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Communications to the Editor

Addition of Aromatic C−H Bonds to η^3-Allenyl/Propargyl Complexes. Organoplatinum-Induced Electrophilic Aromatic Substitution Reactions

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One of the fundamental strategies to achieve C−C coupling between an aromatic ring and an unsaturated carbon−carbon bond is via Friedel−Crafts reactions in which a Lewis acid is often essential.[1] To use organometallic electrophiles for such a purpose is attractive because the metal may activate the ligated organic moiety intrinsically and facilitate the carbon−carbon bond formation in new manners.[2,3] A recently discovered cationic η^3-allenyl/-propargyl complex of platinum, $[Pt(PPh_3)_2(\eta^3\text{-}C_3H_3)](BF_4)$ (**1**), is found to be a potent electrophile and is prone to regioselective nucleophilic addition at the central carbon of the novel η^3-C_3H_3 moiety.[4] The remarkable reactivity of **1** toward a wide variety of hard nucleophiles prompted us to explore the reaction of **1** with soft aromatic species. We report here the unprecedented regioselective addition of aromatic C−H bonds across the C≡C bond of the C_3H_3 fragment. These reactions are found to undergo an organoplatinum-induced electrophilic substitution and lead to aryl vinylation.

Hydropyrrolylation of $[Pt(PPh_3)_2(\eta^3\text{-}C_3H_3)](BF_4)$ (**1**) is accomplished by directly reacting **1** with pyrrole or *N*-methylpyrrole at 25 °C in a dry nitrogen atmosphere. As the electrophilic attack on pyrrole normally occurs at the 2-position, the C−C coupling takes place exclusively between the central carbon of C_3H_3 and the 2-pyrrolyl carbon, thereby generating the central-carbon-substituted η^3-2-pyrrolylallyl complexes $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(2\text{-}C_4H_3NR)CH_2]\}(BF_4)$ (R = H (**2a**), Me (**2b**)) with excellent yields. In the reaction of **1** with indole, the insertion of C_3H_3 into the 3-indolyl C−H bond leads to the formation of $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(3\text{-indolyl})CH_2]\}(BF_4)$ (**3a**). The addition of 3-methylindole to **1** gives rise to the formation of $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(2-(3\text{-methyl})\text{indolyl})CH_2]\}(BF_4)$ (**3b**) at a relatively slow rate.

As to the aryl system, complex **1** can undergo selective addition of the para aryl C−H bond of $PhNMe_2$ to form an arylallyl complex $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(p\text{-}Me_2NC_6H_4)CH_2]\}(BF_4)$ (**4**). Hydroarylation reactions of other electron-riched arenes such as dimethoxy- or trimethoxybenzene to **1** with regioselectivity of electrophilic aromatic substitution are also successful and yield $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(Ar)CH_2]\}(BF_4)$ (Ar = 2,4-$(MeO)_2C_6H_3$ (**5**), 2,4,6-$(MeO)_3C_6H_2$ (**6**)). In contrast, less electron rich aromatics such as benzene, toluene, xylene, and anisole do not react with **1** under the same conditions. Nucleophilic addition to **6** with ^{n}-Bu_4NBH_4, NaSPh, or $Na[CH(SO_2Ph)_2]$ results in $CH_2C[2,4,6\text{-}(MeO)_3C_6H_2]CH_2Nu$ (Nu = H (**7a**), SPh (**7b**), $CH(SO_2Ph)_2$ (**7c**), respectively) (Scheme 1). With respect to the arenes, the overall transformation accomplishes vinylation of arenes, which provides the products as resulting from the Heck or Stille vinylic arylation.[5]

The regiochemistry of the C−H activation in the aromatics appears to be in agreement with the reactivity of electrophilic aromatic substitution. To look for further evidence for the mechanism of electrophilic substitution, a crossover labeling experiment has been carried out. A sample of 1,3,5-$(MeO)_3C_6D_{3-n}H_n$ (n = 0, 1) with d_2:d_3 = 22:78 was mixed with an equimolar amount of 1,3,5-$(MeO)_3C_6H_3$. The resulting 1,3,5-trimethoxybenzene with a labeling distribution of d_0:d_2:d_3 = 50:11:39 was allowed to first react with **1** and followed by treatment with NaSPh. The NMR spectra showed the formation of **7b** with deuterium appearing at the aryl ring and the allyl termini but without stereospecificity. The mass spectroscopy provides the deuterium distribution of d_0:d_1:d_2:d_3 = 28:31:34:7 in the products. Such results strongly support a process with intermolecular hydrogen scrambling during the reaction courses. A mechanism that involves electrophilic aromatic substitution may elucidate these reactions (Scheme 2). The electrophilic **1** replaces an aryl proton to form a metallacyclobutene intermediate. Ensuing protonation of metallacyclobutene then generates the arylallyl complexes. Casey's and our findings concerning synthesis of metallacyclobutene complexes by adding nucleophiles such as Et_3N, Ph_3P, or pyridine to η^3-allenyl/propargyl complexes provide the evidence for such a mechanism.[6]

Although linear η^1-allenyl complexes also are subjected to regioselective nucleophilic addition at the central carbon, they neither show reactivity to the aromatics nor conduct the formation of metallacyclobutenes.[7] The unique bonding mode of the

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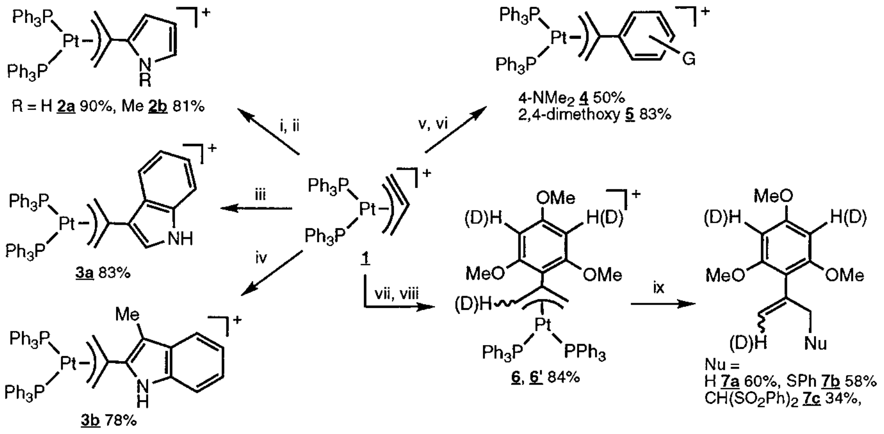
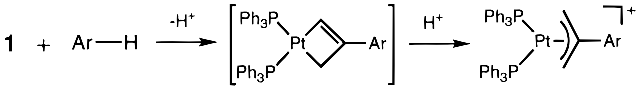
Scheme 1



i: C_4H_4NH, ii: C_4H_4NMe, iii: indole, iv: 3-methylindole, v: $C_6H_5NMe_2$, vi: 1,3-$C_6H_4(OMe)_2$,
vii: 1,3,5-$C_6H_3(OMe)_3$, viii: 1,3,5-$C_6D_3(OMe)_3$/1,3,5-$C_6D_2H(OMe)_3$/1,3,5-$C_6H_3(OMe)_3$ (39:11:50)
ix: $^nBu_4NBH_4$, NaSPh, or Na[$CH(SO_2Ph)_2$],

Scheme 2



severely distorted η^3-allenyl/propargyl ligands[8] confers sufficient and versatile electrophilicity at the center carbon, which leads to remarkably high reactivity as well as subtle chemical selectivity toward different nucleophiles.

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Supporting Information Available: Experimental and spectral details (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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