

研究论文

**CpRu(PPh<sub>3</sub>)<sub>2</sub>SSi<sup>i</sup>Pr<sub>3</sub>与SCNR (R=Ph, 1-Naphthyl)反应的结构、成键与机理的理论研究**

丁养军, 张振伟, 朱树芬, 毕思玮\*

(曲阜师范大学化学科学学院 曲阜 273165)

收稿日期 2006-6-22 修回日期 2007-1-11 网络版发布日期 2007-5-18 接受日期 2007-1-11

摘要 应用密度泛函理论(DFT), 通过CpRu(PH<sub>3</sub>)<sub>2</sub>SSi<sup>i</sup>Pr<sub>3</sub> (Cp=环戊二烯负离子; <sup>i</sup>Pr=异丙基)

与SCNH模型化反应, 探讨了CpRu(PPh<sub>3</sub>)<sub>2</sub>SSi<sup>i</sup>Pr<sub>3</sub>与SCNR (R=苯基, 萘基)的反应机理,

分析了反应所涉及各相关化合物的结构与成键特征. 反应中首先失去一个膦配体, 生成一个中间体. 该中间体中,

硫原子采取sp<sup>2</sup>杂化, 硫原子剩余的一个p轨道与金属中心上的d轨道具有相同的对称性,

因而该p轨道上的孤电子对可与金属中心上的d轨道形成π键, 导致Cp环中心, Ru, S, P和Si原子在同一平面内,

而不是S, P和Si原子偏离该平面. 计算结果预测, S=C双键中的p键打开,

生成含金属中心的四元环螯合物一步为反应的决速步骤. 空间位阻的减小、p共轭体系的生成以及螯合环的存在, 是导致该反应热力学有利的重要原因.

关键词 [密度泛函理论](#) [反应机理](#) [钌配合物](#) [硅烷基转移](#)

分类号

**Theoretical Study of Structures, Bonding and Mechanism on Reaction of CpRu(PPh<sub>3</sub>)<sub>2</sub>SSi<sup>i</sup>Pr<sub>3</sub> with SCNR (R=Ph, 1-Naphthyl)**

DING Yang-Jun, ZHANG Zhen-Wei, ZHU Shu-Fen, BI Si-Wei\*

(College of Chemistry Science, Qufu Normal University, Qufu 273165)

**Abstract** The model reaction mechanism of CpRu(PH<sub>3</sub>)<sub>2</sub>SSi<sup>i</sup>Pr<sub>3</sub> with SCNH, derived from CpRu(PPh<sub>3</sub>)<sub>2</sub>-SSi<sup>i</sup>Pr<sub>3</sub> with SCNR (R=Ph, 1-naphthyl), was investigated by using density functional theory (DFT). The structures and bonding involved in the reaction mechanism were analyzed. The phosphine ligand is first dissociated from the reactant to afford an intermediate in the reaction. The sulphur atom in the intermediate has sp<sup>2</sup> hybridization, and the remaining p orbital is symmetrical to the d orbital of the metal center. Thus, the lone pair on the p orbital can have interaction with the d orbital to form a π bond, which leads to the coplanarity of the center of Cp ring, Ru, P, S and Si atoms, rather than the deviation of P, S and Si atoms from the plane. Our results of calculations predict that formation of a four-membered ring containing metal center is the rate-determining step. Decrease of steric hindrance, formation of p conjugation and occurrence of chelation are responsible for the favorable thermodynamics of the reaction.

**Key words** [density functional theory](#) [reaction mechanism](#) [ruthenium complex](#) [silyl migration](#)

DOI:

通讯作者 毕思玮 [siweibi@126.com](mailto:siweibi@126.com)

扩展功能

本文信息

▶ [Supporting info](#)

▶ [PDF\(395KB\)](#)

▶ [\[HTML全文\]\(39KB\)](#)

▶ [参考文献](#)

服务与反馈

▶ [把本文推荐给朋友](#)

▶ [加入我的书架](#)

▶ [加入引用管理器](#)

▶ [复制索引](#)

▶ [Email Alert](#)

▶ [文章反馈](#)

▶ [浏览反馈信息](#)

相关信息

▶ [本刊中 包含“密度泛函理论”的相关文章](#)

▶ 本文作者相关文章

- [丁养军](#)
- [张振伟](#)
- [朱树芬](#)
- [毕思玮](#)