VIII-E Transition Metal Cluster Chemistry

VIII-E-1 Metathesis Approach to Linkage of Two Tetraplatinum Cluster Units: Synthesis, Characterization, and Dimerization of $[\text{Pt}_4(\mu-\text{OCOCH}_3)_7(\mu-\text{OCO(CH}_2)_n\text{CH}=\text{CH}_2)]$ ($n = 0$–$3$)

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Reaction of $[\text{Pt}_4(\mu-\text{OCOCH}_3)_8]$ (1) with 1 equiv of acrylic acid led to the selective mono-substitution of one of the four in-plane acetates in 1, affording $[\text{Pt}_4(\mu-\text{OCOCH}_3)_7(\mu-\text{OCO})\text{CH}=\text{CH}_2]$ (2a) (eq. 1), whereas treatment with excess amounts of acrylic acid resulted in a full-substitution of four in-plane acetates, yielding $[\text{Pt}_4(\mu-\text{OCOCH}_3)_4(\mu-\text{OCO})\text{CH}=\text{CH}_2]_4$ (3) (Figure 1).

Similarly, mono-substituted heptaacetate complexes $[\text{Pt}_4(\mu-\text{OCOCH}_3)_7(\mu-\text{OCO})\text{CH}=\text{CH}_2]$ (2b–d; $n = 1$–$3$) were prepared. These complexes 2a–d seem to be a suitable precursor for linkage of the Pt$_4$ units. Catalytic intermolecular coupling reactions of 2c and 2d assisted by Grubbs’ catalysts gave the desired dimers $\{[\text{Pt}_4(\mu-\text{OCO})\text{CH}_3]_2\}_2$ (6c; $n = 2$; 6d; $n = 3$) (eq. 2), while metathesis reactions using complexes 2a and 2b did not proceed under the same catalytic condition.

VIII-E-2 Hexapalladium Cluster: Unique Reaction of Cyclic Pd$_3$(CNC$_6$H$_3$Me$_2$-2,6)$_6$ and Linear [Pd$_3$(CNC$_6$H$_3$Me$_2$-2,6)$_8$]$^{2+}$

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Polynuclear clusters with metal–metal bonds have attracted research interest due to their fundamental aspect as surface model of heterogeneous catalyst, as well as potential applications as electrochemical, photoelectric and magnetic materials. Among them, di- and trinuclear complexes with metal–metal bonds have been well documented, and have been used as starting materials to construct new clusters with high nuclearity. Many di- or trinuclear palladium and platinum complexes with isocyano ligands have been formed by electrochemical preparation as well as by redox reactions between metal ions in different formal oxidation states. It has been reported that dicationic dinuclear palladium isocyanide complex [Pd$_2$L$_6$]$^{2+}$ ($L =$ isocyanide) with $d^9$ configuration reacted with Pd$L_x$ sources with $d^{10}$ configuration such as cyclic trinuclear palladium isocyanide complex (Pd$_3$L$_2$) resulted in the selective formation of dicationic linear trinuclear palladium complex [Pd$_3$L$_8$]$^{2+}$, where Pd(0) formally inserted into Pd–Pd bond of [Pd$_2$L$_4$]$^{2+}$ (eq. 1). However, additional reaction of [Pd$_3$L$_8$]$^{2+}$ with “Pd$L_x$” species has not been reported.

Recently we used 2,6-dimethylphenyl-isocyanide as the homoleptic ligand to develop this reaction by preparing [Pd$_3$(CNC$_6$H$_3$Me$_2$-2,6)$_6$][PF$_6$]$_2$ (3) from [Pd(CNC$_6$H$_3$Me$_2$-2,6)$_2$]=$^3$ (1) and [Pd$_2$(CNC$_6$H$_3$Me$_2$-2,6)$_6$][PF$_6$]$_2$ (2). Herein we reported that the additional reaction of 3 and 1 selectively afforded a dicationic hexanuclear palladium complex [Pd$_6$(CNC$_6$H$_3$Me$_2$-2,6)$_{10}$][PF$_6$]$_2$ (4) (eq. 2, $L =$ 2,6-Me$_2$C$_6$H$_3$NC). The crystal structure of the complex 4 was determined by X-ray crystallography and spectroscopic analysis.

VIII-E Transition Metal Cluster Chemistry
VIII-F Synthesis of Transition Metal Catalysts for Organic Transformations

VIII-F-1 Oxidative Addition of RCO₂H and HX to Chiral Diphosphine Complexes of Iridium(I): Convenient Synthesis of Mononuclear Halo-Carboxylate Iridium(III) Complexes and Cationic Dinuclear Triply Halogen-bridged Iridium(III) Complexes and Their Catalytic Performance in Asymmetric Hydrogenation of Cyclic Imines and 2-Phenylquinoline

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Mononuclear iridium(III) complexes of the general formula IrX(H)(O₂CR)[(S)-binap] (2: R = CH₃; 3: R = Ph; 4: R = C₆H₄(C₆F₅)₂-p; a: X = Cl; b: X = Br; c: X = I) were prepared by one-pot reaction of [Ir(μ-X)(cod)]₂ with two equiv of (S)-BINAP [= 2,2’-bis(diphenylphosphino)-1,1’-binaphthyl] and an excess of the corresponding carboxylic acid in toluene. The structure of (S)-2-4 bearing an (S)-BINAP was confirmed to be OC-6-23-A (A-conformation) by X-ray analysis of (S)-4a-c. In this reaction, an iridium(I) complex [Ir(μ-Cl)(S-binap)]⁻ [S⁻] and pentacoordinated iridium(I) complexes IrX(cod)[(S-binap)]⁻ [S⁻] were prepared prior to the oxidative addition of carboxylic acid. Cationic dinuclear iridium(III) complexes of the general formula [[Ir(H)][(S-binap)]₂(μ-X)₃]X⁻ [(S)-8: a: X = Cl; b: X = Br; c: X = I] were generated and their cationic bifacial octahedral dinuclear structure was characterized by spectral data and combustion analysis. The anionic portion of these complexes could be replaced by NaPF₆, leading to the corresponding PF₆⁻ salts, [[Ir(H)][(S-binap)]₂(μ-X)₃]PF₆⁻ [(S)-8: d: X = Cl; e: X = Br; f: X = I]. Iodo-acetate complexes of p-TolBINAP (= 2,2’-bis(di-4-tolylphosphino)-1,1’-binaphthyl) [(S)-9e] and SYNPHOS [= 2,2’,3,3’-tetrahydro(5,5’-bi-1,4-benzodioxin)-6,6’-diyl][bis(diphenylphosphine)] [(S)-10c] were also prepared according to the method used for the BINAP complex (S)-2c and were characterized spectroscopically. Cationic dinuclear complexes of p-TolBINAP [(S)-11e] and SYNPHOS [(S)-12c] were also generated. Using these complexes, the effect of halide variation was studied by asymmetric hydrogenation of 2-phenylpyrrolidine and 2-phenyl-4,5,6,7-tetrahydro-3H-azepine along with 2-phenylquinoline, and the results indicated that iodide complexes were better catalyst precursors for catalytic activity than the corresponding chloride and bromide complexes, but were not superior in enantioselectivity.

VIII-G Early Transition Metal Complexes

VIII-G-1 Synthesis, Structure, and Reactivity of Tantalum and Tungsten Homoenolate Complexes

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Preparation and characterization of homoenolate complexes of tantalum, Cp*Cl₃Ta(CH₂CR₁₂C(=O)OR)₂ (1a: R¹ = H, R² = Et; 1b: R¹ = R² = Me; 1c: R¹ = Me, R² = C₆H₄CH₃-3,4), and tungsten, (Xyl-N)=Cl₃W(CH₂CH₂C(=O)OEt) (7), using zinc homoenolate reagents are described. Intramolecular coordination of the carboxyl moiety to the metal center in these complexes was confirmed by their NMR and IR spectroscopy together with X-ray analyses of 1a and 1b. The insertion reaction of isocyanide into the metal carbon bond of 1a and 7, respectively, resulted in the formation of a diazametallacycle, Cp*Cl₃Ta[N(Xyl)-C(=C=N-Xyl)-C(CH₂CH₂CO₂Et)=N-Xyl] (3a), which possesses a metallacycle structure with an exocyclic ketene-imine moiety, and an η²-iminoacetylenyl tungsten complex, (Xyl-N)=W{C≡(N-Xyl)CH₂CH₂CO₂Et}[CNXyl]Cl₃ (8). The β-proton of the homoenolate moiety of 1a was selectively deprotonated by KN(SiMe₃)₂ to afford an η¹-ethyl acrylate complex, Cp*Cl₃Ta(η¹-ethyl acrylate) (4). In the case of complex 1b, in which the β-positions were protected by dimethyl substituents, reaction with the dialithium salt of diazide afforded a tantalalactone complex 5. The addition of Al(C₆F₅)₃ to 5 afforded a novel zwitterionic complex 6, in which Al(C₆F₅)₃ coordinated to the exocyclic carbonyl oxygen of the tantalalactone.