

Factors influencing cyclometalations in platinum(II) complexes with tertiary phosphine ligands.

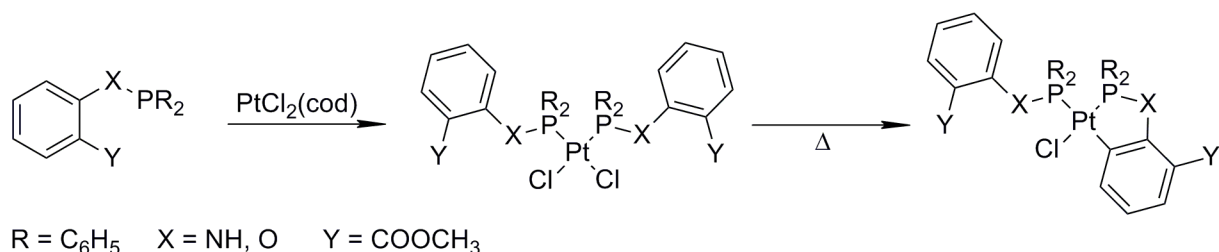
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Intramolecular activation reactions of C-H bonds on aromatic rings are frequently studied in transition metal complexes since resulting cyclometalated complexes are tested and applied in variable areas of research.^[1,2] However, factors influencing proclivity of single complex for cyclometallation are far from being fully understood. We recently performed study of cyclometallations in Pt(II) complexes with phosphinoamine and phosphinophenol ligands via C-H thermal activation to evaluate the importance of ligand substitution on the reactivity of the starting compounds. The presence and positioning (*ortho* and *para*) of the substituents combined with intramolecular hydrogen interactions were found to be crucial for a successful cyclometalation. We have therefore prepared a series of organophosphorus ligands and synthesized their *cis*-Pt(II) complexes from PtCl₂(cod). By means of ³¹P NMR spectroscopy we investigated their propensity for cyclometalation via thermal C-H bond activation on aromatic moieties as well as possible isomerization of *cis* complexes into *trans* isomers. We support our experimental findings by single crystal X-ray diffraction and quantum-mechanical calculations.

Figure 1 Synthetic route to cyclometalated Pt(II) complexes



1 M. Beller, H. Fischer, W. A. Herrmann, K. Öfele, C. Brossmer, *Angew. Chemie Int. Ed. English* **1995**, *34*, 1848.

2 M. Albrecht, *Chem. Rev.* **2010**, *110*, 576.