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Review

The lengths of the metal-to-metal quintuple bonds and reactivity thereof

Anokh K. Nair, N.V. Satyachand Harisomayajula, Yi-Chou Tsai *

Department of Chemistry and Frontier Research Center on Fundamental and Applied Sciences of Matters, National Tsing Hus University, Hsinchu 30013, Taiwan

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ABSTRACT

This article reviews factors affecting the metal–metal bond lengths in the quintuple bonded complexes and reactivity thereof. The metal–metal bond length is the most intriguing metric in the multiple bonded dinuclear complexes. This is not only the case in the well-developed triple and quadruple bonding, but also in the newly-born quintuple bonding. Akin to the wide range of Cr—Cr quadruple bond lengths found among the quadruple bonded complexes, the quintuple bonded dichromium complexes also show a large variation in the Cr—Cr bond lengths, although only fifteen dichromium compounds have been characterized thus far. Donor atoms and steric pressure of the supporting ligands are two main factors affecting the Cr—Cr quintuple bond lengths. The highly reducing nature and low coordination of the quintuple bonded bimetallic complexes render them reactive towards many small inorganic molecules and organic functionalities, and many interesting reactions, such as addition, complexation, cycloaddition and reductive cleavage, were discovered from them.

Anokh K. Nair *was born in Kerala, India, in 1988. He received his BSc from Mahathma Gandhi University in 2008 and MSc from National Institute of Technology, Tiruchirappalli, India in 2010. He is presently a PhD student in Professor Yi-Chou Tsai's group in the Department of Chemistry and Frontier Research Center on Fundamental and Applied Sciences of Matters at National Tsing Hua University. His research interests encompass organic synthesis, synthesis, characterization, and reactivity studies of multiple bonded dinuclear transition metal complexes.*

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* Corresponding author.
E-mail address: yictsai@mx.nthu.edu.tw (Y.-C. Tsai).

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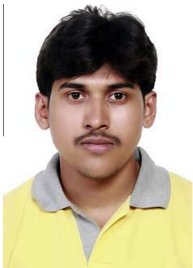

Naga Venkata Satyachand Harisomayajula *received his BSc from Andhra University, and his MSc in 2006 from Andhra University, India. Upon graduation, he went to industry and worked as a Research Scientist for five years. He is currently a PhD student under the supervision of Professor Yi-Chou Tsai in the Department of Chemistry and Frontier Research Center on Fundamental and Applied Sciences of Matters at National Tsing Hua University. His research interest lies in exploring the low-coordinate and low-valent multiple bonded dinuclear complexes.*

Yi-Chou Tsai *obtained his BSc and MSc degrees from the Department of Chemistry, National Taiwan Normal University in Taiwan and his PhD degree from MIT. After a two-year postdoctoral fellowship at Caltech, he joined the Department of Chemistry at National Tsing Hua University in 2003, where he is currently a full professor. His research interest is focused in inorganic and organometallic synthesis, particularly in the synthesis, isolation, and characterization of unusually reactive dinuclear transition metal complexes of unique design and construction.*

Contents

1. Introduction

Synthesis of multiple bonded dinuclear complexes has grasped interest of scientists for many decades and thousands of such complexes have been structurally characterized. A new era of multiple bonded inorganic compounds was initiated by Cotton's landmark discovery of the first quadruple bonded dirhenium complex $[Re_2Cl_8]^{2-}$ in 1964 [1]. Since then, many bimetallic transition metal complexes with a formal quadruple bond have been subsequently characterized [2]. Furthermore, the identification of simple diatomic transition metal molecules with a quintuple (Nb_2) [3] and a sextuple (Cr_2 and Mo_2) [4–10] bond from the metal atom-argon matrix condensation experiments encouraged the interest of scientists for going beyond the element–element bond order of four. On the theoretical side, in 1979, Hoffmann and co-workers speculated that a dinuclear complex featuring a D_{3h} configuration could possibly have a metal–metal quintuple bond [11]. Moreover, Landis and Weinhold, according to their calculations, indicated that the C_{2h} *trans*-bent M_2H_2 (M = Cr, Mo, W) complexes have a formal M–M quintuple bond [12–15]. The hybridization tendencies of s and $d_{x^2-y^2}$ orbitals of transition metals are responsible for the *trans*-bent geometry of M_2H_2. The strong tendency toward $sd_{x^2-y^2}$ hybridization in M_2H_2 results in the strongest M–M σ bonds and bent ligand arrangement around the metal centers [14]. As a matter of fact, the *trans*-bent geometry has been recognized in the multiply bonded dimeric main group compounds. Power and co-workers employed the sterically hindered unidentate terphenyl ligand 2,6-$(2,6\text{-}{}^{i}Pr_2C_6H_3)_2C_6H_2$ (Ar′) to synthesize many *trans*-bent multiply bonded dimeric complexes Ar′EEAr′ (*E* = Group 13 and 14 heavy elements) [16,17]. Inspired by their *trans*-bent Ar′EEAr′ compounds and the quintuple bonded Cr_2H_2 model complex, Power and co-workers subsequently applied Ar′ to stabilize transition metals as well. The quest for a quintuple bonded complex was achieved by the characterization of the first isolable quintuple bonded dichromium