# Density Functional Study on the 1,4-Hydride Migration
# in the $\eta^5$-Naphthalene Manganese Complex [(*exo*-R-$\eta^5$-C$_{10}$H$_8$)Mn(CO)$_3$]

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The mechanism of 1,4-hydride migration in [(*exo*-R-$\eta^5$-C$_{10}$H$_8$)Mn(CO)$_3$] was investigated by density functional theoretical study. Diene hydride intermediate is located, and the Gibbs free energy of activation and the stability of the equilibrium mixture are in good agreement with the experimental results.

It has recently been established that arenes can be activated by coordination to transition metals.[1,2] For example, nucleophilic addition to naphthalene, which is activated by coordination to transition metals, occurs regioselectively at the C1-position, and all of the C-donor additions occurred in the stereospecific *exo* manner. However, recent studies showed a complex behavior due to 1,4-hydride migration. We reported nucleophilic addition to (naphthalene)Mn(CO)$_3^+$, which involves a 1,4-hydride migration in the (*exo*-1-R-$\eta^5$-C$_{10}$H$_8$)Mn(CO)$_3$ derivatives to give an equilibrium mixture of (*exo*-1-R-$\eta^5$-C$_{10}$H$_8$)Mn(CO)$_3$ and (*exo*-1-H-$\eta^5$-C$_{10}$H$_7$-4-R)Mn(CO)$_3$.[3] Recent dynamic NMR studies showed that the activation energy for this migration is corresponding to $\Delta G^\ddagger = 21.0$ kcal/mol at 298 K for R = H.[4] Similar migration also can be found in benzene[5] and anthracene complexes.[6] It is speculated that the 1,4-hydride migration reaction involves the exchange of the endo proton with the proton para to this position and that this generates a highly symmetric diene hydride intermediate ($\eta^4$).[4,6]

Here, we report density functional studies on the mechanism of 1,4-hydride migration in (*exo*-1-R-$\eta^5$-C$_{10}$H$_8$)Mn(CO)$_3$ (R = Me, **1**). Geometry optimization was carried out at the B3LYP/LACVP** level of theory[7–10] using Jaguar v5.5.[11] The stability of all the minima including intermediates and transition states (TSs) was evaluated by calculating the standard Gibbs free energy of each species at 298 K. The standard Gibbs free energy of a molecule was evaluated by

$$\Delta G = E_0 + \text{ZPE} + \Delta\Delta G_{0\to298}. \quad (1)$$

The total energy of the molecule at 0 K ($E_0$) is calculated at the optimum geometry from B3LYP/LACVP** level of theory. Zero-point energy (ZPE) and Gibbs free energy change from 0 to 298 K ($\Delta\Delta G_{0\to298}$) were evaluated at the same level of theory. Thermodynamic quantities were evaluated according to rigid-rotor harmonic oscillator approximation using the computed harmonic frequencies. The local minima and TSs were identified by the analysis of harmonic frequencies from analytical Hessian calculation. Reaction paths were traced by the intrinsic reaction coordinate (IRC) method[12,13] starting from the TSs to confirm that the reactants and products are correct. The choice of the basis set and the flavor of the DFT functional were done by system-

atic tests from our previous work on manganese tricarbonyl cations of phenol and cresols[14,15] to reproduce the X-ray structural data[14] and product selectivity.[15]

Depicted in Scheme 1 is the suggested mechanism for 1,4-hydride migration in the (*exo*-1-R-$\eta^5$-C$_{10}$H$_8$)Mn(CO)$_3$ derivatives.

In Figure 1, showed are the Gibbs free energy diagram relative to complex **1** and the optimized structure from B3LYP/LACVP** calculations. Cyclohexadienyl ring in complex **1** is folded so that five carbon atoms are connected to Mn atom, and dihedral angle was calculated to be 34.4° (experimental results are 36.0° for [(*exo*-1-H-$\eta^5$-C$_{10}$H$_8$)Mn(CO)$_3$],[4] and 33.4° for [(*exo*-1-H-$\eta^5$-C$_{14}$H$_{10}$)Mn(CO)$_3$]).[4,6] In the first step of the migration, the hydride increases its interaction with the metal center accompanied by decreasing interactions between the metal and the carbon atoms carrying the aromatic substituent. At transition state **TS1**, C–H bond distance is elongated to 1.11 Å and H–Mn distance is 2.46 Å. At the same time, the bond distances between Mn and the carbon atoms carrying the aromatic substituent are increased. In the intermediate **2**, the hydride is shared by C and Mn with C–H distance of 1.16 Å and H–Mn distance of 1.83 Å. In **TS2**, hydride is migrated to Mn with H–Mn distance of 1.56 Å. **TS2** is located 19.2 kcal/mol higher in Gibbs free energy relative to **1**. In diene hydride intermediate **3**, hydride is located at Mn symmetrically as for naphthyl ring. Four carbon atoms of the naphthyl ring are located in a plane and binds to Mn in $\eta^4$ manner. The structural features of **TS3**, **4**, **TS4**, and **5** are similar to **TS2**, **2**, **TS1**, and **1**, respectively, except for the differences due to the position of methyl substituent. The
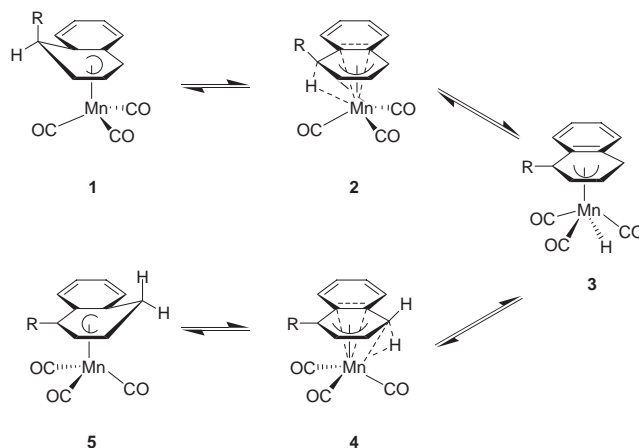


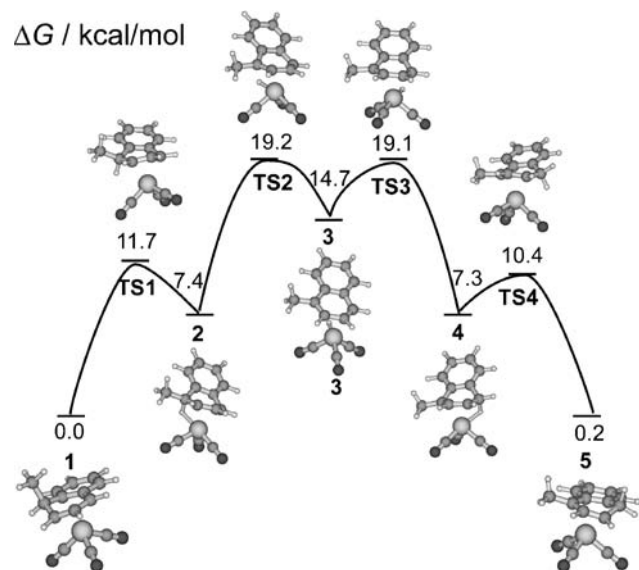**Scheme 1.** Mechanism for 1,4-hydride migration in the present work.

**Figure 1.** Relative Gibbs free energy diagram and the optimized structures of minima and transition states from B3LYP/LACVP** level of theory calculations for the 1,4-hydride migration.

**Table 1.** Gibbs free energy of activation (kcal/mol)

|   | Calculated[a] | Experiments | Notes[b] |
|---|---|---|---|
| **1** | 19.2 | N/A | |
| **6** | 20.0 | 21.0 | Ref 4 |
| **7** | 30.3 | 34.0 | Ref 5 |
| **8** | 17.9 | 14.6 | Ref 6 |

[a]B3LYP/LACVP** level of theory, present work.
[b]Experimental results were from the following references.

movement of the hydrogen atom from **2** to **4** is the rotation around the Mn–$\eta^4$-center of naphthalene axis. At the same time the naphthalene ring is also rotated in the opposite direction. In the course of the reaction, the relative orientations of the three carbonyl ligands and the angles between them remain almost the same.

($exo$-1-H-$\eta^5$-C$_{10}$H$_7$-4-Me)Mn(CO)$_3$ (**5**) is 0.2 kcal/mol higher than **1** in Gibbs free energy, which is in excellent agreement with the experimental equilibrium ratio (**1**:**5**) of 1.24:1 at room temperature.[3] We also performed the calculations on the other molecules shown in ref 3 and found a good correlation between experimental and computational results. (See Supporting Information for details).[16]

Table 1 shows the calculated Gibbs free energy of activation for 1,4-hydride migration. Listed are from B3LYP/LACVP** level of calculation. We also calculated the Gibbs free energy of activation of other three arene complexes shown in Scheme 2. For [($exo$-1-H-$\eta^5$-C$_{10}$H$_8$)Mn(CO)$_3$] (**6**), the results
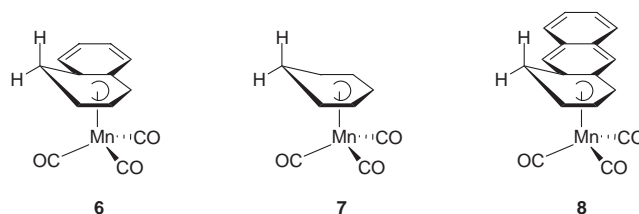


**Scheme 2.**

are in excellent agreement with the experimental results. We performed additional geometry optimization and frequency calculation with LACVP++** in order to check the dependence of thermodynamic quantity on the diffuse function. Inclusion of diffuse function does not affect the result (less than 1.3 kcal/mol) for this reaction.

In summary, we performed DFT calculations on the 1,4-hydride migration reaction of the arene complexes of manganese tricarbonyl compounds. The results for the mixture ratio and the activation energy are in excellent agreement with the experimental results.

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16  Supporting information is available on the CSJ-Journal Web Site, http://www.csj.jp/journals/chem-lett/index.html.