# Addition of Dinuclear Ruthenium Complex to Fullerene: Theoretical Study of Reaction mechanism and Prediction

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[Introduction] A large number of transition-metal complexes of fullerene have been synthesized. However, a new type of complex of transition-metal fullerene is still attractive for us because new properties are expected. Recently, the reaction between $[Ru(CO)_2(\eta^5\text{-}C_5H_5)]_2$ **1** and C_{60} was reported to afford a new fullerene complex $C_{60}[\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)]_2$ **2**, as shown in Scheme 1.[1] In **2**, $CpRu(CO)_2$ is bound with fullerene at the para-positions of a six-member ring of $C_{60}\text{-}I_h$ in an η^1-fasion. This is the first example of a pure η^1-coordination between transition metal and fullerene. However, the formation mechanism and the electronic process are unclear. In this work, we theoretically investigated the reaction between **1** and C_{60} by DFT calculation to elucidate the reaction mechanism and present theoretical prediction of more efficient reaction system.
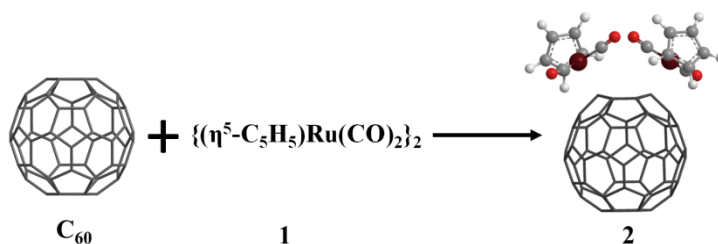
Scheme 1. Reaction between $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ (compound 1) and $C_{60}\text{-}I_h$.

[Computations] All geometry optimizations were carried out by the DFT method with the M06 functional. The LANL2DZ basis set was used for Ru atom. In energy
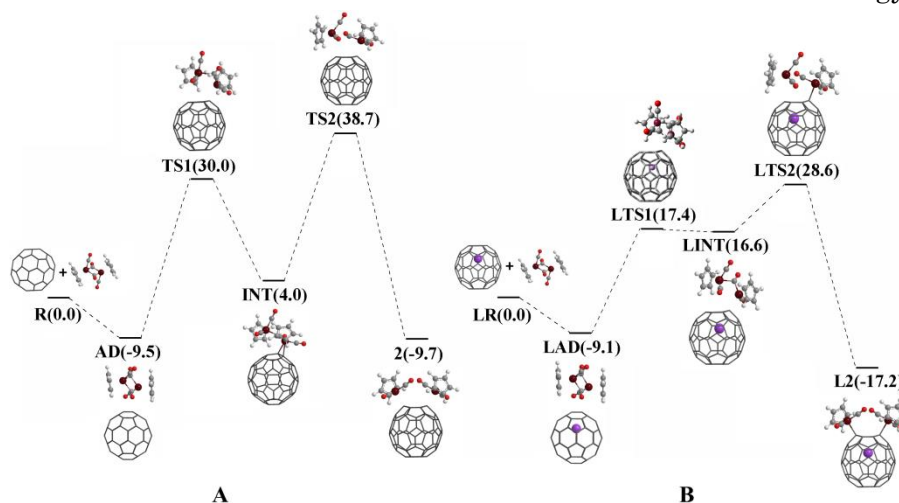

Figure 1. Comparison between the potential energy profiles with and without Li+ cation.

evaluation, another functional wB97XD was employed; the 6-311G(d) basis sets were used for all nonmetal elements and the SDD (Stuttgart-Dresden-Bonn) basis set was employed for the Ru atoms.

[Results and Discussion] The reaction of fullerene with dinuclear Ru complex occurs with very large activation energy (48.2 kcal/mol) and somewhat exo-thermicity (-9.5 kcal/mol), as shown in Figure 1(A). These results are consistent with the experimental report that this reaction is very slow (four to six months) and the yield of product is very small. In the transition state **TS1**, the Ru-Ru bond is elongated very much. In the intermediate **INT**, the Ru-Ru bond is already broken. One Ru is bound with the C atom of C_{60} but another Ru atom is not interact with the C_{60}. One CO ligand is bridging these two Ru atoms. In the second transition state **TS2**, the distant Ru moiety is approaching the C_{60} with changing its orientation toward C_{60}. The analysis of electronic process discloses that the charge transfer (CT) from the Ru complex to C_{60} is important in the reactions, as shown in Figure 2. To theoretically predict a more efficient reaction system, we investigated the reaction between **1** and $Li^+@C_{60}$. As shown in Figure 1(B), this reaction occurs though the similar geometry changes but its activation energy (37.5 kcal/mol) is much smaller and its exo-thermicity is considerably large. The charge-transfer from the Ru complex to $Li^+@C_{60}$ is much larger than in the reaction without Li^+. These results indicate that the Li^+ cation stabilizes very much the LUMO of C_{60} to accelerate the reaction. The reaction at the triplet state occurs with small activation barrier after singlet-triplet excitation, which is in good accordance with the experimental result. Though the Ru-Ru cleavage was experimentally proposed in the reaction at the triplet surface, the Ru-Ru bond cleavage is very unfavorable even at the triplet state. The geometry changes in the reaction at the triplet state are similar to those of the ground state. Not a triplet in the Ru-Ru bond but a CT-type triplet (**1** → C_{60}) participates in the reaction.
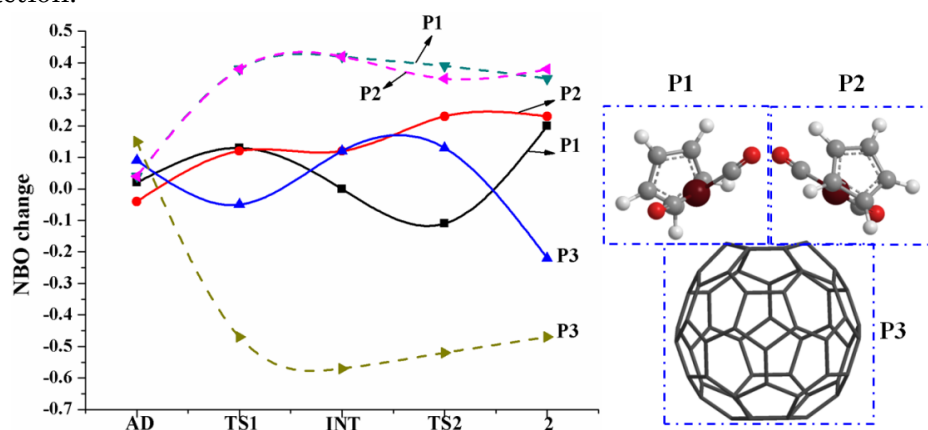

Figure 2. The changes of NBO charge in the reactions with and without Li^+ cation. Solid and dotted lines represent the reaction of C_{60} and that of $Li@C_{60}$, respectively.

Reference
1) Bowles, F. L.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.*, **2014**, 136, 3338−3341.