

## 2008 年中央研究院「年輕學者研究著作獎」得獎人簡介

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學歷：(自大學起；註明起迄年份)

博士:美國麻省理工學院 化學所 1997-2001 年

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國立清華大學化學系 助理教授 2003-

美國加州理工學院 博士後研究員 2001-2003

得獎著作名稱：(請以申請時之格式填入)

- (1) “A Three-Coordinate and Quadruply-Bonded Mo–Mo Complex” *J. Am. Chem. Soc.* **2006**, *128*, 13980.
- (2) “Inverted-Sandwich Dichromium(I) Complexes Supported by two -Diketiminates: A Multi-Electron Reductant and Syntheses of Chromium Dioxo and Imido” *J. Am. Chem. Soc.* **2007**, *129*, 8066.
- (3) “Structural Transformations in Dinuclear Zinc Complexes Involving Zn–Zn Bonds” *Chem. Commun.* **2007**, 4125.

得獎著作簡介：(2000 字左右)

我的得獎著作主要是探討低價數且低配位數(或稱配位未飽合)的過渡金屬化合物的化學。當代無機化學合成一項重要的研究課題是合成高活性且穩定的金屬化合物可以有選擇性的活化小分子，如化學活性很低的氮氣。因此，具高立體阻礙之低配位金屬化合物便是無機合成化學家的首要目標，因為低價數且低配位數，所以金屬之間易有罕見的特殊鍵結。

第一篇論文發表於美國化學學會誌 *J. Am. Chem. Soc.* **2006**, *128*, 13980-13981。該報導是探討第一個具有低配位數的金屬-金屬四重鍵的雙鉬化合物，但其中每一個鉬金屬的配位數只有傳統的具金屬-金屬四重鍵的化合物的一半。自 1964 年 Cotton 教授發現金屬和金屬間可以有四重鍵結以來，金屬與金屬間的鍵結吸引合成化學家和理論計算學家的重視，這些成果在所有的無機化學教課書都可以看到，可見其重要性。本研究結果首度突破了四十幾年來對金屬-金屬四重鍵的鍵結理論，為吾人對金屬-金屬多重鍵結開創出一新的思維。

第二篇為發表於英國皇家化學會的 *Chem. Commun.* **2007**, 4125 的論文是探討罕見的一價鋅之間的鍵結及化學。長久以來大家都認為鋅的氧化數只有 0 和 2，但是其同族的汞化合物卻常以氧化數 1 的形式存在。因此，自 2004 年一價鋅被發


現以來，吾人對氧化數為 1 的鋅的化合物深感興趣。此論文中所合出的雙鋅化合物具有很有趣的鋅-鋅單鍵，其鍵結經由理論計算配合得知為一單鍵，此結果有助於大家對氧化數為 1 鋅化合物有更進一步瞭解。

第三篇論文也是發表於美國化學學會誌 *J. Am. Chem. Soc.* **2007**, *129*, 8066-8067。本篇論文是探討罕見的低配位的一價鉻的化學。一價鉻被認為是鉻金屬化合物催化有機烯類進行聚合反應過程中非常重要的物種。同時鉻的氧化數的多樣性也為大家所熟知。正因如此，本論文中的低配位的一價鉻化合物展現非常特殊的化學活性，特別是對含氮的有機化合物有特別高的活性，可助吾人瞭解過渡金屬在固氮過程中所扮演的角色。其它與有機炔類和烯類的反應正進行探討中。

#### 評審簡評：

蔡易州博士刊登在 *Journal of the American Chemical Society* 和 *Chemical Communications* 的文章，都是 impact factor 很高的期刊。對一位年輕學者而言，這是非常卓越的成就。蔡博士主要研究低價數且低配位數(或稱配位未飽合)的過渡金屬化合物的化學。蔡博士的研究成果包括發現了第一個具有低配位數的金屬-金屬四重鍵的雙鉬化合物，但是其中每一個鉬金屬的配位數只有傳統的具金屬-金屬四重鍵的化合物的一半。He 也發現探討一價鋅之間的鍵結及化學及低配位的一價鉻的化學。在其領域具有尖端權威的國外評審委員，特別推崇蔡博士研究的創新性以及他所發表的論文的高品質，並認為他未來的前途無可限量。

## 2008 Academia Sinica Research Award for Junior Research Investigators

<p>Name : Yi-Chou Tsai</p> 	<p>Education: Ph.D., Massachusetts Institute of Technology, 1997- 2001 M.Sc., National Taiwan Normal University, 1992-1994 B.Sc., National Taiwan Normal University, 1987-1991</p> <p>Employer(s)/Job Title(s): Assistant Professor, 2003- Postdoctoral Fellow, California Institute of Technology 2001-2003</p>
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### Award publications :

- (1) "A Three-Coordinate and Quadrupty-Bonded Mo–Mo Complex" *J. Am. Chem. Soc.* **2006**, *128*, 13980.
- (2) "Inverted-Sandwich Dichromium(I) Complexes Supported by two -Diketiminates: A Multi-Electron Reductant and Syntheses of Chromium Dioxo and Imido" *J. Am. Chem. Soc.* **2007**, *129*, 8066.
- (3) "Structural Transformations in Dinuclear Zinc Complexes Involving Zn-Zn Bonds" *Chem. Commun.* **2007**, 4125.

### Summary of the Award publications ( around 2000 words ) :

My published work was focusing on exploring the chemistry of low-valent and low-coordinate (or the so called coordination unsaturated) transition metal complexes. One hot topic of the contemporary inorganic chemistry research is to synthesize isolable reactive complexes, which are aimed to selectively activate chemically-inert small molecules, such as N<sub>2</sub>. In this regard, low-coordinate complexes stabilized by sterically encumbered ancillary ligands have been the first priority target to inorganic chemists. While low-valent and low-coordinate mononuclear complexes have garnered considerable attention, reports on coordination-unsaturated dinuclear complexes are still scarce. Coordination unsaturated dinuclear complexes are potentially interesting not only in their inherent high reactivity, but also in the formation of unusual metal-metal bonds, which feature unusual electronic structures. I will briefly state how remarkable of these work published in the following three papers.

The first paper entitled "A Three-Coordinate and Quadrupty Bonded Mo-Mo

Complex” was published in *J. Am. Chem. Soc.* **2006**, *128*, 13980-13981. In this work, we described the synthesis and characterization of a quadruply-bonded dimolybdenum complex stabilized by two diamido ligands. Since Professor Cotton’s seminal discovery of the first quadruply bonded dirhenium complex  $[\text{Re}_2\text{Cl}_8]^{2-}$  in 1964, in which each Re atom is ligated by four ligands and the whole molecule displays  $D_{4h}$  symmetry, such quadruply bonded dinuclear complexes  $\text{M}_2\text{L}_8$  have dominated over the past 40 years. Accordingly, the synthesized dimolybdenum complex in this work represents the first compound, where each metal center is coordinated by only two nitrogen donor atoms, and a quadruple bond exists between two Mo atoms. Moreover, the said dimolybdenum compound is not only interesting in structure motif, but remarkable in electronic structure. The conventional interaction between metal and ligands is mainly sigma bonding in Cotton’s type of quadruply bonded dinuclear complexes and the delta bond is formed via the overlap of a pair of  $d_{xy}$  orbitals. However, based on sophisticated DFT calculations, a strong pi interaction between Mo and N atoms was found in our dimolybdenum complex and consequently the delta bond is formed by the interaction between a pair of  $d_{x^2-y^2}$  orbitals. This work widens the scope of the field of the chemistry of metal-metal bonding. We therefore are convinced that this remarkable result will be included in inorganic text books in the near future.

The second paper entitled “Structural transformations in dinuclear zinc complexes involving Zn-Zn bonds” was published in *Chem. Commun.* **2007**, 4125-4127. In this work, we described the syntheses and characterizations of two Zn(I)-Zn(I) bonded complexes. Unlike the ubiquitous Hg(I) compounds, the first Zn(I) compound  $\text{Cp}^*\text{Zn-ZnCp}^*$  was just recently reported. Thereafter, several Zn(I)-Zn(I) bonded complexes were subsequently reported, however, those were merely about synthetic work. In this paper, we are the first trying to understand structural transformation between a dinuclear Zn(II) compound and a dinuclear Zn(I)-Zn(I) bonded complex upon reduction of the former compound, experimentally and theoretically, and a computed plausible mechanism was thereby proposed and was experimentally proved later by us (unpublished results). This work illustrates that the molecular chemistry of zinc can still yield surprises and helps chemists understand the chemistry of the unusual Zn(I)-Zn(I) bond.

The third paper entitled “Inverted-Sandwich Dichromium(I) Complexes Supported by Two beta-Diketiminates: A Multielectron Reductant and Syntheses of Chromium Dioxo and Imido” was published in *J. Am. Chem. Soc.* **2007**, *129*, 8066-8067. Various oxidation states of Cr have been found, but low-coordinate monovalent Cr complexes

have not yet been discovered. Cr(I) complexes have long been thought as critical intermediates in Cr-catalyzed olefin polymerization reactions. Therefore, in this report, we synthesized a remarkable inverted-sandwich dichromium complex stabilized by two monoanionic beta-diketiminato and an arene ligands. The synthesized dichromium complex behaves as a source of two Cr(beta-diketiminato), which is capable of effecting the cleavage of the N-N double bond of azobenzene, O-O double bond of molecular dioxygen, and reduction of organic azides to give rise to the formation of corresponding Cr-imido, -dioxo and -bisimido complexes, respectively. Accordingly, the result in this paper opens a door to explore the chemistry of two-coordinate univalent Cr complex towards small molecules and organic functionalities.