

## Communications to the Editor

### Addition of Aromatic C–H Bonds to $\eta^3$ -Allenyl/Propargyl Complexes. Organoplatinum-Induced Electrophilic Aromatic Substitution Reactions

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Received November 17, 1997

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.<sup>1</sup> 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.<sup>2,3</sup> A recently discovered cationic  $\eta^3$ -allenyl/propargyl complex of platinum,  $[\text{Pt}(\text{PPh}_3)_2(\eta^3\text{-C}_3\text{H}_3)](\text{BF}_4)$  (**1**), is found to be a potent electrophile and is prone to regioselective nucleophilic addition at the central carbon of the novel  $\eta^3\text{-C}_3\text{H}_3$  moiety.<sup>4</sup> 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  $\text{C}_3\text{H}_3$  fragment. These reactions are found to undergo an organoplatinum-induced electrophilic substitution and lead to aryl vinylation.

Hydropyrrolylation of  $[\text{Pt}(\text{PPh}_3)_2(\eta^3\text{-C}_3\text{H}_3)](\text{BF}_4)$  (**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  $\text{C}_3\text{H}_3$  and the 2-pyrrolyl carbon, thereby generating the central-carbon-substituted  $\eta^3$ -2-pyrrolylallyl complexes  $\{\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(2\text{-C}_4\text{H}_3\text{NR})\text{CH}_2]\}(\text{BF}_4)$  (R = H (**2a**), Me (**2b**)) with excellent yields. In the reaction of **1** with indole, the insertion of  $\text{C}_3\text{H}_3$  into the 3-indolyl C–H bond leads to the formation of  $\{\text{Pt}(\text{PPh}_3)_2$

$[\eta^3\text{-CH}_2\text{C}(3\text{-indolyl})\text{CH}_2]\}(\text{BF}_4)$  (**3a**). The addition of 3-methylindole to **1** gives rise to the formation of  $\{\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(2\text{-}(3\text{-methyl})\text{indolyl})\text{CH}_2]\}(\text{BF}_4)$  (**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  $\text{PhNMe}_2$  to form an arylallyl complex  $\{\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(p\text{-Me}_2\text{NC}_6\text{H}_4)\text{CH}_2]\}(\text{BF}_4)$  (**4**). Hydroarylation reactions of other electron-rich arenes such as dimethoxy- or trimethoxybenzene to **1** with regioselectivity of electrophilic aromatic substitution are also successful and yield  $\{\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{Ar})\text{CH}_2]\}(\text{BF}_4)$  (Ar = 2,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**5**), 2,4,6-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**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 <sup>n</sup>-Bu<sub>4</sub>NBH<sub>4</sub>, NaSPh, or Na[CH(SO<sub>2</sub>Ph)<sub>2</sub>] results in  $\text{CH}_2\text{C}(2,4,6\text{-}(\text{MeO})_3\text{C}_6\text{H}_2)\text{CH}_2\text{Nu}$  (Nu = H (**7a**), SPh (**7b**), CH(SO<sub>2</sub>Ph)<sub>2</sub> (**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.<sup>5</sup>

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)<sub>3</sub>C<sub>6</sub>D<sub>3–n</sub>H<sub>n</sub> (*n* = 0, 1) with d<sub>2</sub>:d<sub>3</sub> = 22:78 was mixed with an equimolar amount of 1,3,5-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>. The resulting 1,3,5-trimethoxybenzene with a labeling distribution of d<sub>0</sub>:d<sub>2</sub>:d<sub>3</sub> = 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<sub>0</sub>:d<sub>1</sub>:d<sub>2</sub>:d<sub>3</sub> = 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<sub>3</sub>N, Ph<sub>3</sub>P, or pyridine to  $\eta^3$ -allenyl/propargyl complexes provide the evidence for such a mechanism.<sup>6</sup>

Although linear  $\eta^1$ -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.<sup>7</sup> The unique bonding mode of the

(1) (a) March, J. *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure* 4th ed.; John Wiley & Sons: New York, 1992. (b) Olah, G. A. *Friedel–Crafts Chemistry*; Wiley: New York, 1973. (c) Roberts, R. M.; Khalaf, A. A. *Friedel–Crafts Alkylation Chemistry*; Marcel Dekker: New York, 1984. (d) Olah, G. A. *Friedel–Crafts & Related Reactions*; Wiley: New York, 1963–1965; Vol. 2. (e) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578.

(2) Trost, B. M.; Fortunak, J. M. D. *Organometallics* **1982**, *1*, 7.

(3) (a) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043. (b) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053 and the references therein. (c) Casey, C. P.; Woo, L. K.; Fagan, P. J.; Palermo, R. E.; Adams, B. R. *Organometallics* **1987**, *3*, 447.

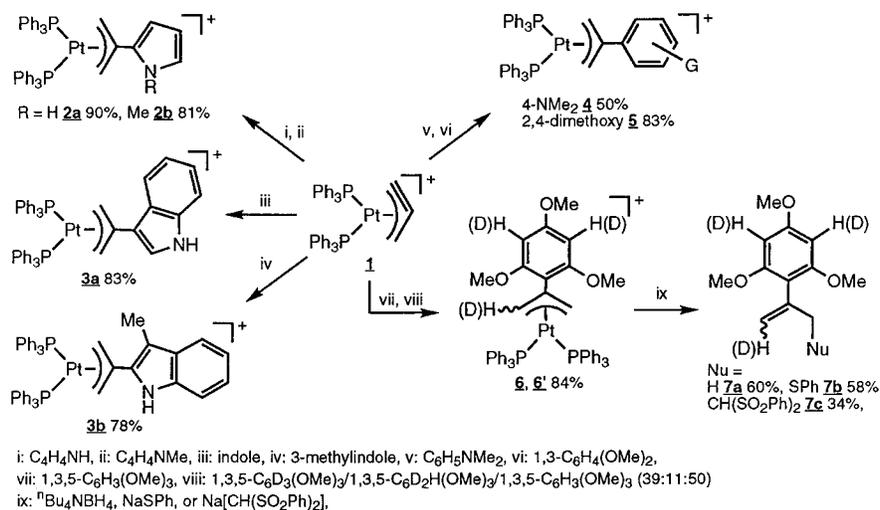
(4) (a) Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Am. Chem. Soc.* **1993**, *115*, 1170. (b) Casey, C. P.; Yi, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 6597. (c) Huang, T.-M.; Hsu, R.-H.; Yang, C.-S.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1994**, *13*, 3657. (d) Baize, M. W.; Furilla, J. L.; Wojcicki, A. *Inorg. Chim. Acta* **1994**, *233*, 1. (e) Wojcicki, A. *New J. Chem.* **1994**, *18*, 61. (f) Plantevin, V.; Blosser, P. W.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1994**, *13*, 3651. (g) Baize, M. W.; Plantevin, V.; Gallucci, J. C.; Wojcicki, A. *Inorg. Chim. Acta* **1995**, *235*, 1. (h) Tsai, F.-Y.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Organomet. Chem.* **1996**, *520*, 85.

(5) (a) Heck, R. F. *Org. React.* **1982**, *27*, 345. (b) Malleron, J.-L.; Fiaud, J.-C.; Legros, J.-Y. *Handbook of Palladium-Catalyzed Organic Reactions*; Academic Press Inc.: San Diego, CA, 1997.

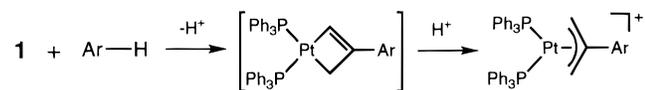
(6) (a) Chen, J.-T.; Cheng, Y.-C.; Chen, Y.-K.; Huang, T.-M.; Yu, C.-Y.; Lee, G.-H.; Wang, Y. *Organometallics*. Submitted for publication. (b) Casey, C. P.; Nash, J. R.; Yi, C. S.; Selmecky, A. D.; Chung, S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 722.

(7) (a) Hsu, R.-H.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1997**, *16*, 1159. (b) Chen, J.-T.; Chen, Y.-K.; Chu, J.-B.; Lee, G.-H.; Wang, Y. *Organometallics* **1997**, *16*, 1476. (c) Su, C.-C.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Am. Chem. Soc.* **1994**, *116*, 4999.

## Scheme 1



## Scheme 2



severely distorted  $\eta^3$ -allenyl/propargyl ligands<sup>8</sup> confers sufficient and versatile electrophilicity at the center carbon, which leads to

(8) Baize, M. W.; Blosser, P. W.; Plantevin, V.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1996**, *15*, 164.

remarkably high reactivity as well as subtle chemical selectivity toward different nucleophiles.

**Acknowledgment.** We thank the National Science Council, Taiwan, ROC for financial support.

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

JA973926O