عنوان مقاله:

Computational Study of Multiple Pathways and Ion-Pairing in Oxidative Addition of Iodomethane to a Binuclear Organoplatinum(II) Complex containing Imine and Phosphine Bridging Ligands

محل انتشار:

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خلاصه مقاله:

A density functional theory (DFT) study of the reaction of [Me۲Pt(μ-NN)(μ-dppm)PtMe۲] (۱) (NN = phthalazine, dppm = bis(diphenylphosphino)methane) with two equivalents of iodomethane in acetone (A) and benzene (B) reveals a mechanism in agreement with spectrocopic and kinetic data reported earlier by Rashidi and coworkers, for which computation permits additional insights. Following initial oxidation at one platinum(II) centre to form mixed valence outer-sphere ion-pairs containing a PtII→PtIV interaction, [Me۳Pt(+)(μ-NN)(μ-dppm)PtMe۲·I(-)] (۶A, ۷B), two competing mechanisms are found for the second oxidative addition at the remaining platinum(II) centre. In one mechanism (Path I), a rearrangement of intermediate ۶A and ۷B to form [Me۳Pt(κ۱-NN)(μ-dppm)(μ-I)PtMe۲] (۲aA, ۲aB) occurs prior to oxidative addition giving, after subsequent steps, outer-sphere ion-pairs [Me۳Pt(κ۱-NN)(μ-dppm)(μ-I)PtMe۳(+)·I(-)] (۱۰A, ۱۰B), followed by dissociation of phthalazine and formation of the product complex [Me۳Pt(μ-dppm)(μ-I)۲PtMe۳] (۴A, ۴B) containing two PtIV centres.. In the other mechanism (Path ۱I), oxidative addition occurs at the PtII centre of ۷A and ۷B, leading also to ۱۰A and ۱۰B. Paths I and II are competitive in acetone, but Path I is preferred in benzene. The first oxidative addition computes as having a lower barrier than the second, in accord with .experiment, and we attribute this to the occurrence of a Pta···Ptb interaction assisting the first oxidative addition at Ptb

کلمات کلیدی:

platinum, oxidation, organoplatinum, Reaction mechanisms, DFT