

A DFT study of fullerene C₆₀ transition metal complexes structure and dynamic

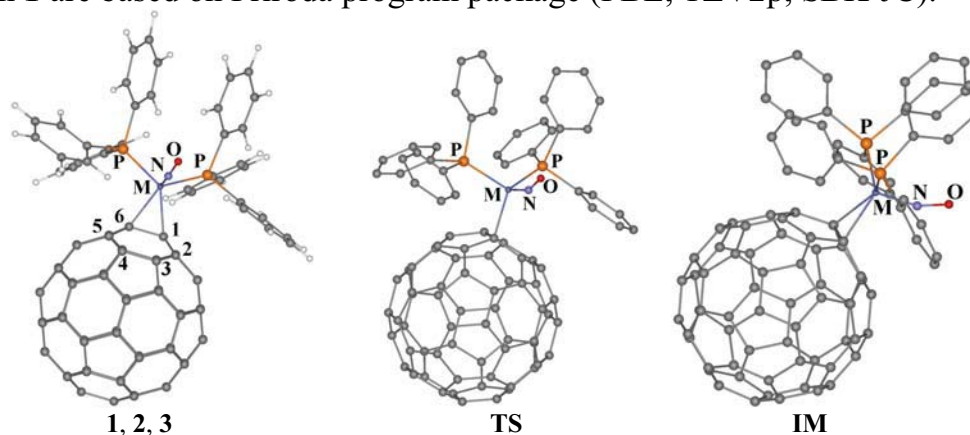
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Since the first preparation of organometallic complexes of fullerene^{1,2} many compounds of this type have been synthesized and structurally characterized by means of X-ray, NMR and DFT.³⁻⁵ Such systems have good prospects as catalysts in organic reactions and as new materials in optoelectronics. Data on dynamic processes in transition metal complexes of fullerene are relatively rare, e.g. variable-temperature and EXCY ¹³C NMR studies on [M(NO)(PPh₃)₂(η²-C₆₀)] (M = Co, Rh, Ru) **1-3** show the presence of C₆₀ – metal moiety rotation with low activation barrier and haptotropic migration processes with ΔG[#] = ca. 9, 10 and 14 kcal/mol, correspondingly.⁵

The DFT calculations reported in this paper on complexes **1-3** structures and activation barrier of haptotropic migration of metal moiety over the whole fullerene surface in **1** are based on Priroda program package (PBE, TZV2p, SBK-JC).⁶



η²,η²-Rearrangement over the whole surface of fullerene proceeds in **1** as intermolecular [1, 3]-shift of the Co metal atom via transition state **TS** (ΔG = 12.2 kcal/mol) and intermediate **1-IM** (ΔG = 7.6 kcal/mol): **1** → **1-TS** → **1-IM** → **1-TS** → **1-IM** → **1**. Theoretically calculated data on geometry, structure and conformation of **1-3** and activation barrier for **1-TS** of metal migration in **1** thus are in good agreement with experimental data.

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- [1] Fagan P.J., Calabrese J.C., Malone B., *Acc. Chem. Res.*, **25**, 134 (1997).
- [2] Hawkins J.M., *Acc. Chem. Res.*, **25**, 150 (1997).
- [3] Nunzi F., Sgamellotti A., Re N., Floriani C., *Organometallics*, **19**, 1628 (2000).
- [4] Stefens A.H., Green M.L.H., *Adv. Inorg. Chem.*, **44**, 1 (1997).
- [5] Green M.L.H., Stefens A.H., *Chem. Commun.*, 793 (1997).
- [6] Laikov D. N., *Chem. Phys. Lett.*, **V. 281**, 151 (1997).