VIII-E Transition Metal Cluster Chemistry

VIII-E-1 Metathesis Approach to Linkage of Two Tetraplatinum Cluster Units: Synthesis, Characterization, and Dimerization of [$Pt_4(\mu\text{-}OCOCH_3)_7(\mu\text{-}OCO(CH_2)_nCH{=}CH_2)$] ($n$ = 0–3)

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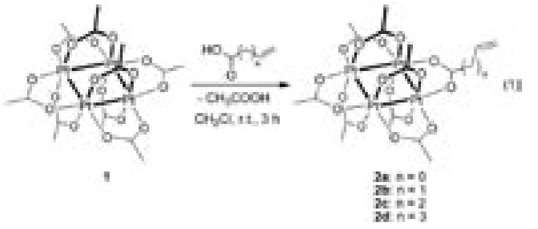
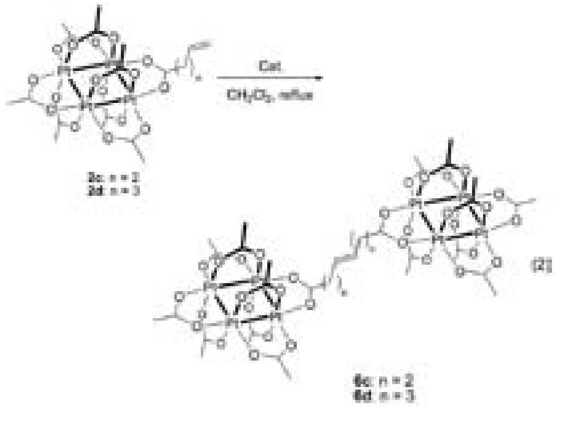
Reaction of [$Pt_4(\mu\text{-}OCOCH_3)_8$] (**1**) with 1 equiv of acrylic acid led to the selective mono-substitution of one of the four *in*-plane acetates in **1**, affording [$Pt_4(\mu\text{-}OCOCH_3)_7(\mu\text{-}OCOCH{=}CH_2)$] (**2a**) (eq. 1), whereas treatment with excess amounts of acrylic acid resulted in a full-substitution of four *in*-plane acetates, yielding [$Pt_4(\mu\text{-}OCOCH_3)_4(\mu\text{-}OCOCH{=}CH_2)_4$] (**3**) (Figure 1). Similarly, mono-substituted heptaacetate complexes [$Pt_4(\mu\text{-}OCOCH_3)_7\{\mu\text{-}OCO(CH)_nCH{=}CH_2\}$] (**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 [$\{Pt_4(\mu\text{-}OCOCH_3)_7\}_2\{\mu\text{-}OCO(CH_2)_nCH{=}CH(CH_2)_n(\mu\text{-}OCO)\}$] (**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 $Pd_3(CNC_6H_3Me_2\text{-}2,6)_6$ and Linear $[Pd_3(CNC_6H_3Me_2\text{-}2,6)_8]^{2+}$

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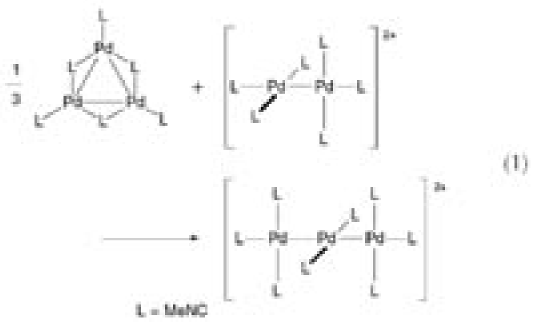
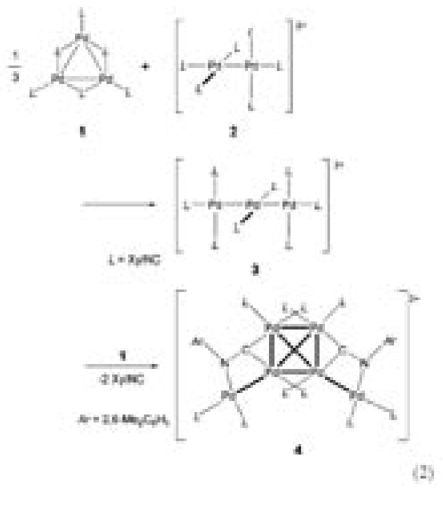
Polynuclure clusters with metal–metal bonds have attracted research interest due to their fundamental aspect as surface model of heterogeneous catalyst, as well as potential applications as electrochemical, photoelectric and magnetic mareials. Among them, di- and trinuclear complexes with metal–metal 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 isocyanide 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 $[Pd_2L_6]^{2+}$ (L = isocyanide) with d^9 configuration reacted with Pd^0L_x sources with d^{10} configuration such as cyclic trinuclear palladium isocyanide complex $(Pd^0L_2)_3$ resulted in the selective formation of dicationic linear trinuclear palladium complex $[Pd_3L_8]^{2+}$, where Pd(0) formally inserted into Pd–Pd bond of $[Pd_2L_6]^{2+}$ (eq. 1). However, additional reaction of $[Pd_3L_8]^{2+}$ with "Pd^0L_2" species has not been reported.



Recently we used 2,6-dimethylphenyl-isocyanide as the homoleptic ligand to develop this reaction by preparing [$Pd_3(CNC_6H_3Me_2\text{-}2,6)_8$][$PF_6$]$_2$ (**3**) from [$Pd(CNC_6H_3Me_2\text{-}2,6)_2$]$_3$ (**1**) and [$Pd_2(CNC_6H_3Me_2\text{-}2,6)_6$][$PF_6$]$_2$ (**2**). Herein we reported that the additional reaction of **3** and **1** selectively afforded a dicationic hexanuclear palladium complex [$Pd_6(CNC_6H_3Me_2\text{-}2,6)_{10}$][$PF_6$]$_2$ (**4**) (eq. 2, L = 2,6-$Me_2C_6H_3NC$). The crystal structure of the complex **4** was determined by X-ray crystallography and spectroscopic analysis.



VIII-F Synthesis of Transition Metal Catalysts for Organic Transformations

VIII-F-1 Oxidative Addition of RCO_2H 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 $IrX(H)(O_2CR)[(S)\text{-binap}]$ (**2**: R = CH_3; **3**: R = Ph; **4**: R = $C_6H_4CH_3$-*p*; **a**: X = Cl; **b**: X = Br; **c**: X = I) were prepared by one-pot reaction of $[Ir(\mu\text{-}X)(cod)]_2$ 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 (Λ-conformation) by X-ray analysis of (*S*)-**4a-c**. In this reaction, an iridium(I) complex $\{Ir(\mu\text{-}Cl)[(S)\text{-binap}]\}_2$ [(*S*)-**5a**] and pentacoordinated iridium(I) complexes IrX(cod)[(*S*)-binap] [(*S*)-**7b**: X = Br; (*S*)-**7c**: X = I] were generated prior to the oxidative addition of carboxylic acid. Cationic dinuclear iridium(III) complexes of the general formula $[\{Ir(H)[(S)\text{-binap}]\}_2(\mu\text{-}X)_3]X$ [(*S*)-**8**: **a**: X = Cl; **b**: X = Br; **c**: X = I] were prepared 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 $NaPF_6$, leading to the corresponding PF_6 salts, $[\{Ir(H)[(S)\text{-binap}]\}_2(\mu\text{-}X)_3]PF_6$ [(*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'-bi naphthyl) [(*S*)-**9c**] and SYNPHOS [= 2,2',3,3'-tetra hydro(5,5'-bi-1,4-benzodioxin)-6,6'-diyl]bis(diphenylph osphine)] [(*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*)-**11c**] 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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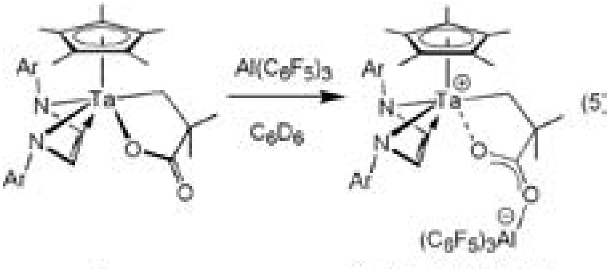
Preparation and characterization of homoenolate complexes of tantalum, $Cp^*Cl_3Ta(CH_2CR^1{}_2C(=O)OR^2)$ (**1a** : R^1 = H, R^2 = Et; **1b** : R^1 = R^2 = Me; **1c** : R^1 = Me, R^2 = $C_6H_4CH_3$-4), and tungsten, $(Xyl\text{-}N{=})Cl_3W(CH_2CH_2C(=O)OEt)$ (**7**), using zinc homoenolate reagents are described. Intramolecular coordination of the carbonyl 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, $Cp^*Cl_3Ta[N(Xyl)\text{-}C(=C=N\text{-}Xyl)\text{-}C(CH_2CH_2CO_2Et)=N\text{-}Xyl]$ (**3a**), which possesses a metallacyclic structure with an exocyclic ketene-imine moiety, and an η^2-iminoacyl tungsten complex, $(Xyl\text{-}N{=})W\{C(=N\text{-}Xyl)CH_2CH_2CO_2Et\}(CNXyl)Cl_3$ (**8**). The β-proton of the homoenolate moiety of **1a** was selectively deprotonated by $KN(SiMe_3)_2$ to afford an η^4-ethyl acrylate complex, $Cp^*Cl_2Ta(\eta^4\text{-ethyl acrylate})$ (**4**). In the case of complex **1b**, in which the β-positions were protected by dimethyl substituents, reaction with the dilithium salt of diazadiene afforded a tantalalactone complex **5**. The addition of $Al(C_6F_5)_3$ to **5** afforded a novel zwitterionic complex **6**, in which $Al(C_6F_5)_3$ coordinated to the exocyclic carbonyl oxygen of the tantalalactone.



5 **6** : Ar = 4-MeOC$_6$H$_4$