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[Cp*Rh(CO)$_2$Me]BF$_4$和二环庚二烯的反应机理研究

Mechanistic Study on Reaction of [Cp*Rh(CO)$_2$Me]BF$_4$ with nbd

中文关键词：共聚；　催化剂；　铑；　二环庚二烯；　环张力；　机理

英文关键词：copolymerization; catalyst; Rh; nbd; ring strain; mechanism

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中文摘要：

[Cp*Rh(CO)$_2$Me]BF$_4$与二环庚二烯反应生成的含五元环产物可以作为烯烃/羰基共聚的潜在催化剂。本文采用密度泛函(DFT)方法对该类反应的机理进行了研究。研究表明，甲基转移是整个反应的决速步骤。计算得到，该步反应的活化焓变为71.67 kJ·mol^{-1}，跟实验中得到的相应的焓变值(72 ± 2 kJ·mol^{-1})吻合得很好。计算结果同时证实，该反应在热力学上非常有利。结构分析表明，二环庚二烯和金属中心配位后，二环庚二烯内的环张力得以释放以及螯合环的生成是导致热力学有利的主要原因。

英文摘要：

The product of the reaction of [Cp*Rh(CO)$_2$Me]BF$_4$ with nbd is a potential catalyst for the catalytic alternating copolymerization of CO and alkenes. The mechanism for the reaction has been completely studied by using density functional theory (DFT). The energetics and structures involved in this reaction have been fully discussed. Our results of calculations reveal that the methyl migration is the rate-determining step with the calculated activation enthalpy being $\Delta H^{\ddagger}$ = 71.67 kJ·mol^{-1}, well in agreement with the experimental observations ($\Delta H^{\ddagger}$ = 72 ± 2 kJ·mol^{-1}). The relief of ring strain in nbd after coordinating to the metal center and the chelation effect involved in the product play a crucial role for the stabilization of product, which makes the reaction much favorable thermodynamically.

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