VIII-B Early Transition Metal Chemistry Directed to Olefin Polymerization

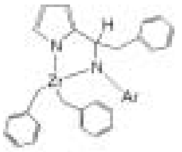
Recent development of well-defined single site transition metal catalysts enables us to precisely control not only catalytic activity for α-olefin polymerization but also microstructure of polymers. The nitrogen-based polydentate ligands such as phenoxyimine, 2,6-bis(*N*-aryliminomethyl)pyridine, and α-diimine derivatives, which serve the polymerization catalysts as supporting ligands, have attracted particular interest in terms of their advantageous feasibility and flexibility in design to introduce sterically and electronically demanding features on the ligand. Despite these merits, the catalysts supported by these ligands have been found to be occasionally deactivated by the alkylation of the C=N bond of the ligand. The alkylation of the C=N moiety of the nitrogen-based ligand was thus anticipated to have a capability to make a cationic alkyl species more stable and, in particular case, enhance its catalytic activity compared to the corresponding catalyst bearing the unalkylated ligand. In this contribution, we have investigated such the alkylation of the ligand related to the polymerization activity and mechanism.

VIII-B-1 Intramolecular Benzylation of an Imino Group of Tridentate 2,5-Bis(*N*-aryliminomethyl)-pyrrolyl Ligands Bound to Zircnoium and Hafnium Gives Amido-Pyrrolyl Complexes That Catalyze Ethylene Polymerization

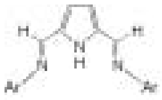
TSURUGI, Hayato[1]; YAMAGATA, Tsuneaki[1]; MASHIMA, Kazushi[2]
([1]Osaka Univ.; [2]IMS and Osaka Univ.)

[*Organometallics* **23**, 2797–2805 (2004)]

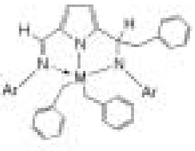
We already reported that an intramolecular benzylation of the imino moiety of bidentate iminopyrrolyl ligands afforded an amido-pyrrolyl complexes **1** and they exhibited better catalytic activity for ethylene polymerization compared to the corresponding bis(iminopyrrolyl) dichloro complexes of zirconium. In this contribution, we prepared amido-pyrrolyl complexes of zirconium (**3a-d**) and hafnium (**4a-f**) by the reaction of tetrabenzyl-zirconium and -hafnium with 2,5-bis(*N*-aryliminomethyl)pyrrole ligands (**2a-e**), respectively. During the course of the reaction, one of two imino moieties of the ligand was selectively benzylated to give unique dianionic tridentate ligands, which stabilized dibenzyl complexes of zirconium and hafnium. The coordinative unsaturation around the metal center was compensated by not only the donation of the imino moiety but also the η^2-coordination of one of the two benzyl ligands, as confirmed by spectral data together with X-ray analysis of **3b** and **3c**. The zirconium complexes **3b** and **3c** bearing bulky substituents at the nitrogen atoms of the ligand exhibited high catalytic activities (**3b**, 131 (kg-PE)(mol-cat)$^{-1}$h^{-1} at 60 °C; **3c**, 458 (kg-PE)(mol-cat)$^{-1}$h^{-1} at 75 °C) upon combined with 1000 equiv. of MMAO. Lewis-base free cationic alkyl complexes **5b**, **5c**, **6b**, and **6c** were prepared by alkyl abstruction from the corresponding dibenzyl complexes of zirconium **3b**,**c** and hafnium **4b**,**c** and the resulting cationic complexes **5c** and **6c** were found to catalyze the ethylene polymerization without MMAO.



1 : Ar = 4-MeOC$_6$H$_4$
4-MeC$_6$H$_4$



2



3 : M = Zr
4 : M = Hf

a : Ar = 2-MeC$_6$H$_4$
b : Ar = 2,6-Me$_2$C$_6$H$_3$
c : Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$
d : Ar = 4-MeOC$_6$H$_4$
e : Ar = 4-MeC$_6$H$_4$

5 : M = Zr
6 : M = Hf

VIII-C Linear Metal Clusters: Bonding and Reactivity

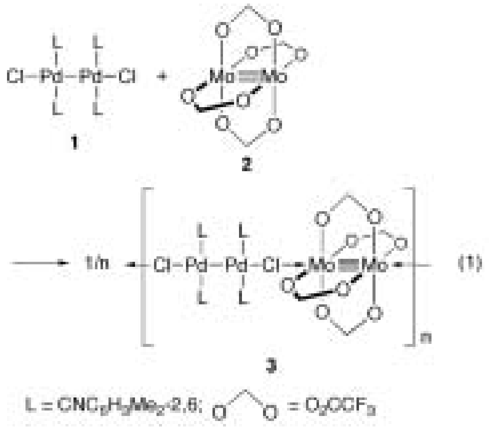
Assembled metal complexes with highly controlling their nuclearity and dimensionality have extensively investigated and quasi-one-dimensional materials, especially transition-metal linear-chain complexes, have attracted particular interest in view of their novel electronic, magnetic, and optical properties. In this contribution, we prepared two linear chain compounds comprised of Mo–Mo multiple bond in their chain.

VIII-C-1 An Infinite Zigzag Chain of Alternating Cl–Pd–Pd–Cl and Mo–Mo Units

MASHIMA, Kazushi[1]; YI, JianJun[2]; MIYABAYASHI, Takayuki[2]; OHASHI, Masato[2]; YAMAGATA, Tsuneaki[2]
([1]IMS and Osaka Univ.; [2]Osaka Univ.)

[*Inorg. Chem.* **43**, 6596–6599 (2004)]

Treatment of $Pd_2Cl_2(CNC_6H_3Me_2\text{-}2,6)_4$ (**1**) and $Mo_2(O_2CCF_3)_4$ (**2**) in dichloromethane afforded an infinite zigzag chain $\{[Pd_2Cl_2(CNC_6H_3Me_2\text{-}2,6)_4][Mo_2(O_2CCF_3)_4]\}_n$ (**3**), where two metal–metal bonded dinuclear Pd–Pd and Mo–Mo units were bridged by chloro atoms (equation 1). The Mo–Mo distance (2.1312(3) Å) of **3** is significantly elongated compared to that of **2** (2.090(4)) Å) and lies in the range of that of the quadruple Mo–Mo bonded complexes (Figure 1). Such the elongation might be attributed to the axial donation of the chloro atoms of the Pd–Pd unit to the Mo–Mo moiety.



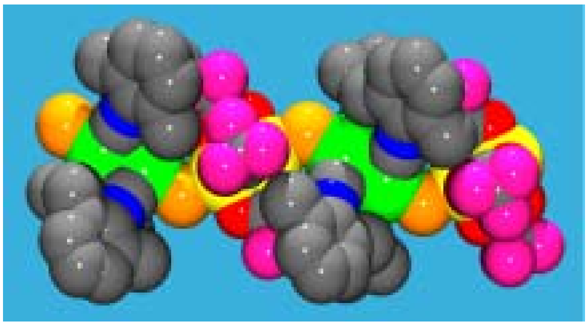


Figure 1. The structure of the infinite zigzag chain of **3**. Mo: yellow; Pd: green; Cl: orange; F: purple; O: red; N: blue; C: gray.

VIII-C-2 Unique Oxidative Metal–Metal Bond Formation of Linearly Aligned Tetranuclear Rh–Mo–Mo–Rh Clusters

MASHIMA, Kazushi[1]; RÜFFER, Tobias[2]; OHASHI, Masato[2]; SHIMA, Asuka[2]; MIZUMOTO, Hitoshi[2]; KANEDA, Yutaka[2]
([1]IMS and Osaka Univ.; [2]Osaka Univ.)

[*J. Am. Chem. Soc.* **126**, 12244–12245 (2004)]

The construction of one-dimensional, covalently bonded metal strings has attracted much interest in view of fundamental bonding nature as well as promising applications as extensive electronic and optoelectronic materials. Two major synthetic approaches to these compounds have been conducted by (a) using polydentate ligands such as oligo-α-pyridylamido ligands or by (b) partial oxidation of d^8 square-planar complexes to form metal–metal bonds (*e.g.* platinum blue). Our effort has been focused on aligning transition metals by using a tridentate ligand 6-diphenylphosphino-2-pyridonate (pyphos), in which three different elements, P, N, and O, were linearly laid out by the rigid pyridone framework and could act as coordination sites for arrangement of more than two kinds of transition metals in linear manner. And we have demonstrated linear hetelometallic clusters containing both group VI and group X metals by use of the quadruply-bounded dimolybdenum(II) complex, $Mo_2(pyphos)_4$ (**1**) as a core part of metal strings such as $Mo_2Pd_2Cl_2(pyphos)_4$ (**2**) .

As the next stage of our continuous study, we confronted the synthesis of a new series of heterometallic tetranuclear clusters containing group IX metals with appropriate geometries of square planar as well as octahedral to be supported by the two PPh_2 groups. Herein we report the synthesis of linearly aligned tetranuclear complexes bearing the Rh–Mo–Mo–Rh array (equaition 2) and their unique oxidative reaction (equation 3). We found that rhodium metals at both axial positions of the Mo_2 in **4** electronically communicated through the Mo_2 core and, as a result, oxidative reaction Rh(I)/Rh(II) induced the formation of metal-metal bonds.