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機能集積型金属触媒の創製を基盤とする人工光合成の高度化

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Development of Multifunctional Transition Metal Complexes toward Efficient Transformation of Carbon Dioxide

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二酸化炭素のような不活性分子の効率的分子変換反応の開発を目指し、複数の機能を備えた均一系機能集積型金属触媒として、金属-金属結合をもつ異種金属二核錯体の創製と反応性の調査に取り組んだ。その結果、PZnP-ピンサー型配位子をもつパラジウムならびにルテニウム錯体の合成と構造解析に成功し、これらがルイス酸機能をもつ複合機能遷移金属錯体として働くことを明らかとした。

Aiming at the development of efficient molecular transformation of inert molecules such as carbon dioxide, synthesis and reactivity of bimetallic complexes with metal-metal bonds were investigated. As a result, we succeeded in synthesis and structural analyses of palladium and ruthenium complexes having PZnP-pincer-type ligands, which work as multifunctional transition metal complexes that possess Lewis acidic sites on the ligand.

1. 研究内容

Organometallic catalysis employing bimetallic complexes has emerged as an important strategy in synthetic chemistry. Such bimetallic catalysts are expected to be multi-functional catalysts due to their unique electronic property, coordination ability, and redox behavior at the metal-metal bonds, which are highly promising toward development of efficient transformation reactions of unreactive molecules such as carbon dioxide. However, metal-metal bonds are generally unstable and difficult to make, and efficient synthesis of such bimetallic complexes and their application in synthetic chemistry have been a great challenge. The main purpose in this research is to develop new hetero bimetallic complexes having a metal-metal bond that would be applicable to

transformation reactions of carbon dioxide utilizing the multi-functional property of the metal-metal bond.

After several investigations, we have found that the treatment of (*o*-diphenylphosphino)phenylboronate **1a** with 0.7 equivalent of ZnMe₂ in toluene at 100°C afforded bis(*o*-diphenylphosphino)phenylzinc **2a** in 80% yield, which was easily isolated by reprecipitation of the crude mixture from THF/hexane (Figure 1). X-ray analysis disclosed that **2a** forms a dimer in the crystalline state, where one of phosphorus atoms coordinates to zinc of the other molecule (Figure 2-a). The reaction was also applicable to (*o*-dicyclohexylphosphino)phenylboronate **1b**, affording the corresponding bis(*o*-dicyclohexylphosphino)phenylzinc **2b** in 47% isolated yield, which exists as a monomer in

the crystalline state (Figure 2-b). Previously, we have developed the Ru-catalyzed *ortho* C–H borylation reaction of arylphosphines with HBpin to afford *o*-phosphinophenylboronic acid pinacol esters in high yields. Therefore, these arylboronates can be prepared easily by Ru-catalyzed C–H borylation of commercially available arylphosphines. This method realizes the highly efficient, practical synthesis of bis(*o*-phosphino)phenylzinc derivatives from commercially available arylphosphines in two steps without the use of organolithium reagents.

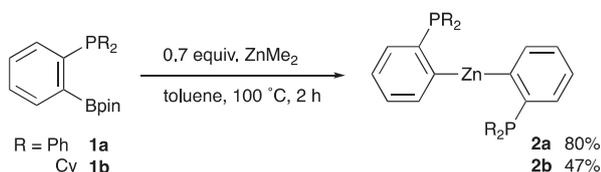


Figure 1

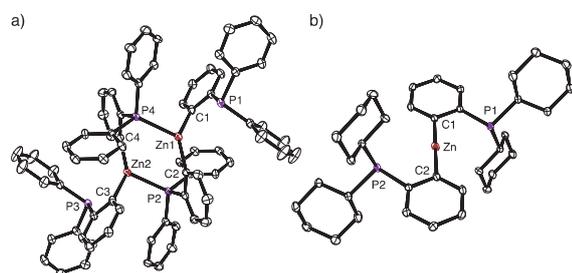


Figure 2. ORTEP drawings of 2a (a) and 2b (b) at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for 2a: Zn1–C1=2.002(3), Zn1–C2=2.003(4), Zn1–P4=2.478(1), Zn1–P1=2.941(1), C1–Zn1–C2=142.2(1); for 2b: Zn1–C1=1.9407(16), Zn1–C2=1.9407(16), C1–Zn1–C2=180.0.

Having bis(*o*-phosphinophenyl)zinc derivatives in hand, we examined to use them as PZnP-pincer type ligands for complexation with various transition metals expecting facile formation of bimetallic complexes having zinc-transition metal bonds. It was found that the reaction of 2a with Pd(PPh₃)₄ in benzene at room temperature afforded a palladium complex 3a having a PZnP-

pincer ligand and PPh₃ as supporting ligands in 95% yield (Figure 3). The ³¹P NMR showed a singlet at $\delta = 44.1$ and a broadening peak around $\delta = 14$, which correspond to phosphorous atoms of the PZnP-ligand and PPh₃, respectively. X-ray analysis revealed that the geometry around Pd is distorted tetrahedral judged from the Zn–Pd–P3 angle (166.21(2)°) and $\Sigma(\text{Pd}) = 365.4^\circ$, but relatively close to square planar compared to the structures of phenylene-tethered PBP–Pd complexes (Figure 4-a). The Pd–Zn length (2.6399(5) Å) is almost comparable to the sum of covalent radii (2.61 Å). The C1–Zn–C2 angle bends to 149.3(1)° from the original linear structure, which is similar to the value of the acridine–ZnPh₂ complex (149.0°). Furthermore, NBO analyses clarified that the Pd–Zn bond consists of donor/acceptor interactions between an occupied $d_{x^2-y^2}$ orbital of Pd and an unoccupied s-type orbital of Zn, leading to the stabilization energy of 7.5 kcal/mol (Figure 4-b). These data support that the coordination bond

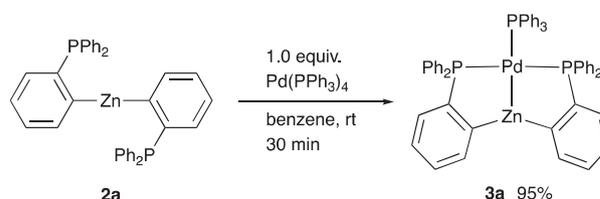


Figure 3

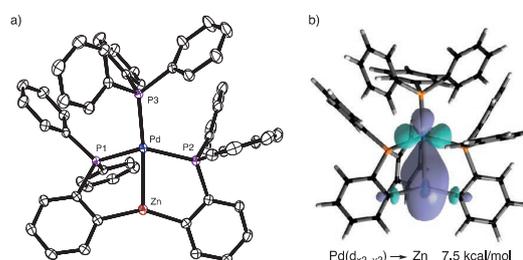


Figure 4. a) ORTEP drawing of 3a at 30% probability level. Hydrogen atoms and a solvent molecule (Et₂O) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd–Zn=2.6399(5), C1–Zn–C2=149.3(1). b) NBO analysis on 3a.

exists between a Lewis basic Pd atom and a σ -accepting Zn atom with the PZnP-tridentate structure. This is the first example of the synthesis of the phenylene-tethered PZnP-Pd complex that bears a neutral, coordinatively unsaturated Zn atom as a Z-type metalloligand.

The versatility of bis(*o*-phosphinophenyl)zinc **2** as PZnP-pincer type ligands was further demonstrated in the complexation with Ru(0). A PZnP-ruthenium tricarbonyl complex **4a** was easily accessible by the reaction of **2a** with 0.33 equiv. of Ru₃(CO)₁₂ in benzene at 100°C (Figure 5). Furthermore, the reaction of **2b** also proceeded smoothly to give the PZnP-Ru complex **4b** having PCy₂ side arms, demonstrating the high utility of this method to prepare a variety of PZnP-metal complexes. These

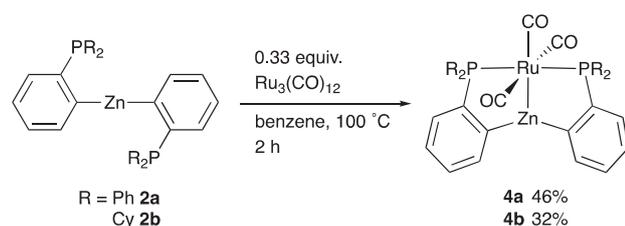


Figure 5

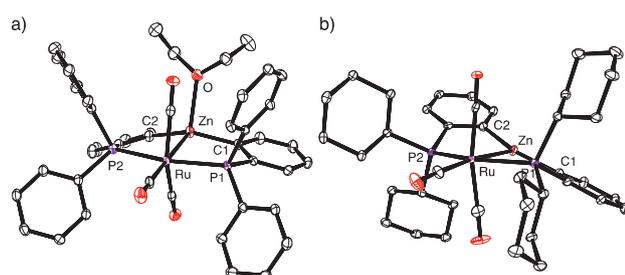


Figure 6. ORTEP drawing of **4a** (a) and **4b** (b) at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **4a**: Ru–Zn = 2.7343(5), Ru–P1 = 2.3490(9), Ru–P2 = 2.3604(9), Zn–C1 = 2.013(3), Zn–C2 = 2.012(3), Zn–O = 2.297(3), P1–Pd–P2 = 164.01(3), C1–Zn–C2 = 145.3(1); for **4b**: Ru–Zn = 2.697(1), Ru–P1 = 2.416(2), Ru–P2 = 2.364(3), Zn–C1 = 1.990(10), Zn–C2 = 1.975(9), P1–Pd–P2 = 153.13(9), C1–Zn–C2 = 152.6(4).

complexes were structurally characterized by X-ray analyses using single crystals obtained from toluene/Et₂O for **4a** and toluene/pentane for **4b** (Figure 6). It is noteworthy that a Et₂O molecule coordinates on the Zn atom of **4a** in the crystalline state, proving that the Zn-metalloligand is able to accept a Lewis basic substrate with keeping the Ru–Zn bond. This is highly promising for the synergetic activation of substrates such as carbon dioxide at the M–Zn bond to realize unique carboxylation reactions in synthetic chemistry.

We have developed an efficient method to access bis(*o*-phosphinophenyl)zinc derivatives via boron-zinc double transmetalation between *o*-phosphinophenylboronate and dialkylzinc for the first time. This method enables two-step synthesis of phenylene-tethered PZnP-pincer type ligands from commercially available arylphosphines. The facile preparation of PZnP-palladium and -ruthenium complexes is also achieved, demonstrating high versatility of the diarylzinc compounds as isolable PZnP-pincer type ligands. The structural analyses revealed that the Zn atom works as a Lewis acidic site, indicating that these Zn-transition metal bonds are highly promising for cooperative activation and transformation of unreactive molecules such as carbon dioxide. This study demonstrates feasibility of these Zn-Pd and Zn-Ru bimetallic complexes as multi-functional metal catalysts. Development of other bimetallic complexes and their application to transformation of carbon dioxide are in progress.

2. 発表 (研究成果の発表)

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