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First Example of a Rapid Reversible Inter-Ring η^5,η^5-Haptotropic Rearrangement in an Anionic Metal Tricarbonyl Complex Containing a Dibenzopentalene Ligand

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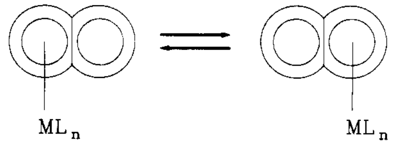
Summary: The first examples of migration of an organometallic group between two fused five-membered rings in transition-metal π-complexes have been found for anionic (9-methyl-10-benzylindeno[1,2-*a*]indene)manganese tricarbonyl complexes. The activation parameters of the rearrangement have been established with the aid of dynamic NMR spectroscopy.

In recent years numerous authors[1] have studied reversible inter-ring metallotropic rearrangements of transition-metal π-complexes of polycyclic aromatic systems (eq 1), in which a metal carbonyl or an organometallic group migrates along the plane of the π-system from one ring to another. A great number of such rearrangements in fluorenyl π-complexes and related systems have been investigated, where migration is taking place between five- and six-membered rings,[2-8] as well as in naphthalene,[9-13] acenaphthene[11-14] and acenaphthylene,[15] biphenylene,[15] and biphenyl[16] complexes, where transfer occurs between two six-membered rings. Thus, the processes of this type represent a fairly common characteristic property of the



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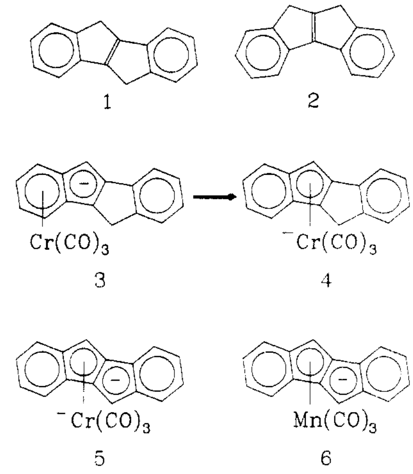
Scheme I



π-complexes of transition metals with polycyclic aromatic systems, and some of them should be regarded as a new type of metallotropic tautomerism.

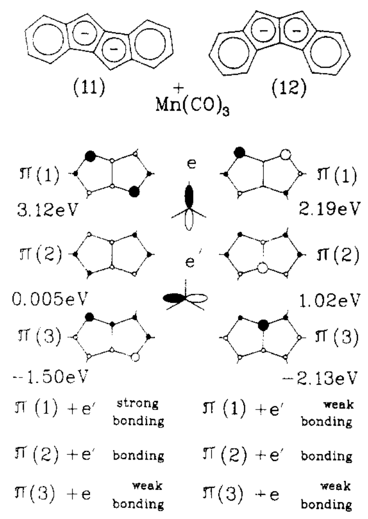
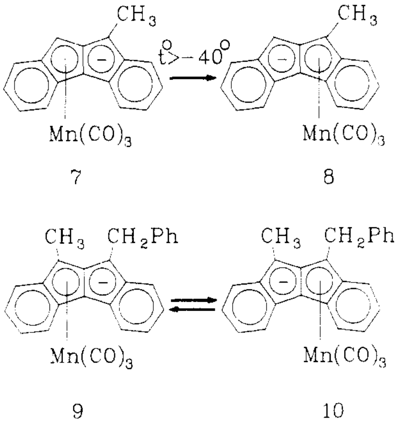


Figure 1. Main bonding interactions in complex anions **6** and **7**.

Scheme II



The mechanism of rearrangements of this type was theoretically examined by Albright, Hofmann, and coworkers in terms of the orbital interaction concept[1] with the use of extended Hückel theory. It was established that the main contribution to the bonding in the ground state of π-complexes of this type comes from the interaction of the two higher occupied molecular orbitals with the lower unoccupied molecular orbitals of the organometallic and metal carbonyl fragments. In most cases the path of least motion from ring to ring through the middle of the carbon–carbon bond, which is common for these rings, is forbidden because in this case both the bonding interactions are lost. More preferable is metal migration over the polycycle periphery via an intermediate η^3-allyl structure. Such an analysis for pentalene complexes with d^6 organometallic fragments predicts a lower activation barrier in cationic complexes as compared to that in the corresponding anion. However, data on inter-ring haptotropic rearrangements in π-complexes containing a pentalene fragment have so far been absent in the literature. In the course of systematic studies of haptotropic rearrangements of transition-metal π-complexes with polycyclic aromatic systems we have synthesized η^6 chromium tricarbonyl and η^5 manganese tricarbonyl complexes of two dibenzopentalenes: 5,10-dihydroindeno[2,1-*a*]indene (**1**) and the isomeric 9,10-dihydroindeno[1,2-*a*]indene (**2**), differing in the type of condensation of the indene fragments[17-19] (Scheme I). It was found that the anionic η^6 complex **3** rearranges readily and irreversibly to the η^5 isomer **4**, but in the dianionic complex **5** no η^5,η^5 rearrangement was observed.[17,19] Similarly, the corresponding anionic manganese tricarbonyl complex **6** fails to undergo a rearrangement of the $\eta^5 \rightarrow \eta^5$ type. A quite different situation was observed for anionic manganese tricarbonyl complexes of the isomeric hydrocarbon **2**. The anionic complex **7** easily and irreversibly converts into **8**, within the temperature interval -80 to -40 °C in THF-d_8 (Scheme II). The interconversion of two the isomeric disubstituted complexes **9** and **10** proceeds rapidly and reversibly at temperatures from -40 to +20 °C in THF-d_8. The process can be easily followed by observing the characteristic reversible temperature dependence of positions and line shapes of the signals due to the methyl protons and the CH_2 groups of the benzyl substituents as indicators in their ^1H NMR spectra. A complete line shape analysis of the methyl signals enables us to calculate the activation parameters of the rearrangement **9** ⇄ **10** ($\Delta H^{\ddagger} = 54.6 \pm 0.3$ kJ/mol, $\Delta S^{\ddagger} = -28$ J/(mol K)) as well as dynamic equilibrium parameters ($\Delta H^{\circ} = -0.66 \pm 0.3$ kJ/mol, $\Delta S^{\circ} = -2.8$ J/(mol K)).

According to IR spectra the salts **9** and **10** exist as contact ion pairs. The negative activation entropy probably means that the potassium cation is more solvated in the transition state than in interconverting complexes. Thus, we have found the first rapid (on the NMR time scale) η^5,η^5 rearrangement in a π-complex containing a dibenzopentalene ligand.

A difference in the dynamic behavior of the anionic complexes **6**, on the one hand, and **7–10**, on the other, becomes clear from the analysis of nodal properties, energies, and coefficients of the $2p_z$ AO's of the high-energy occupied molecular orbitals of isomeric dianions **11** and **12** shown in Figure 1 (the central pentalene fragment alone being given) according to INDO calculation data.

The two anionic ligands **11** and **12** are different in symmetry. If the trivial element of symmetry (σ_{xy} plane) is excluded from consideration, there is a C_2 axis in **11** perpendicular to σ_{xy}, which passes though the center of in-

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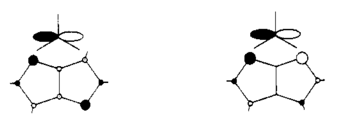

13 14

π (1) + e′ strong bonding π (1) + e′ very strong bonding

Figure 2. Proposed intermediates in inter-ring η^5,η^5-haptotropic rearrangements of anionic manganese tricarbonyl complexes of isomeric indeno[1,2-*a*]- and indeno[2,1-*a*]indenes.

version lying in the middle of C_{5a}–C_{10a}. For **12** there is a σ_2 plane perpendicular to σ_{xy}, passing through C_4–C_{9a}. In accord with this, nodal properties of two upper occupied, bonding π-MO's of both dianions **11** and **12** cannot be classified relating to the common symmetry element. There is also no common element of symmetry with vacant e and e′ orbitals of the $Mn(CO)_3^+$ fragment, retained along the reaction path.

Qualitatively, however, it may be concluded that for the trans anion **11** $\pi(1)$ + e, $\pi(1)$ + e′, $\pi(2)$ + e, and $\pi(2)$ + e′ interactions may occur. The first two are strong and stabilize the ground state. While the $Mn(CO)_3^+$ group is moving from one ring to another, only one $\pi(1)$ + e′ interaction is retained under the condition that the $Mn(CO)_3^+$ group shifts to the periphery of the system. The intermediate must have the structure **13** (Figure 2). However, with further movement this bonding interaction disappears. Thus, the inter-ring η^5,η^5 rearrangement as an intramolecular process for complex **6** is completely prohibited.

In the case of cis anion **12** $\pi(1)$ may participate only in one bonding $\pi(1)$ + e interaction, while $\pi(1)$ + e′, $\pi(2)$ + e, and $\pi(2)$ + e′ will be very weak. According to this, bonding of the $Mn(CO)_3^+$ group in complex **9** in the ground state is weakened in comparison with that in **6**. In intermediate **14** with rearrangement of complex **9**, the $\pi(1)$ + e interaction is lost while $\pi(1)$ + e′ becomes very strong.

Therefore, **14** must be more stable than **13**. The obligatory withdrawal of the $Mn(CO)_3^+$ group over the ligand contour is not necessary; i.e., as in the case of the cation (pentalene)cyclopentadienyliron[1] the transition on the least motion principle becomes "partially allowed".

The synthesis of the complexes **3**–**10** and their characteristics have been described.[19,20]

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Registry No. **7**, 125610-38-0; **8**, 125610-39-1; **9**, 125610-40-4; **10**, 125610-41-5; **11**, 65583-99-5; **12**, 72866-14-9.

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Unusual Trigonal-Bipyramidal Coordination of Gallium by an Aza Crown Ether. Synthesis and Molecular Structure of $[Ga(CH_3)_2][C_{12}H_{25}N_2O_4][Ga(CH_3)_3]_2$

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Summary: Reaction of diaza-18-crown-6, $C_{12}H_{26}N_2O_4$, with trimethylgallium in a toluene/heptane mixture affords the crystalline complex $[Ga(CH_3)_2][C_{12}H_{25}N_2O_4][Ga(CH_3)_3]_2$. The title compound contains two trimethylgallium units and one dimethylgallium unit. The dimethylgallium unit resides within the cavity of the aza crown with the gallium atom bonding to two oxygen atoms and a nitrogen atom in addition to the two methyl carbon atoms. As the gallium atom, the two carbon atoms, and the nitrogen atom constitute a basal plane while the two oxygen atoms of the crown are found to reside above and below the plane (O–Ga–O bond angle 157.2 (2)°), the coordination of the core gallium atom may be described as distorted trigonal bipyramidal.

The last decade witnessed a proliferation of advances in the chemistry of gallium. Seminal discoveries concerning gallium compounds have found utility in the diagnosis of disease[1-3] as well as in the production of semiconductor materials.[4-10] This laboratory has an interest in the chemistry of gallium as it relates to the liquid inclusion compounds known as liquid clathrates, $[M_2R_6X][CE{\cdot}M']$ (M = Al, Ga; R = alkyl; X = halide; CE = oxygen-based crown ethers; M′ = alkali-metal ion).[11] It

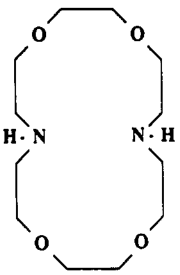

Figure 1. The mixed nitrogen–oxygen donor crown ether diaza-18-crown-6, $C_{12}H_{26}N_2O_4$.

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