

Cyclopalladation of Schiff bases of thiosubstituted benzylideneanilines

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Cyclopalladation processes are important in solving the current chemical problems of the activation of the C–H bonds by transition metal compounds. Various applications of cyclometalated complexes to organic synthesis and other fields of chemistry are known. In the intramolecular activation of C–H bonds, palladium has been historically classified as a typical electrophile. The cyclopalladation of various N-donor ligands like amine, imines, azobenzenes, arylhydrazones and their chemistry is extensively studied. Their ease of formation and resistance towards hydrolysis make them attractive for reactivity studies. The cyclopalladation of imines is mainly achieved by using palladium(II) acetate as a palladating agent because other palladating agents like PdCl_4^- , PdCl_2 , $\text{PdCl}_2(\text{RCN})_2$ etc. have strong affinity towards metal catalysed hydrolysis of Schiff bases. The Schiff bases bearing an additional donor group at the suitable position to maintain chelate structure provide extra stability to the cyclopalladated complexes. On that basis, we have designed several thiosubstituted Schiff bases belonging to the class 2-(alkylthio)-N-(benzylidene)anilines (**1**, **2**) [$\text{C}_6\text{H}_4(\text{R})\text{-CH=N-C}_6\text{H}_4\text{X}$; R = H(**a**), 4- CH_3 (**b**), 4- OCH_3 (**c**), 4- Cl (**d**), 4- NO_2 (**e**); X = 2- SCH_3 (**1**), 2- SCH_2Ph (**2**)], a family of tridentate (C, N, S) donor ligands. The ligands react with $\text{Pd}(\text{OAc})_2$ in dry benzene under reflux for 1 h. The brown precipitate is collected and reacted with LiCl in MeOH-CHCl_3 mixture affording orange brown cyclopalladated species having the coordination sphere $[\text{Pd}(\text{C, N, S})\text{Cl}]$ (**3**, **4**). The mode of ligand binding is established with the help of high resolution $^1\text{H NMR}$ and IR data. The elemental analyses data are also reported.

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