displaced toward a metal. The equilibrium geometries are connected by three paths competitive in energy. The first of these is a "slide-rotation-slide", $i{\to}j{\to}k{\to}l$ $(\equiv i)$ in *6*. The second is the "slide + 60° scan" shown in *7*, $i{\to}j{\to}m{\to}n{\to}l$ $(\equiv i)$ and the third the "120° scan" $l{\to}n{\to}m{\to}o{\to}p$. The calculated barriers are 38 kJ/mol for the first path, 42 kJ/mol for the last two. The first two would produce the magnetic site equivalencing observed by Deeming,[6] with an experimental activation energy of 63 kJ/mol.

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