

# 行政院國家科學委員會專題研究計畫成果報告

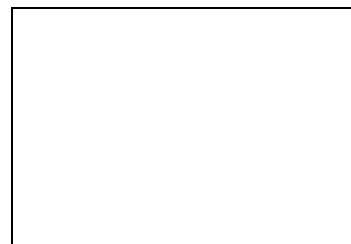
計畫名稱：有機金屬錯合物官能基轉換及催化反應(二)

**Novel Organometallic Functional Transformation  
and Catalysis (II)**

計畫編號：NSC87-2113-M002-001

執行期限：86年8月1日至87年7月31日

主持人：陳竹亭 執行機構：台灣大學化學系



## 一、中文摘要

炔丙基及丙二烯基有機金屬錯合物的親核加成反應形成氮代三亞甲基甲烷，金屬環丁烯，及中央碳取代的丙烯基錯合物。

**關鍵詞：**炔丙基，丙二烯基，親核加成反應

### Abstract

Addition of amines, phosphines, and electron-rich aromatic derivatives to the  $\eta^3$ -allenyl/propargyl complexes lead to the formation of  $\eta^3$ -azatrimethylenemethane, metallacyclobutene, and central carbon-substituted  $\eta^3$ -allyl complexes via C-N, C-P, and C-C bond formation, respectively.

Keywords:  $\eta^3$ -allenyl/propargyl complexes, nucleophilic addition.

## 二、緣由與目的

The transition metal complexes with unsaturated hydrocarbon of  $\pi$ -coordination have long been the focus of organometallic chemistry. Those with non-classical organometallic interactions are of particular interest, for they often empower new activity to the organic moieties [1]. For example, organic allyls ( $C_3R_3^-$ ) often bond with metal in a  $\eta^3$ -form rather than a  $\eta^1$ -form. The chemistry involving  $\eta^3$ -allyl complexes has been extensively studied and proved to contribute crucially to organic synthesis [2]. Propargyl which may be conceived as the alkyne analog of allyl has a tautomeric

isomer of allenyl. Similar to allyl, propargyl and allenyl ( $C_3R_3^-$ ) which also have three-carbon skeletons and unsaturated hydrocarbyl functionalities, ought to allow rich chemistry with metal. Indeed, transition metal complexes of allenyl and propargyl have been drawing attention for three decades, since the first reported synthesis of metal  $\eta^1$ -allenyl [3]. Besides, organometallic propargyl and allenyl have revealed their synthetic utility in many organic reactions [3, 4]. However, mononuclear allenyl or propargyl metal complexes with non-classical  $\sigma,\pi$ -bonding were actually unexplored until recently.

It has been known that metal  $\eta^1$ -propargyl can transform into the thermodynamically more stable  $\eta^1$ -allenyl tautomer [5]. The mechanistic studies indicate the involvement of 1,3-metal shift in this process of tautomerization. Comparing such a metal shift with the  $\eta^1$ -to- $\eta^3$ -to- $\eta^1$  fluxional motion of allyl [6], it would be chemically logical to expect the  $\eta^3$ -bonding interaction between metal and the allenyl and/or propargyl ligands. Recent development in metal  $\eta^3$ -allenyl/propargyl chemistry has filled such a category and opened a new page in organometallic chemistry. We choose to use the nomenclature of  $\eta^3$ -allenyl/propargyl, because the organic ligands with a general  $C_3R_3$  form are shown to bond with metal through three carbon atoms with hybridization of allenyl and propargyl features. Such a bonding mode of  $\eta^3$ - $C_3R_3$  groups remarkably enhances their electrophilic character, especially at the central carbon, and makes them as potent organometallic carbon electrophiles [7]. In fact, the

cationic mononuclear  $\eta^3$ -allenyl/propargyl complexes are found prone to external attack by various hard and soft nucleophiles. This report covers the addition of amines, phosphines, as well as electron-rich aromatic which strongly suggest the character of potent carbon electrophiles for the  $\eta^3$ -allenyl/propargyl complexes

### 三、報告内容

#### I. Addition of Aromatic C-H Bond to An $\eta^3$ -Allenyl/Propargyl Complex. Organoplatinum-Induced Electrophilic Aromatic Substitution Reactions

The regioselective addition of a C-H bond of the pyrrole, indole, or benzene derivatives to the  $\eta^3$ -allenyl/propargyl ligand of  $\{\text{Pt}(\text{PPh}_3)_2(\eta^3\text{-C}_3\text{H}_3)\}(\text{BF}_4)$  (**1**) generates the pyrrolyl-, indolyl-, or aryl-substituted  $\eta^3$ -allyl complexes  $\{\text{Pt}(\text{PPh}_3)_2(\eta^3\text{-CH}_2\text{C}(\text{Ar})\text{-CH}_2)\}(\text{BF}_4)$  (Ar = 2-pyrrolyl **2a**, 2-N-methylpyrrolyl **2b**, 3-indolyl **3a**, 2-3-methylindolyl **3b**, 4-dimethylamino-phenyl **4**, 2,4-dimethoxyphenyl **5**, 2,4,6-trimethoxyphenyl **6**), respectively. The regiochemistry of the C-H activation and a crossover labeling experiment support electrophilic substitution mechanism. Further nucleophilic addition to **6** leads to demetallation and achieves aryl vinylation.

#### II. Synthesis of Metallacyclobutenes Complexes of Late Transition Metals via Nucleophilic Addition of Allenyl or Propargyl Complexes.

The regioselective addition of  $\text{NEt}_3$ ,  $\text{PPh}_3$ , or pyridine to the central carbon of an  $\eta^3$ -allenyl/-propargyl complex of platinum  $\{\text{Pt}(\text{PPh}_3)_2(\eta^3\text{-C}_3\text{H}_3)\}(\text{BF}_4)$  (**1**) leads to the formation of the new cationic platinacyclobutenes  $\{(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{C}(\text{Nu})\text{CH})\}(\text{BF}_4)$  (Nu =  $\text{NEt}_3$  (**2a**),  $\text{PPh}_3$  (**2b**),  $\text{C}_6\text{H}_5\text{N}$  (**2c**)) via formation of a C-N or C-P bond, respectively. Complex **2c** can transform into  $\{\text{cis-Pt}(\text{PPh}_3)_2(\text{Py})(\eta^1\text{-CHCCH}_2)\}(\text{BF}_4)$  (**3**). The reverse reaction has not been observed. It is

suggested that nucleophilic addition of **1** likely involves the external attack at the central carbon of the  $\eta^3$ -allenyl/propargyl ligand. Protonation of **1** yields  $\{\text{Pt}(\text{PPh}_3)_2(\eta^3\text{-CH}_2\text{C}(\text{PPh}_3)\text{CH}_2)\}(\text{BF}_4)_2$  (**7**). Addition of  $\text{PPh}_3$  to labile  $\eta^1$ -allenyliridium complex (OC-6-42)- $\text{Ir}(\text{Cl})(\text{PPh}_3)_2(\text{OTf})(\text{CO})(\eta^1\text{-CHC-CH}_2)$  (**4**) results in an iridacyclobutene  $\{(\text{Cl})(\text{PPh}_3)_2(\text{CO})\text{Ir}[\text{CH}_2\text{C}(\text{PPh}_3)\text{CH}]\}(\text{OTf})$  (**5**). The single crystal X-ray structure of **5** has been determined.

#### III. A New Stable Intermediary Mode between $\eta^3$ -2-Aminoallyl Complexes and Metallacyclobutanimes. Synthesis and Structural Characteristic of $\eta^3$ -Azatrimethylenemethane and N-Protonated, N-Alkylated, N-Arylated $\eta^3$ -Azatrimethylenemethane Complexes of Pt and Pd.

Regioselective addition of ammonia, primary or secondary amines, aniline, or amino derivatives either to a neutral ( $\eta^1$ -allenyl)platinum complex  $\text{trans-Pt}(\text{Br})(\text{PPh}_3)_2(\eta^1\text{-CHCCH}_2)$  (**1**) or to a cationic  $\eta^3$ -allenyl/propargyl platinum complex  $[\text{Pt}(\text{PPh}_3)_2(\eta^3\text{-C}_3\text{H}_3)](\text{BF}_4)$  (**2**) provide the synthesis of cationic N-protonated, N-alkylated, and N-arylated  $\eta^3$ -azatrimethylenemethane complexes  $\{\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NRR}')\text{CH}_2]\}(\text{X})$  (R = H R' = H (**3a**), Me (**3b**), Et (**3c**),  $^i\text{Pr}$  (**3d**),  $^t\text{Bu}$  (**3e**),  $\text{c-C}_6\text{H}_{11}$  (**3f**), Ph (**3g**),  $\text{CH}_2\text{CH}_2\text{OH}$  (**3h**), R = R' = Et (**3i**),  $\text{c-C}_3\text{H}_6$  (from azetidine **3j**), Ph (**3k**), R = Me R' = Ph (**3l**); X = Br,  $\text{BF}_4$ ), respectively. Addition of amides to **1** gave a neutral  $\eta^3$ -azatrimethylenemethane complex  $\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NSO}_2\text{Ph})\text{CH}_2]$  (**4m**). Similar reactions using palladium complexes yield  $\{\text{Pd}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NRR}')\text{CH}_2]\}(\text{X})$  (R = H R' =  $^i\text{Pr}$  (**7d**), Ph (**7g**), R = R' = Et (**7i**); X = Br,  $\text{BF}_4$ , OTf),  $\text{Pd}(\text{Br})(\text{PPh}_3)[\eta^3\text{-CH}_2\text{C}(\text{NEt}_2)\text{-CH}_2]$  (**8i**) and  $\text{Pd}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NR})\text{CH}_2]$  (R =  $\text{SO}_2\text{Ph}$  (**9m**),  $\text{p-SO}_2\text{C}_6\text{H}_4\text{Me}$  (**9n**)). Synthesis of three complexes,  $\{\text{M}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NHR})\text{CH}_2]\}^+$  (M = Pt R =  $\text{SO}_2\text{Ph}$  (**3m**); M = Pd R =  $\text{SO}_2\text{Ph}$  (**7m**),  $\text{p-SO}_2\text{C}_6\text{H}_4\text{-Me}$  (**7n**)), can not be done by hydroamination reactions, but has been succeeded using protonation of  $\eta^3$ -N-TMM complexes **4m**,

**9m**, and **9n**, respectively. Spectroscopic and crystallographic characterizations indicate that these N-TMM species exhibit intermediary structural features between  $\eta^3$ -2-aminoallyl and metallacyclobutanimine complexes.

### Summary

We have extended the nucleophilic addition of  $\eta^3$ -allenyl/propargyl complexes to C-N, C-P, and C-C bond formation. The resulting products include  $\eta^3$ -azatrimethylenemethane, metallacyclobutene, and central carbon-substituted  $\eta^3$ -allyl complexes.

### Acknowledgement.

計畫主持人及計畫下研究人員要在此感謝國科會對此計畫的支持。

### References

- [1] J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, In *Principles and Applications of Organotransition Metal Chemistry*, University Science Books: Mill Valley, CA, **1987**; Chps. 2, 3.
- [2] (a) L. S. Hegedus, *Transition Metals in the Synthesis of Complex Organic Molecules*, University science Books: Mill Valley, CA, **1994**; Chp. 9. (b) B. M. Trost, T. R. Verhoeven, In *Comprehensive Organometallic Chemistry*, G. Wilkinson FRS., F. G. A. Stone, E. W. Abel, Eds., Pergmon: Elmsford, New York, **1982**; Vols. 8. (c) J. Tsuji, *Tetrahedron* **42** (1986) 4361. (d) B. M. Trost, *Acc. Chem. Res.* **13** (1980) 385. (e) B. M. Trost, *Angew. Chem. Int. Ed. Engl.* **25** (1986) 1. (f) P. J. Harrington, W. Oppolzer, D. J. Krysan, In *Comprehensive Organometallic Chemistry II*, E. W. Abel, F. G. A. Stone, G. Wilkinson FRS., Eds. Elsevier: Oxford, U.K., **1995**; Vol. 12. (g) B. M. Trost, D. L. Van Vranken, *Chem. Rev.* **96** (1996) 395. (h) H. Kurosawa, S. Ogoshi, *Bull. Chem. Soc. Jpn.* **71** (1998) 973.
- [3] (a) J. K. P. Ariyaratne, M. L. H. Green, *J. Organomet. Chem.* **1** (1963) 90. (b) M. D. Johnson, C. Mayle, *J. Chem. Soc. (D)* (1969) 192. (c) J. P. Collman, J. N. Cawse, J. W. Kang, *Inorg. Chem.* **8** (1969) 2574. (d) A. Wojcicki, *Adv. Organomet. Chem.* **12** (1974) 31. (e) C. P. Casey, E. A. Austin, *J. Am. Chem. Soc.* **110** (1988) 7106. (f) A. Wojcicki, C. E. Schuchart, *Coord. Chem. Rev.* **105** (1990) 35. (g) Doherty, J. F. Corrigan, A. J. Carty, E. Sappa, *Adv. Organomet. Chem.* **37** (1996) 39.
- [4] (a) F. Thon, M. Verny, R. Vessière, *The Chemistry of the Carbon-Carbon Triple Bond, Part I*; S. Patai, Ed.,s Wiley: New York, **1978**, Chp. 10. (b) M. Veber, K. N. V. Doung, F. Gaudemer, A. Gaudemer, *J. Organomet. Chem.* **18** (1979) 688. (c) L. N. Lewis, J. C. Huffman, K. G. Caulton, *J. Am. Chem. Soc.* **102** (1980) 403. (d) H. Hopf, T. L. Jacobs, *The Chemistry of Allenes*; S. R. Landor, Ed., Academic Press: London, **1982**, vol 2, Chp. 4.2, 4.3. (e) C. J. Elsevier, H. Kleijn, K. Ruitenber, P. J. C. S. Vermeer, *J. Chem. Soc., Chem. Commun.* (1983) 1529. (f) J. Tsuji, H. Watanabe, I. Minami, I. Shimizu, *J. Am. Chem. Soc.* **107** (1985) 2196. (g) B. Cazes, *Pure & Appl. Chem.* **62** (1990) 1867. (h) T.-W. Tseng, I.-Y. Wu, Y.-C. Lin, C.-T. Chen, M.-C. Cheng, Y.-J. Tsai, Y. Wang, *Organometallics* **10** (1991) 43. (j) M. E. Welker, *Chem. Rev.* **92** (1992) 97. (k) C.-C. Su, J.-T. Chen, G.-H. Lee, Y. Wang, *J. Am. Chem. Soc.* **116** (1994) 4999.
- [5] (a) R.-S. Keng, Y.-C. Lin, *Organometallics* **9** (1990) 289. (b) M.-C. Chen, R.-S. Keng, Y.-C. Lin, Y. Wang, M.-C. Cheng, G.-H. Lee, *J. Chem. Soc., Chem. Commun.* (1990) 1138. (c) S. Ogoshi, Y. Fukunishi, K. Tsutsumi, H. Kurosawa, *Inorg. Chim. Acta* **265** (1997) 9.
- [6] K. Vrieze, In *Dynamic Nuclear Magnetic Resonance Spectroscopy*, L. M. Jackson, F. A. Cotton, Eds., Academic: New York, **1975**.
- [7] (a) J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, In *Principles and Applications of Organotransition Metal Chemistry*, University Science Books: Mill Valley, CA, **1987**; Chp. 7. (b) C. P. Casey, M. W. Meszaros, P. J. Fagan, R. K. Bly, S. R. Marder, E. A. Austin, *J. Am. Chem. Soc.* **108** (1986) 4043. (c) C. P. Casey, M. W. Meszaros, P. J. Fagan, R. K. Bly, R. E. Colborn, *J. Am. Chem. Soc.* **108** (1986) 4053. and the references therein. (d) C. P. Casey, L.

K. Woo, P. J. Fagan, R. E. Palermo, B. R. Adams, *Organometallics* 3 (1987) 447.

[8] A. Wojcicki *New. J. Chem.* 18 (1994) 61.1138.