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Facile Synthesis and Utilization of Bis(o-phosphinophenyl)zinc as Isolable PZnP-pincer Ligands Enabled by Boron-Zinc Double Transmetallation

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| Journal: | <i>Dalton Transactions</i> |
| Manuscript ID | DT-COM-04-2022-001222 |
| Article Type: | Communication |
| Date Submitted by the Author: | 19-Apr-2022 |
| Complete List of Authors: | Fukuda, Kazuishi; Tokyo Institute of Technology, Department of Chemistry Harada, Takuma; Tokyo Institute of Technology, Department of Chemistry Iwasawa, Nobuharu; Tokyo Institute of Technology, Department of Chemistry Takaya, Jun; Tokyo Institute of Technology, Department of Chemistry |
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Facile Synthesis and Utilization of Bis(*o*-phosphinophenyl)zinc as Isolable PZnP-pincer Ligands Enabled by Boron-Zinc Double Transmetalation

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Bis(*o*-phosphinophenyl)zinc derivatives were successfully synthesized by the reaction of *o*-phosphinophenylboronates with dimethylzinc via boron-zinc double transmetalation. The transmetalation was significantly accelerated by the presence of the *ortho* PR₂ substituent to give diarylzinc selectively. These organozinc compounds act as isolable phenylene-tethered PZnP-pincer ligands, affording PZnP-palladium and ruthenium complexes with a σ -accepting Zn-metalloligand.

Tridentate ligands containing a Lewis acidic metal or metalloid element (E) as a σ -acceptor (Z-type ligand) at the central position have emerged as a new class of pincer type ligands for transition metals.¹ Such Z-type pincer ligands activate the transition metal electrophilically, enabling a reverse electronic perturbation compared to the case of σ -donating, L-type ligands such as phosphines. The unique reactivity and synthetic utility have been demonstrated particularly with the phenylene-tethered PEP-ligands and their metal complexes, in which the M–E bond is supported by two *o*-phosphinophenyl linkages (Figure 1-a).² This type of PEP-ligands is generally synthesized from *o*-phosphinophenyllithium and the corresponding electrophiles (X_nECl₂). The obtained (*o*-PR₂C₆H₄)E_n compounds are isolable and utilized for complexation with transition metals to afford various PEP-M complexes. This method is widely applicable to a variety of PEP-pincer ligands including group 13,^{3,4} 14,⁵ 15,⁶ and 16⁷ elements as σ -acceptors, and unique reactivities and catalytic applications have been developed.

In spite of the high versatility of the *o*-phosphinophenyl linkage, the corresponding chemistry of group 12 elements has remained unexplored. Bennett reported the pioneering work on the synthesis and structural analysis of PHgP-metal

complexes utilizing bis(*o*-diphenylphosphino)phenyl)mercury as a PHgP-ligand.⁸ Regarding Zn, bis(*o*-phosphinophenyl)zinc derivatives **A** are possible candidates as Z-type PZnP-pincer ligands, however, their synthesis and complexation behavior have not been investigated to date. Recently, Miloserdov, Macgregor and Whittlesey reported the *in situ* generation of a ruthenium complex bearing bis(*o*-diphenylphosphino)phenyl)zinc as a PZnP-ligand through the reaction of a ruthenacycle complex [Ru(PPh₃)(C₆H₄PPh₂)₂H(ZnMe)] with ZnMe₂ and CO via Ru–C/Zn–C bond exchange (Figure 1-b).⁹ However, this method

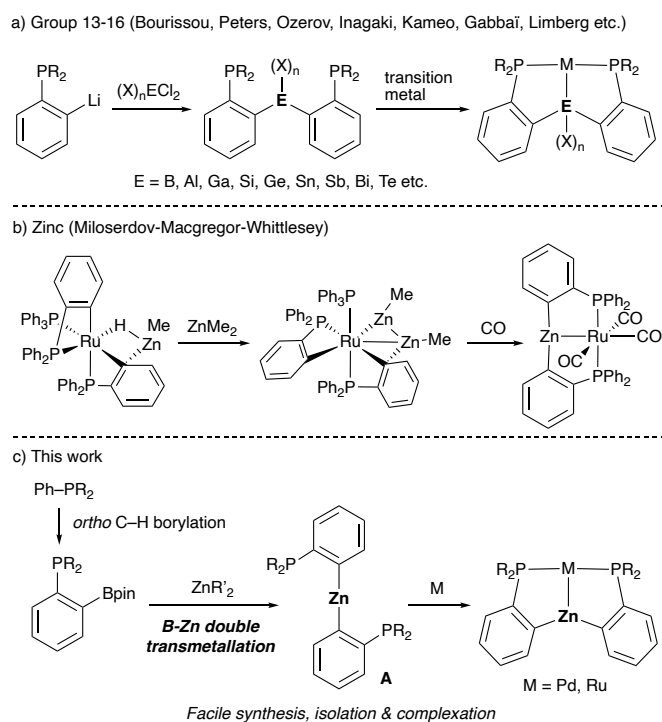


Fig. 1 Z-type PEP-pincer metal complexes utilizing the *o*-phosphinophenyl linkage

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Electronic Supplementary Information (ESI) available: Details of experimental procedures, spectral data, analytical data, and theoretical calculations. CCDC 2156957 (**2a**), 2156958 (**2b**), 2156959 (**3a**), 2156960 (**4a**), and 2156961 (**4b**). For ESI and crystallographic data in CIF; See DOI: 10.1039/x0xx00000x

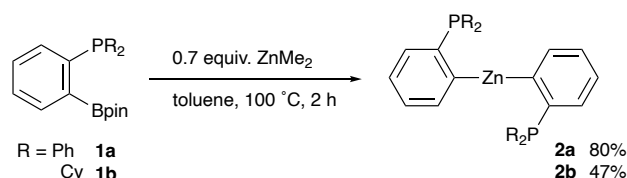
lacks generality and versatility for the synthesis of various PZnP-metal complexes. The development of an efficient method for the preparation of bis(*o*-phosphinophenyl)zinc derivatives as isolable, handy PZnP-ligands is highly desirable to further promote investigation and utilization of PZnP-metal complexes.¹⁰

Herein we report the facile synthesis of bis(*o*-phosphinophenyl)zinc derivatives **A** as isolable Z-type PZnP-pincer ligands and their complexation with transition metals (Figure 1-c). We developed a highly efficient boron-zinc double transmetallation reaction between *o*-phosphinophenylboronates and dialkylzinc, realizing the practical two-step synthesis of the PZnP-ligands from commercially available arylphosphines. The preparation and structural analyses of PZnP-palladium and ruthenium complexes were also achieved, demonstrating the versatility of bis(*o*-phosphinophenyl)zinc as Z-type PZnP-pincer ligands.

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.^{11,12} In our continuous research on the utilization of the borylation products, it was found that the treatment of (*o*-diphenylphosphino)phenylboronate **1a** with 1.0 equiv. of ZnEt₂ in toluene at room temperature afforded triphenylphosphine in 79% yield after acidic hydrolysis (Table 1, Entry 1). This result suggested that an arylzinc compound was generated *in situ* via boron-zinc transmetallation. ZnMe₂ was also employable instead of ZnEt₂ although prolonged reaction time or heating at 100 °C were required for high conversion due to the lower reactivity of ZnMe₂ than ZnEt₂ (Entries 2 and 3).¹³ Furthermore, the loading of ZnEt₂ can be reduced to 0.7 and 0.5 equiv. with keeping the yield of PPh₃ comparable to that with 1.0 equiv. (Entries 4 and 5), indicating the generation of diarylzinc, not monoarylzinc (ArZnEt), *in situ*. The reaction of phenylboronate, a substrate without a PPh₂ substituent at an *ortho* position, did

not occur at room temperature (Entry 6) and proceeded slowly with an excess amount of ZnEt₂ at 100 °C (Entry 7). Therefore, it is disclosed that the *ortho* PPh₂ substituent exhibits a significant effect to promote the boron-zinc transmetallation reaction.

To confirm the formation of diarylzinc, we tried isolation and structural analysis of the generated arylzinc compound. The mixture of **1a** and 0.7 equiv. of ZnMe₂ in toluene was heated at 100 °C for 2 h, and after removal of volatiles, the obtained crude product was reprecipitated from THF/hexane to give bis(*o*-diphenylphosphino)phenylzinc **2a** in 80% yield (Scheme 1).¹⁴ 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 ³¹P NMR in C₆D₆ exhibited a singlet at δ = 3.5, suggesting that **2a** exists as a monomer in the solution as it is a typical value for free triarylphosphines. 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). These diarylzincs are soluble into THF, Et₂O, and benzene, but not into hexane, and easily hydrolyzed by a small amount of water. It should be noted that these arylboronates can be prepared by Ru- or Rh-catalyzed C–H borylation of arylphosphines.^{11a,12b,15} Therefore, 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. The boron-zinc transmetallation between arylboronic acid derivatives and dialkylzinc has been widely utilized for the



Scheme 1. Preparation of bis(*o*-phosphinophenyl)zinc 2

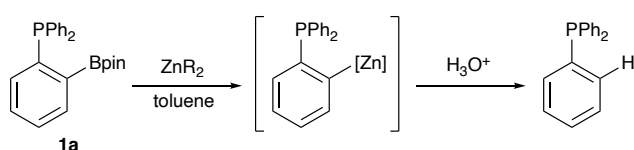


Table 1. Transmetallation of *o*-phosphinophenylboronate with alkylzinc

| Entry | Zn | Equiv. | Temp./°C | Time/h | Yield/% ^a |
|----------------|-------------------|--------|----------|--------|----------------------|
| 1 | ZnEt ₂ | 1.0 | rt | 2 | 79 |
| 2 | ZnMe ₂ | 1.0 | rt | 12 | 56 ^b |
| 3 | ZnMe ₂ | 1.0 | 100 | 2 | 72 |
| 4 | ZnEt ₂ | 0.7 | rt | 2 | 85 |
| 5 | ZnEt ₂ | 0.5 | rt | 2 | 77 |
| 6 ^c | ZnEt ₂ | 0.7 | rt | 2 | ND ^d |
| 7 ^c | ZnEt ₂ | 3.0 | 100 | 2 | 28 ^d |

^a The combined yields of triphenylphosphine and triphenylphosphine oxide, which is formed during work-up, are depicted. These yields are determined by GC analysis. ^b The reaction for 2 h afforded PPh₃ in 21% yield. ^c Phenylboronic acid pinacol ester was employed instead of **1a**. ^d GC yield of benzene.

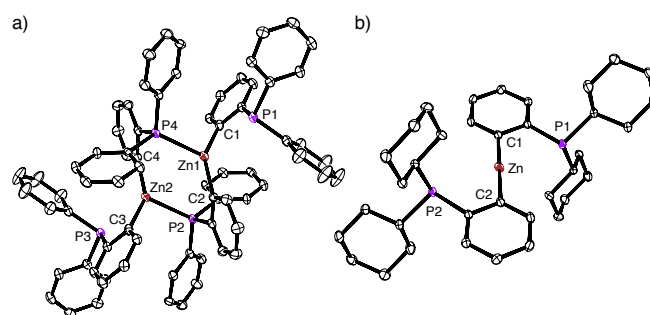
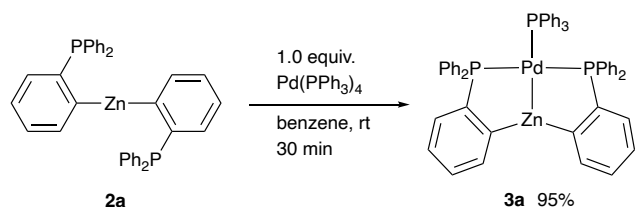


Fig. 2 ORTEP drawings of **2a** (a) and **2b** (b) at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **2a**: Zn1–C1 = 2.002(3), Zn1–C2 = 2.003(4), Zn1–P4 = 2.478(1), Zn1–P1 = 2.941(1), C1–Zn1–C2 = 142.2(1); for **2b**: Zn1–C1 = 1.9407(16),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

generation of arylzinc reagents, which are proposed to be monoarylzinc (ArZnR) generally.¹⁶ Arylboronic acids and arylboroxines are often employed as aryl sources, however, the use of arylboronates has scarcely been reported despite their easy availability through various C–H borylation reactions.¹⁷ Moreover, the reaction usually necessitates heating with an excess amount of ZnEt_2 for a long time to generate arylzinc reagents sufficiently.^{18,19} In sharp contrast to these precedents, our investigations clarified that 1) the boron-zinc transmetallation of arylboronate is significantly accelerated by the *ortho* PPh_2 substituent and proceeds even at room temperature, and 2) boron-zinc *double* transmetallation, where both alkyl groups on zinc transmetallate to two molecules of boronate, proceeds to give *diarylzinc* selectively in the presence of the *ortho* PR_2 substituent. These findings reveal new aspects of the boron-zinc transmetallation reaction for organic synthesis.

Having bis(*o*-phosphinophenyl)zinc derivatives in hand, we examined to use them as PZnP-pincer type ligands for complexation with various transition metals. Gratifyingly, it was found that the reaction of **2a** with $\text{Pd}(\text{PPh}_3)_4$ in benzene at room temperature afforded a palladium complex **3a** having a PZnP-pincer ligand and PPh_3 as supporting ligands in 95% yield (Scheme 2). The ^{31}P NMR showed a singlet at $\delta = 44.1$ and a broadened peak around $\delta = 14$, which correspond to phosphorus atoms of the PZnP-ligand and PPh_3 , respectively. X-ray analysis revealed that the geometry around Pd is distorted tetrahedral judged from the Zn–Pd–P3 angle ($166.21(2)^\circ$) and $\Sigma(\text{Pd}) = 365.4^\circ$, but relatively close to square planar compared to the structures of phenylene-tethered PBP-Pd complexes.^{3c,j} The Pd–Zn length ($2.6399(5) \text{ \AA}$) is almost comparable to the sum of covalent radii (2.61 \AA).²⁰ The C1–Zn–C2 angle bends to $149.3(1)^\circ$ from the original linear structure, which is similar to the value of the acridine-coordinated diphenylzinc ($(\text{C}_{13}\text{H}_9\text{N})\text{ZnPh}_2$) (149.0°).²¹ 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). These data support that the coordination bond 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.¹⁰



Scheme 2. Complexation of **2a** with $\text{Pd}(0)$

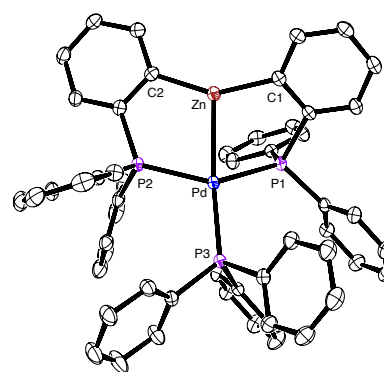


Fig. 3 ORTEP drawing of **3a** at 30% probability level. Hydrogen atoms and a solvent molecule (Et_2O) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd–Zn = $2.6399(5)$, Pd–P1 = $2.3270(7)$, Pd–P2 = $2.3095(7)$, Pd–P3 = $2.3917(7)$, Zn–C1 = $1.983(3)$, Zn–C2 = $1.973(3)$, C1–Zn–C2 = $149.3(1)$, P1–Pd–P2 = $140.41(3)$, P3–Pd–Zn = $166.21(2)$.

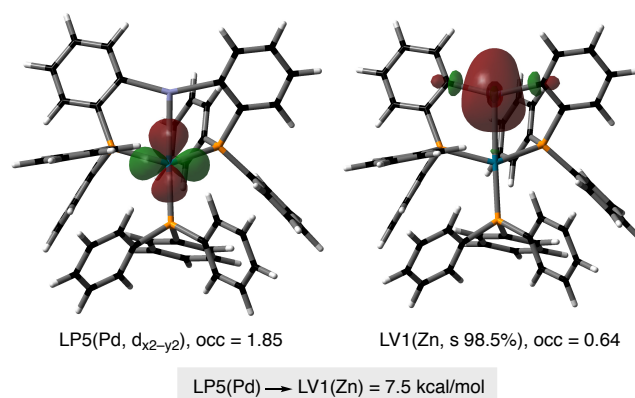


Fig. 4 Donor and acceptor orbitals for the Pd–Zn bond and the stabilization energy calculated by NBO analysis. LP denotes a lone pair orbital, LV denotes a lone vacancy (unoccupied valence orbital), and occ denotes the electron occupancy.

The versatility of bis(*o*-phosphinophenyl)zinc **2** as PZnP-pincer type ligands was further demonstrated in the complexation with $\text{Ru}(0)$. A PZnP-ruthenium tricarbonyl complex **4a** was easily accessible by the reaction of **2a** with 0.33 equiv. of $\text{Ru}_3(\text{CO})_{12}$ in benzene at 100°C (Scheme 3), whereas the previous method requires several steps to access the complex as shown in Figure 1-b.⁹ Furthermore, the reaction of **2b** also proceeded smoothly to give the PZnP-Ru complex **4b** having PCy_2 side arms, demonstrating the high utility of this method to prepare a variety of PZnP-metal complexes. These complexes were structurally characterized by X-ray analyses using single crystals obtained from toluene/ Et_2O for **4a** and toluene/pentane for **4b** (Figure 5). It is noteworthy that a Et_2O 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 at the M–Zn bond to realize unique catalysis in synthetic chemistry. Further investigations on the synthesis and utilization of various PZnP-metal complexes are in progress.

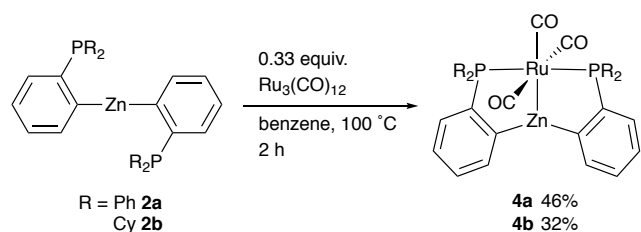
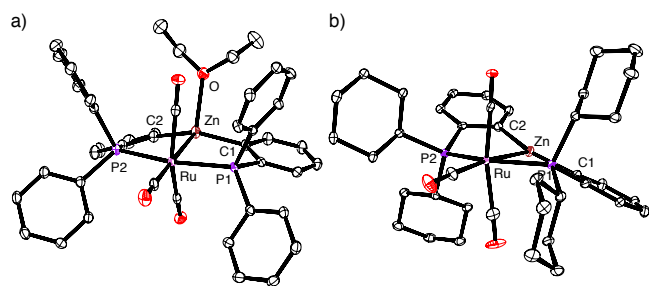
Scheme 3. Complexation of **2** with Ru(0)

Fig. 5 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 = 2.6983(5), Ru–P1 = 2.3954(9), Ru–P2 = 2.385(1), Zn–C1 = 1.975(4), Zn–C2 = 1.978(4), P1–Pd–P2 = 153.13(3), C1–Zn–C2 = 152.7(1).

We have developed an efficient method to access bis(*o*-phosphinophenyl)zinc derivatives via boron-zinc double transmetallation 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. These results are highly promising for further exploration of the chemistry of Z-type pincer ligands in organometallic and synthetic chemistry.

Data availability

Details of experimental procedures, spectral data, crystallographic information, and theoretical calculations can be found in the ESI. Crystallographic data were deposited in the CCDC with deposition numbers 2156957–2156961 for **2a**, **2b**, **3a**, **4a**, and **4b**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by JSPS KAKENHI Grant Numbers 20H02732, 20H04806, 20K21189 and JST, PRESTO Grant Number JY290145, Japan, and Tokuyama Science Foundation,

Shorai Foundation for Science and Technology, and Toyota Riken Scholar.

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- 14 For the preparation of **2** in a large scale, ZnMe₂ was employed because removal of the generated MeBpin by evaporation was easy. We confirmed that the diarylzinc **2a** was generated as a major species in the solution regardless of the alkylzinc reagent when monitoring the reaction of **1a** with 1.0 equiv. of ZnEt₂ or ZnMe₂ by ³¹P NMR. See the SI.
- 15 The boronate **1a** was prepared by the Ru-catalyzed C–H borylation of PPh₃ in a 30 mmol scale. See the SI.
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