

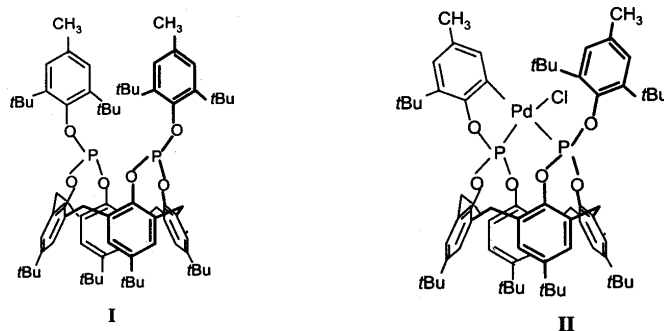
Cyclometallation in calixarenes: Synthesis and structural characterization of a novel cyclopalladated calix[4]arene bisphosphite

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Calixarenes¹, a class of phenolic macrocycles, continue to find applications in diverse fields, especially in catalysis and solvent extraction of metal ions. Phosphorus containing calixarenes² with P(III) centres (notably phosphanes, phosphites or phosphinites) provide an attractive platform for anchoring transition metal-based catalysts which would have several distinct advantages over the conventional transition metal homogeneous catalysts. Recent reports on calixarenes have explored this aspect³. In this context, our present report on a novel cyclopalladated calixarene bisphosphite unfolds a new facet of calixarene chemistry.

The novel symmetrically bridged calix[4]arene bisphosphite-**I** has been isolated from the reaction of *p*-*tert*-butylcalix[4]arene with ROPCl_2 ($\text{R} = 2,6\text{-Bu}^t_2, 4\text{-ME-C}_6\text{H}_2$) in the presence of NaH, followed by column chromatography over silica gel. Reaction of **I** with $\text{PdCl}_2(\text{NCPH})_2$ or $\text{PdCl}_2(\text{COD})$ gives the cyclopalladated *p*-*tert*-butylcalix[4]arene bisphosphite-**II**, unprecedented in calixarene chemistry. Structural studies reveal that the aryl rings of the phenolic substituents in the cyclopalladated complex-**II** are oriented perpendicular to each other unlike in the case of the calixarene bisphosphite ligand-**I** although in both the compounds the calixarene framework adopts a distorted cone conformation.



References

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