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Trimerization of Acetylene in the Presence of ($PH_2CH_2CH_2PH_2$)IrCl as a Catalyst. A Computational Study

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1. Introduction:

Syntheses of benzene and benzenoid-based structures are very important synthetically and medicinally. Their catalytic preparations have advantages over thermal preparations as they take place at milder conditions and are more regioselective. Since the trimerization of alkynes in the presence of nickel catalyst, trimerization of alkynes in the presence of a number of transition metal catalysts have been reported.[1] Transition metal catalysts of group 9 Co and Rh have been extensively used in experiments and a number of theoretical studies on this trimerizations have been reported.[2] Though there have also been a number of experimental studies on the trimerization of alkynes in the presence of Ir catalyst, theoretical studies about this catalyst have been limited and to the best of our knowledge there are only two theoretical studies on the trimerization of acetylenes as models for alkynes in the presence of CpIr and TpIr catalysts (Cp = cyclopentadienyl, Tp = hydrotris(pyrazolyl)borate).[3] These two studies showed that there are two possible reaction mechanisms; intramolecular [4+2] cycloaddition and Schore mechanisms. While in the case of CpIr, intramolecular [4+2] cycloaddition is more favorable than Schore mechanism, in the case of TpIr the two mechanisms are competitive and when there are electron-withdrawing methoxy carbonyl substituents, only one mechanism is possible; that is Schore mechanism.

Continuing to our study on the trimerization of acetylene in the presence of transition metal catalysts, in this work the trimerization of acetylene in the presence of $[(cod)IrCl]_2$ and dppe, where ($PH_2CH_2CH_2PH_2$) and acetylene were used as models for dppe and alkynes, were studied theoretically in detail, focusing on the possibility of intramolecular [4+2] cycloaddition and Schore mechanism shown in Scheme and which of them is more favorable. This study can give more information about the catalytic cycles and therefore can help in designing better catalysts.

2. Computational methods:

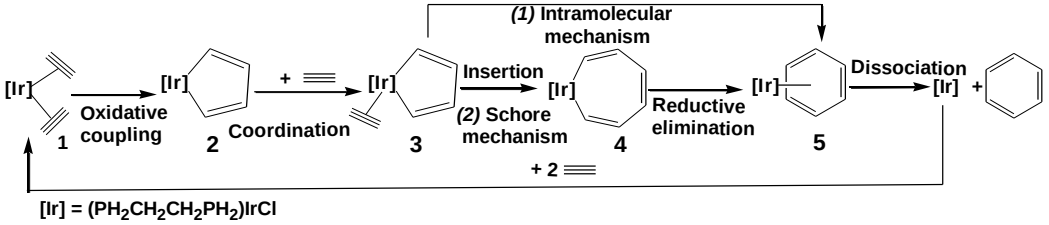
Density functional theory (DFT) calculations with B3LYP and M06 functionals were performed to verify the feasibility of the reaction mechanism suggested in Scheme. In calculations we used two basis sets called I (LANL2DZ + f polarization function for Ir, 6-31G** for C and H, and 6-31+G** for P and Cl) and II (LANL08 for Ir, 6-311G(d,p) for C and H, and 6-311+G(d,p) for P and Cl). The structures of intermediates and transition states were optimized with the B3LYP/I method, whereas to obtain better enegetics we performed single point energy calculations at the B3LYP/II and M06/II levels. Unless explicitly stated otherwise, the potential energies corrected with the zero-point energy (ZPE) at the B3LYP/I level are used in discussion.

3. Results and Discussion:

We found two pathways for each of intramolecular [4+2] cycloaddition and Schore mechanisms depending on the orientation of the $PH_2CH_2CH_2PH_2$ and Cl ligands. The optimized structures and potential energy profiles corrected with zero-point energy (ZPE) for more favorable pathway in both mechanisms are shown in Figure. In the initial stage of the reactions oxidative coupling of two coordinating alkyne molecules takes place to lead to iridacyclopentadiene intermediate and then the reaction pathways are separated into the cycloaddition and Schore mechanisms. Prior to oxidative coupling, as shown in Figure, the stable bis alkyne Ir(I) complex **1a** is isomerized to less stable **1b** with an activation energy of 16.3 kcal/mol. Following this isomerization, oxidative coupling in **1b** takes place with an activation energy of 8.3 kcal/mol to give iridacyclopentadiene **2a**. The oxidative coupling of **1a** to **2a** requires higher activation energy (28.9 kcal/mol). Although **2a** is coordinatively unsaturated, it is more stable than coordinatively saturated **1a** and **1b** due to the formation of three σ-bonds at the expense of cleavage of weak two π bonds. The shape of **2a** is the square pyramid where one of the C atoms (C1) in the iridacyclopentadiene ring is located at the axial position. For the formation of benzene molecule, interaction of π orbitals in the iridacyclopentadiene ring with the third acetylene molecule is necessary. However, acetylene coordination to the vacant site in **2a** would not give a proper structure. Acetylene π complex **3b** suitable for this reaction is yielded when the third acetylene molecule approaches between the axial C1 atom and basal Cl ligand to the Ir atom. The formation of **3b** through weak reactant complex **7b** requires only a small activation energy of 3.2 kcal/mol. From this π complex, there are two reaction pathways; one is intramolecular [4+2] cycloaddition and the other is Schore mechanism. The [4+2] cycloaddition takes place via C_s symmetric

TS4 to form η^4-benzene Ir(I) complex **5b1** with an activation energy of 8.2 kcal/mol. This small activation energy can be ascribed to the high exothermicity of this step (−52.4 kcal/mol) which can be ascribed to the formation of two σ bond and coordination of four atoms from benzene ring to $(PH_2CH_2CH_2PH_2)IrCl$ fragment. **5b1** isomerizes through **TS5** and **TS6** to two other benzene Ir complexes, **5a2** and **5b2** which are more stable than **5b1** by 12.3 and 17.1 kcal/mol, respectively. In Schore mechanism the π complex **3b** isomerizes to iridabicyclo[3.2.0]heptatriene complex **6b** via $\mathbf{TS_{3b\text{-}6b}}$ with an activation energy of 10.3 kcal/mol. There is a highly strain imposed on the four-membered ring in **6b**. Therefore, the transformation of **6b** to puckered iridacycloheptatriene **4b1** takes place with a low activation energy of 6.1 kcal/mol. **4b1** isomerizes to the planar iridacycloheptatriene **4b2**.While **4b2** is more stable than **4b1** with the B3LYP calculations, it is less stable at the M06 level. This is because B3LYP functional does not take dispersion interaction into account. There is another pathway from bicycle **6b** in which it is rearranged to **5b1**. While this reaction directly giving benzene complex **5b1** through **TS11** requires an activation energy of 12.5 kcal/mol, the highest activation barrier in the reaction through **4b1** is 13.5 kcal/mol and the corresponding **TS10** is less stable than **TS11** by 11.7 kcal/mol, to show that the reaction through **TS11** is more favorable. Comparison of the two mechanisms showed that the intramolecular [4+2] cycloaddition mechanism is more favorable, because the step from **3b** in this mechanism requires a lower activation energy compared to that in the Schore mechanism (8.2 and 10.3 kcal/mol). However, this small difference suggests that the favorable mechanism could change with electronic and/or steric effects of substituted groups in ligands.

Scheme. proposed Scheme for trimerization of acetylene in the presence of $(PH_2CH_2CH_2PH_2)IrCl$ as a catalyst.



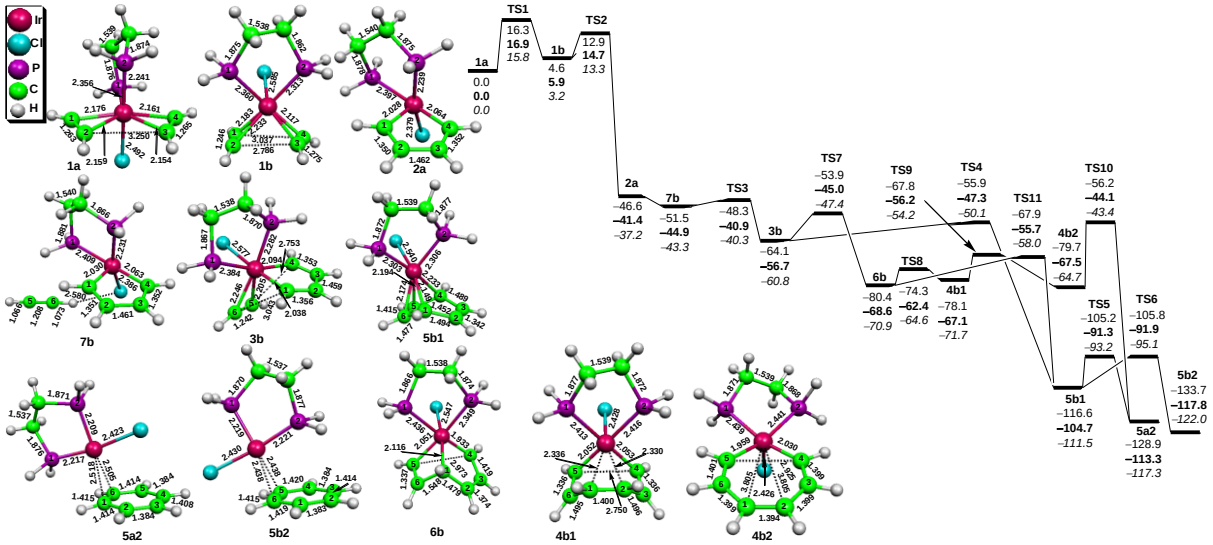


Figure. Some of the optimized structures in intramolecular [4+2] cycloaddition and Schore mechanisms and the energy profile for the trimerization of acetylene in the presence of $(PH_2CH_2CH_2PH_2)IrCl$ as a catalyst. All bonds are in Å. All energies are ZPE-corrected and at B3LYP/I (normal), B3LYP/II (bold) and M06/II (italic) relative **1a** + acetylene.

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