

P_n ring size dependence on NHC-induced ring contraction reactions of $[\text{CoCp}''(\eta^4\text{-P}_4)]$ and $[\text{FeCp}^*(\eta^5\text{-P}_5)]$. A DFT Study.

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Cyclopolyphosphorus rings (*cyclo*- P_n) as ligands, isolobal to aromatic carbon rings, have intrigued chemists for the past few decades.¹⁻³ The reactivity of transition metal stabilized *cyclo*- P_n [TM-*cyclo*- P_n] through phosphorus has led to several facile transformations with retention, expansion, fragmentation, and even contraction of the ring.⁴⁻⁹ In a recent report, Sheer et al. observed carbene induced facile ring contraction of $[\text{CoCp}''(\eta^4\text{-P}_4)]$, and $[\text{Ta}(\text{CO})_2\text{Cp}''(\eta^4\text{-P}_4)]$ ($\text{Cp}'' = 1,2,4\text{-tri-tert-butyl-cyclopentadienyl}$, $\text{Cp}' = 1,3\text{-di-tert-butyl-cyclopentadienyl}$).^{5,6} However, a similar reaction with $[\text{FeCp}^*(\eta^5\text{-P}_5)]$ ends up giving an intermediate with ring retention.⁸ In order to answer these discrepancies, arising as the ring size increases, we have computed the energetics for the ring contraction with variation in ring size (Figure 1). We have employed different theoretical tools for a qualitative picture of the overall reaction. It is observed that the inherent ring strain in the P_n ring plays a decisive role in determining the ring contraction capability of [TM-*cyclo*- P_n] complex. We have further analysed the role of different metal, nucleophile on the ring-contraction energetics. An isolobal perspective on these reactions affords a more simplistic picture of the overall reaction.¹⁰

We also report the mechanism of ring contraction by NHC in triple decker complexes with varying valence electron count (VEC), the role of halogens in inducing ring contraction and product distribution in double decker and triple decker complexes.^{5,11,12}

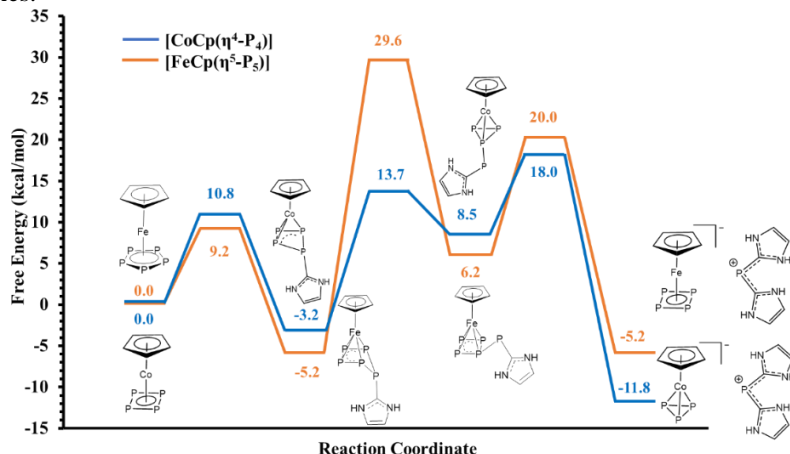


Figure 1. Free energy landscape for the carbene induced ring-contraction reaction of $[\text{CoCp}(\eta^4\text{-P}_4)]$ and $[\text{FeCp}(\eta^5\text{-P}_5)]$ computed at B3LYP/Def2SVP level of theory with the IEFPCM solvation model for THF solvent at 298 K.

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