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# Atom Swapping on Aromatic Rings: Conversion from Phosphinine Pincer Metal Complexes to Metallabenzenes Triggered by O<sub>2</sub> Oxidation

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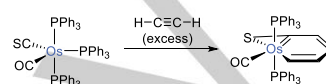
**Abstract:** Herein, we report a novel synthetic method for metallabenzene by swapping phosphorous atom in an aromatic phosphinine ring with transition metal fragments. Oxidation of a phosphine-phosphinine-phosphine pincer iridium complex by O<sub>2</sub> triggered replacement of the phosphorous atom of the phosphinine ring by an iridium fragment to afford iridabenzene. Dianionic rhodabenzene was also synthesized from a phosphinine rhodium complex by oxidation of the phosphorous atom followed by the subsequent reduction by metallic potassium. The aromaticity of newly synthesized irida- and rhoda-benzenes were evaluated experimentally and theoretically.

## Introduction

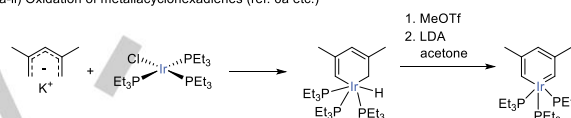
Since Kekulé proposed the correct structure of benzene in 1865, tremendous progress has been made in the chemistry of aromatic compounds, which have widespread applications ranging from materials to pharmaceuticals. Heterobenzenes, where one (or more) CH group of benzene is replaced with other elements, show distinguishable properties from benzene like Lewis basicity and electrophilicity as exemplified by pyridine. In 1979, the concept of heterobenzene was expanded to metallabenzene, heterobenzene with a transition-metal-based fragment by Thorn and Hoffman in their theoretical prediction of manganos- and rhoda-benzenes.<sup>1</sup> Transition-metal-based metallabenzene have attracted great attention<sup>2</sup> because the conjugation of d-orbital to  $\pi$ -system will afford unique characters such as steric, redox, and optical property. Introducing a transition metal to an aromatic system enables synthesis of unprecedented class of compounds which cannot be achieved by main group elements, such as spiro-aromatic compounds with planar geometry.<sup>3</sup> After Thorn and Hoffman's theoretical prediction,<sup>1</sup> it was firstly reported experimentally that transition metals can participate in the aromatic conjugation in the synthesis of osmabenzene by Roper and coworkers.<sup>4</sup> Following this pioneering work, various metallabenzene have been reported among late transition metals such as Mo, Re, Fe, Ru, Os, Ir, Ni and Pt.<sup>2h</sup>

### a) Major synthetic methods of metallabenzene

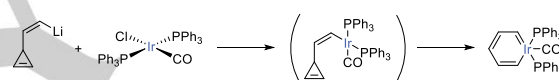
a-i) Cyclization of alkynes (ref. 4 etc.)



a-ii) Oxidation of metallacyclohexadienes (ref. 6a etc.)

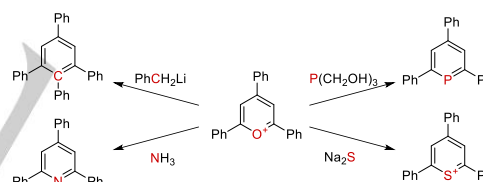


a-iii) Isomerization of cyclopropenylethynyl metal complexes (ref. 7a etc.)

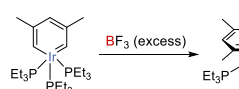


### b) Exchange of heteroatoms on an aromatic ring

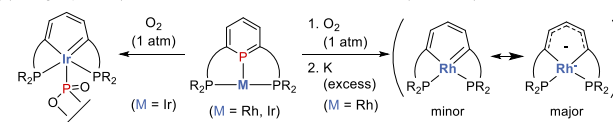
b-i) Heterobenzene-to-heterobenzene conversion (ref. 9)



b-ii) Metallabenzene-to-heterobenzene conversion (ref. 11)



### c) (Main-group-based)-heterobenzene-to-metallabenzene conversion (This work)



**Scheme 1.** a) Synthetic methods of metallabenzene, b) Exchange of heteroatom in aromatic rings and c) Atom-swapping method for the synthesis of metallabenzene presented in this manuscript

The major synthetic methods of metallabenzene can be classified into three categories as shown in Scheme 1a:<sup>2d</sup> a-i) cyclization of alkynes with metal complexes,<sup>4,5</sup> a-ii) oxidation of metallacyclohexadienes,<sup>6</sup> and a-iii) isomerization of cyclopropenylethynyl metal complexes.<sup>7</sup> Because the scope of each methodology is confined by the character of transition metal centers, metallabenzene lack of general synthetic methodology,<sup>7b</sup> and the limited metals are reported to be included in the aromatic system. Therefore, a novel synthetic method of

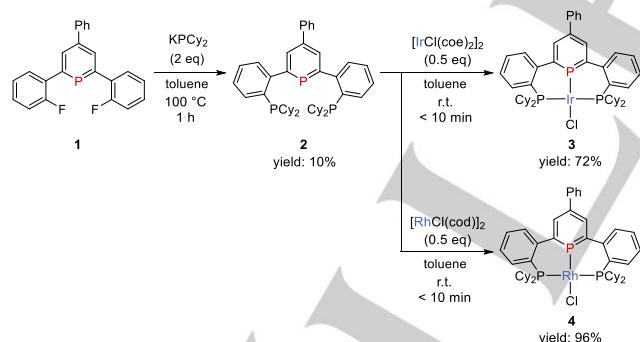
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metallabenzene is desirable to enable access to unexplored metallabenzenes and to broaden the applications of metallabenzenes. In this context, we focused on an atom-swapping strategy on an aromatic ring. As reported examples, treatment with appropriate nucleophiles can convert pyrylium into other (hetero)benzenes<sup>8,9</sup> such as benzene,<sup>9a</sup> pyridine,<sup>9b</sup> phosphinine,<sup>9c</sup> or thiopyrylium<sup>9d</sup> (Scheme 1b-i). Thiopyrylium can be converted to benzene by the reaction with a carbanion as well.<sup>10</sup> As for metallabenzene-to-(main-group-based)-heterobenzene conversion, one example has been reported for the conversion of iridabenzene to boratabenzene by treatment of iridabenzene with an excess amount of boron trifluoride (Scheme 1b-ii).<sup>11</sup> On the other hand, to the best of our knowledge, there is no report about conversion from main-group based heterobenzenes to metallabenzenes.

Here in this paper, we report a conversion of phosphinine to metallabenzene, where phosphorous atom is replaced by transition metal fragments, triggered by oxidation of the phosphorous atom by molecular oxygen (Scheme 1c). A new method, *atom-swapping* methodology enabled an access to rhodabenzene, which remained as a big challenge since it was predicted to be unstable by theoretical calculations.<sup>12–14</sup>

## Results and Discussion

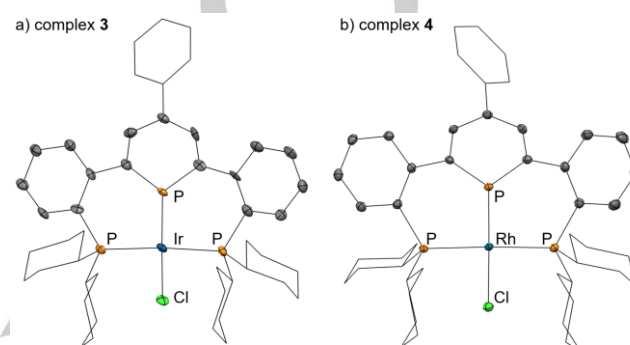
We designed phosphine-phosphinine-phosphine pincer complexes **3** and **4** in order to achieve the stable coordination of phosphinine to the transition metal. The desired complexes were synthesized over two steps from the literature-reported fluorophenyl-substituted phosphinine **1**<sup>15</sup> through  $S_NAr$  reaction with  $KPCy_2$  followed by coordination to iridium or rhodium. The structures of **2–4** were spectroscopically characterized, and those of **3** and **4** were also determined by single-crystal X-ray crystallographic analysis (Figure 1).



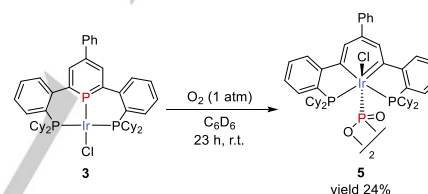
**Scheme 2.** Synthesis of phosphine-phosphinine-phosphine pincer complexes **3** and **4**

When benzene solution of phosphinine pincer complex **3** was exposed to atmospheric pressure of  $O_2$  gas for two days, crystals of iridabenzene **5** were grown in the reaction mixture (24% crystal yield, Scheme 3; *vide infra* for detailed discussion on the mechanism shown in Scheme 7). The structure of iridabenzene **5** was identified by single-crystal X-ray crystallographic analysis (Figure 2). Two iridabenzenes were bridged by  $\mu$ - $P^1, P^2$ -dimetaphosphite dianion ( $P_2O_4^{2-}$ ), which shows the phosphorous atom was oxygenated and replaced by iridium atom in the reaction. The structure of iridabenzene six-membered ring in **5** is almost symmetrical about the  $C3-Ir1-Cl1$  plane to have similar

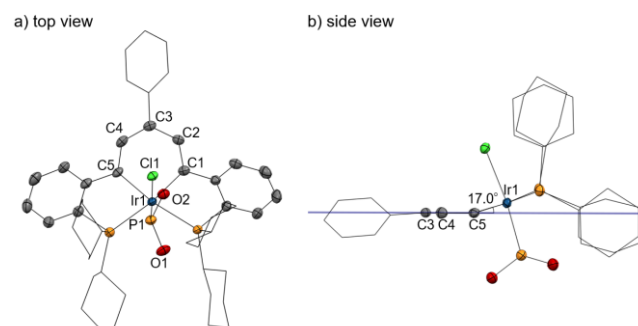
bond lengths between  $Ir1-C1$  and  $Ir1-C5$ ,  $C1-C2$  and  $C4-C5$ ,  $C2-C3$  and  $C4-C3$ . The six membered ring of iridabenzene **5** is not planar but rather bent: the  $C1-Ir1-C5$  plane is tilted significantly from the pentadienyl plane composed by five carbons  $C1-C5$  by  $17^\circ$ . This angle is slightly larger than other reported iridabenzenes,<sup>11,16</sup> which are ranging from 5 to 10 degrees. However, minimal bond alternation namely,  $C1-C2$  1.379(5),  $C2-C3$  1.399(5),  $C3-C4$  1.400(5),  $C4-C5$  1.372(5), suggests the aromatic character of iridabenzene **5**.  $^1H$  NMR chemical shift of the proton on the iridabenzene ring appeared in low-magnetic field at 7.58 ppm ( $CD_2Cl_2$ ), which implies the existence of aromatic ring current on the iridabenzene ring (*vide infra* for further analysis on aromaticity).



**Figure 1.** X-ray crystal structures of complexes **3** and **4** (thermal ellipsoids are drawn with 50% probability; hydrogen atoms are omitted, and cyclohexyl group and phenyl group were simplified for clarity).



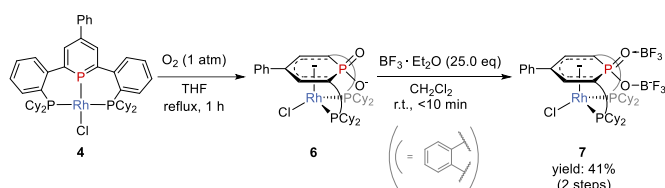
**Scheme 3.** Formation of iridabenzene **5** by  $O_2$  oxidation of complex **3**



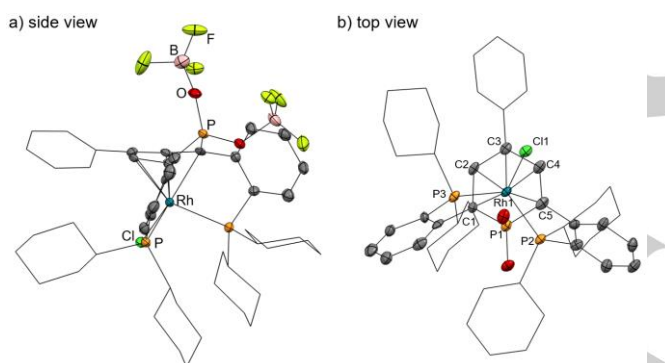
**Figure 2.** X-ray crystal structure of iridabenzene **5** (thermal ellipsoids are drawn with 50% probability; hydrogen atoms are omitted, and cyclohexyl group and phenyl group were drawn as wireframe for clarity; the other part was omitted for clarity). Selected bond distances ( $\text{\AA}$ ):  $Ir1-C1$  2.046(4),  $Ir1-C5$  2.037(4),  $C1-C2$  1.379(5),  $C2-C3$  1.399(5),  $C3-C4$  1.400(5),  $C4-C5$  1.372(5),  $Ir1-Cl1$  2.4506(9),  $Ir1-P1$  2.2546(10),  $Ir1-P2$  2.4256(10),  $Ir1-P3$  2.4036(9).

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Simple treatment of rhodium complex **4** with O<sub>2</sub> did not afford a rhodabenzene. Unlike iridium complex **3**, reaction of complex **4** with oxygen gas reached to full conversion of complex **4** in an hour to afford  $\eta^5$ -pentadienyl complex **6** where phosphorous atom on phosphinine was oxidized and the rhodium center was coordinated by the  $\pi$ -electrons of the  $\lambda^5$ -phosphacycle (Scheme 4). This structure was spectroscopically characterized and the  $\eta^5$ -pentadienyl structure was confirmed by single crystal X-ray diffraction analysis as complex **7** after trapping oxygen atom on phosphorous by two molecules of BF<sub>3</sub> (Figure 3) as well as spectroscopic analysis. Phosphacycle on complex **7** showed bond alternation namely, P1–C1 1.803(4), C1–C2 1.393(5), C2–C3 1.446(5), C3–C4 1.402(6), C4–C5 1.456(5), P1–C5 1.763(4), which suggests that the phosphacycle has non-aromatic character.



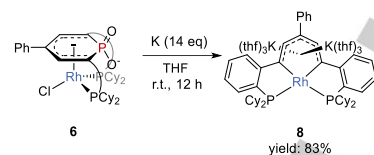
**Scheme 4.** Formation of  $\eta^5$ -pentadienyl complex **6** and trapping with BF<sub>3</sub>



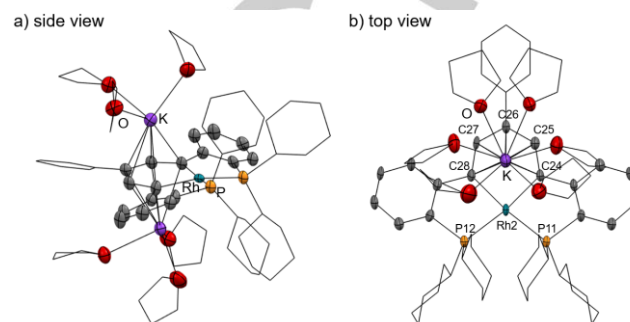
**Figure 3.** X-ray crystal structure of  $\eta^5$ -pentadienyl complex **7** (thermal ellipsoids are drawn with 50% probability; hydrogen atoms are omitted, and cyclohexyl group and phenyl group were simplified for clarity). Selected bond distances (Å): P1–C1 1.803(4), P1–C5 1.763(4), C1–C2 1.393(5), C2–C3 1.446(5), C3–C4 1.402(6), C4–C5 1.456(5), Rh1–C1 2.265(3), Rh1–C2 2.226(4), Rh1–C3 2.318(4), Rh1–C4 2.240(4), Rh1–C5 2.150(3).

Further treatment of  $\eta^5$ -pentadienylrhodium complex **6** with excess amount of metallic potassium in THF afforded dianionic rhodabenzene **8**. The structure of **8** was spectroscopically characterized and <sup>1</sup>H NMR chemical shift of a proton on the rhodabenzene ring appeared at 8.08 ppm (THF-*d*<sub>6</sub>) which suggests the existence of strong aromatic ring current on the rhodabenzene ring. The single crystal suitable for X-ray diffraction analysis could be grown by slow evaporation from THF solution at –25°C and the X-ray structure is shown in Figure 4.<sup>17</sup> Rhodabenzene was contacted by two potassium cations from both sides while rhodabenzene plane was almost planar. The structure of rhodabenzene six-membered ring in **8** have symmetrical structure and similar bond lengths between Rh2–C24 2.064(7) and Rh2–C28 2.071(7), C24–C25 1.386(10) and C27–C28 1.397(11), C25–C26 1.420(10) and C26–C27 1.433(9).

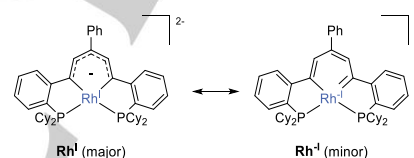
This minimal bond alternation suggests the aromatic character of rhodabenzene **8** (*vide infra* for further analysis on aromaticity).



**Scheme 5.** Formation of dianionic rhodabenzene **8** using potassium metal as a reductant



**Figure 4.** X-ray crystal structure of rhodabenzene **8** (thermal ellipsoids are drawn with 50% probability; hydrogen atoms and disordered rhodium atom are omitted, and cyclohexyl group, phenyl group, and THF are simplified for clarity). Selected bond distances (Å): Rh2–C24 2.064(7), Rh2–C28 2.071(7), C24–C25 1.386(10), C25–C26 1.420(10), C26–C27 1.433(9), C27–C28 1.397(11), Rh2–P11 2.261(2), Rh2–P12 2.277(2).



**Scheme 6.** Possible resonance structures of rhodabenzene dianion **8**

As shown in Scheme 6, rhodabenzene dianion **8** can adopt two resonance structures, namely Rh(I) anionic complex with pentadienyl anion (Scheme 6, left) and Rh(-I) dianionic complex (Scheme 6, right). The coupling constant between rhodium and phosphorous in <sup>31</sup>P NMR (<sup>1</sup>J<sub>PRh</sub> = 123.0 Hz) support Rh(I) character (left in Scheme 6), as is comparable with the <sup>1</sup>J<sub>PRh</sub> values of reported dicarbonyl Rh(I) ate complexes (128 Hz to 142 Hz)<sup>18</sup> while <sup>1</sup>J<sub>PRh</sub> values of Rh(-I) complexes are ranging from 150 Hz to 209 Hz.<sup>19</sup> The coupling constant between rhodium and carbon in <sup>13</sup>C NMR of rhodabenzene dianion **8** (<sup>1</sup>J<sub>CRh</sub> = 36.6 Hz) is also comparable with the <sup>1</sup>J<sub>CRh</sub> values of reported dicarbonyl Rh(I) ate complexes (24 Hz to 38 Hz).<sup>18</sup> In addition, the distorted square planar geometry also support Rh(I) character as Rh(I) species generally favors square planar geometry whereas Rh(-I) species favors tetrahedral geometry.

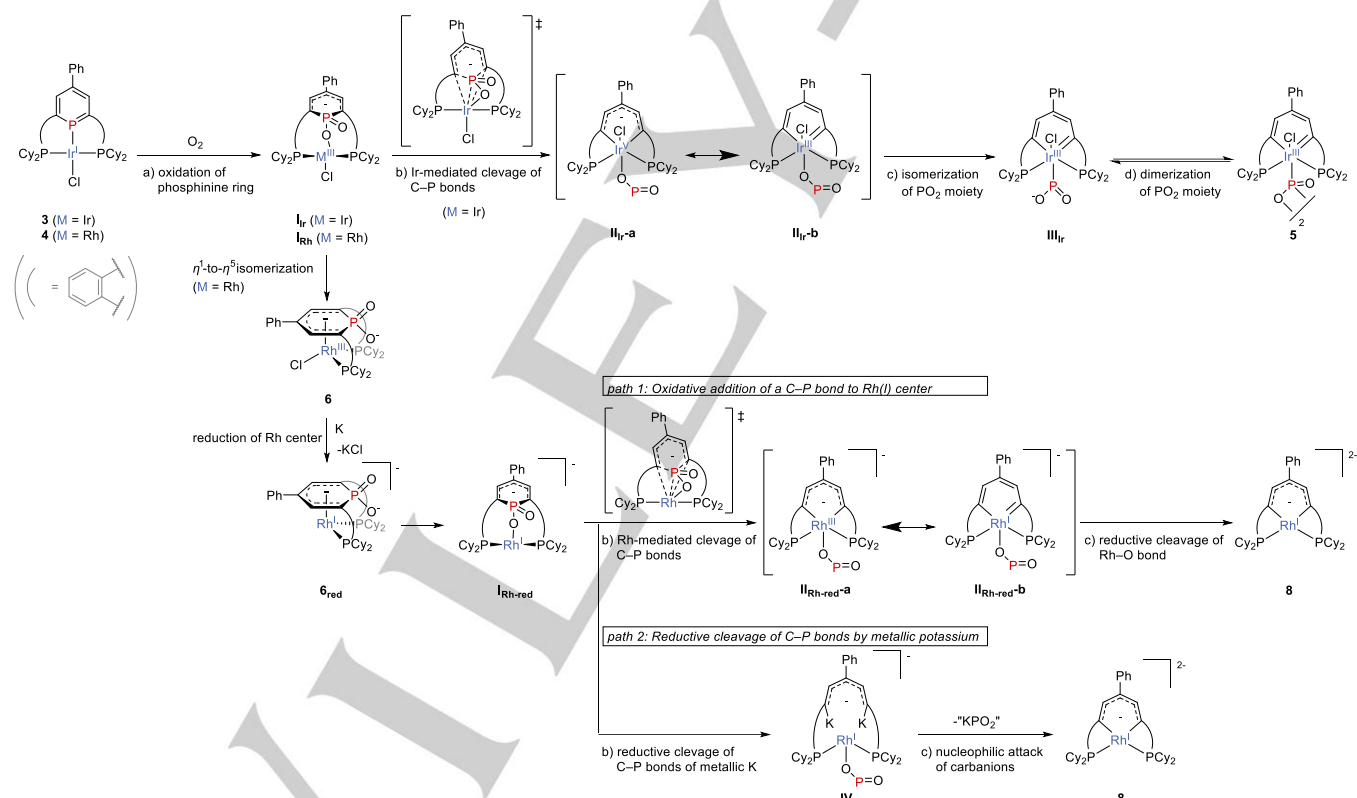
To the best of our knowledge, this is the first successful synthesis of rhodabenzene after 40 years since it was first theoretically predicted. Although some attempts for the synthesis of rhodabenzene from rhodacyclohexadiene<sup>12</sup> or cyclopropenylethenyl anion<sup>13</sup> were reported, the synthesis has remained unachieved challenge. In precedented theoretical investigations with DFT calculations, rhodabenzene<sup>14</sup> were predicted to be unstable and easily isomerize to cyclopentadienyl rhodium complex, which has indeed made it difficult to isolate

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rhodabenzene. Rhodabenzene **8** was, in sharp contrast, stable enough to be isolated and spectroscopically fully characterized, probably due to the dianionic character and two rigid supporting phosphine ligands preventing **8** from isomerization into a cyclopentadienyl complex.

Possible mechanisms for the formation of iridabenzene **5**, pentadienyl rhodium complex **6**, and rhodabenzene **8** are shown in Scheme 7 (See Supporting Information for DFT calculations for the formation of iridabenzene **5**). In the case of iridium, phosphinine iridium complex **3** was oxidized by O<sub>2</sub> to form intermediate **I<sub>Ir</sub>** where phosphorous atom of phosphinine was oxidized (step a). Oxidation of phosphorous atom enhances the reactivity of the C–P bond of phosphinine toward oxidative addition. Oxidative addition of a C–P bond to Ir(III) and subsequent migration of metaphosphite (PO<sub>2</sub><sup>-</sup>) moiety occurred in a concerted manner to afford Ir(V) intermediate **II<sub>Ir-a</sub>** (step b). This intermediate can be drawn by another resonance structure **II<sub>Ir-b</sub>**, which has Ir(III) center and one carbene ligand. Afterward, the metaphosphite ligand isomerized from O-coordination to P-coordination to afford intermediate **III<sub>Ir</sub>** (step c). Finally, dimerization of metaphosphite moiety afforded iridabenzene **5** (step d).<sup>20</sup> As for step a, treatment of a phosphinine with hydrogen peroxide or oxygen gas is known to afford corresponding λ<sup>5</sup>-

phosphinine derivatives.<sup>21</sup> As for step b, reactions which involve oxidative addition of C–P bond have been reported.<sup>22</sup> For rhodium complex **4**, oxidation of phosphinine ring (step a) proceeded in the same way as the case for iridium complex **3** to afford intermediate **I<sub>Rh</sub>**. However, in the case of rhodium, the Rh-mediated cleavage of the C–P bond has a much higher barrier possibly because oxidation of Rh(III) center to Rh(V) is difficult (See Supporting Information for DFT calculations). Intermediate **I<sub>Rh</sub>** then eventually isomerized to a stable η<sup>5</sup>-pentadienyl Rh(III) complex **6** without cleavage of the C–P bonds. Contrastively, reduction of complex **6** affords intermediate **I<sub>Rh-red</sub>** by the reduction of Rh(III) to Rh(I) and subsequent isomerization. Two possible pathways are postulated from **I<sub>Rh-red</sub>** to rhodabenzene **8** (Scheme 7, paths 1 and 2): One is the oxidative addition of a C–P bond to the Rh(I) accompanied by the concerted migration of the metaphosphite moiety to afford intermediate **II<sub>Rh-red-a</sub>**. Reductive cleavage of the Rh–O bond yields dianionic rhodabenzene **8**. This transformation from **I<sub>Rh-red</sub>** to **II<sub>Rh-red-a</sub>** is analogous to **I<sub>Ir</sub>** to **II<sub>Ir-a</sub>** (Scheme 7, path 1). Alternatively, reductive cleavage of the two C–P bonds of the phosphacycle in intermediate **I<sub>Rh-red</sub>** could afford intermediate **IV**. Nucleophilic attack of the carbyl potassium moieties on the rhodium center produces dianionic rhodabenzene **8** (Scheme 7, path 2).



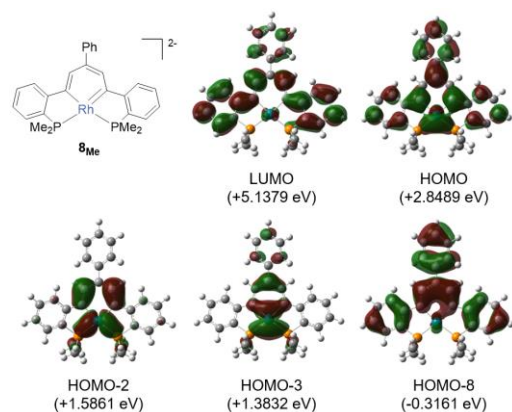
**Scheme 7.** Mechanisms of the formation of iridabenzene **5**, pentadienyl rhodium complex **6**, and rhodabenzene **8** (See Supporting Information for DFT calculations in the formation of iridabenzene **5**)

To elucidate the electronic structures of the metallabenzene **5** and **8**, we employed DFT calculations for simplified model compounds **5<sub>Me</sub>** and **8<sub>Me</sub>** (Computational details are described in the Supporting Information). Figure 5 shows the π-orbitals of rhodabenzene **8<sub>Me</sub>**. High-lying orbital energies are due to dianionic character of **8<sub>Me</sub>**. HOMO-8 spread all over the 5 carbons and rhodium center of rhodabenzene ring, which shows that the d-orbital of rhodium significantly participates in π-conjugation on

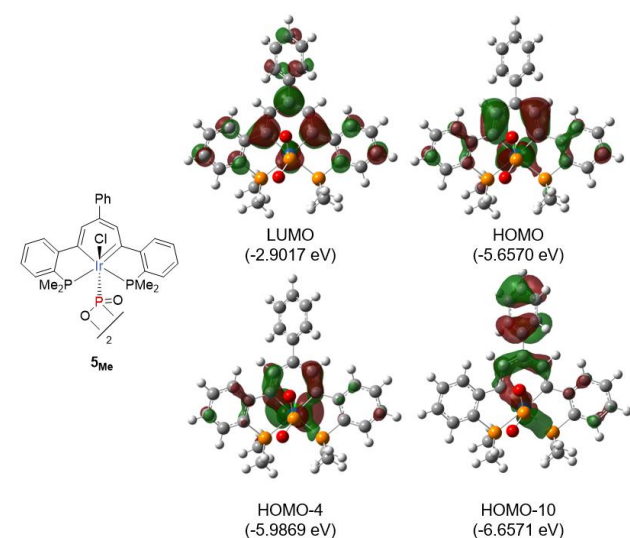
the rhodabenzene ring. The other molecular orbitals shown in Figure 5 (LUMO, HOMO, HOMO-2, and HOMO-3) also showed large contribution of the d-orbitals of rhodium to the π-conjugation and their electron configuration has analogy to those of benzene. This contribution of the rhodium center results in characteristic deep purple color of rhodabenzene **8** (see Supporting Information for UV/Vis spectrum and TD-DFT calculation). In Figure 6, the representative π-conjugated orbitals of iridabenzene **5<sub>Me</sub>** are listed.

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Due to its asymmetric chemical environment above and below the iridabenzene plane, the shape of orbitals is distorted. However, contribution of the d-orbitals is largely observable as well in iridabenzene. In addition, Nucleus-independent chemical shift (NICS)<sup>23,24</sup> calculations are performed (see Supporting Information for the detailed analysis). NICS(1)<sub>zz</sub> value of iridabenzene **5**<sub>Me</sub> was calculated to -6.4 ppm (PO<sub>2</sub> side) and -1.2 ppm (Cl side), which indicates slight aromatic character of **5**<sub>Me</sub>. On the other hand, NICS(1)<sub>zz</sub> value of rhodabenzene **8**<sub>Me</sub> was calculated to +2.6 ppm (average of two faces), which reflects slightly anti-aromatic character of **8**<sub>Me</sub>. This tendency is also supported by the anisotropy of the induced current density (ACID)<sup>25,26</sup> analysis. The ring current of iridabenzene ring **5**<sub>Me</sub> is negligible (Figure S44, Supporting Information), which accords the small absolute value of NICS(1)<sub>zz</sub>. Rhodabenzene **8**<sub>Me</sub> exhibits the slight paratropic ring current (Figure S45, Supporting Information), which accords the positive NICS(1)<sub>zz</sub> value. According to these results, iridabenzene **5** is thought to have small but significant aromatic character in both structural property and magnetic property. Aromaticity of rhodabenzene **8** is still elusive. Experimental results (bond lengths and <sup>1</sup>H NMR chemical shift) indicate its aromatic character whereas computational results (NICS and ACID analysis) indicate slightly antiaromatic character of rhodabenzene **8**.



**Figure 5.** Selected molecular orbitals of **8**<sub>Me</sub> calculated at the B3LYP/def2-SVP level.



**Figure 6.** Selected molecular orbitals of **5**<sub>Me</sub> calculated at the B3LYP/def2-SVP level (The other iridabenzene part was omitted for clarity).

## Conclusion

In conclusion, we established an *atom-swapping* methodology for the synthesis of metallabenzene, namely conversion from phosphinine metal complexes to metallabenzenes. Treatment of phosphinine iridium complex **3** with O<sub>2</sub> afforded iridabenzene **5**. For analogous phosphinine rhodium complex **4**, simple oxidation with O<sub>2</sub> gave pentadienyl rhodium complex **6** instead of the corresponding rhodabenzene. Subsequent reduction of **6** by potassium metal resulted in the formation of dianionic rhodabenzene **8**. Successful synthesis of an unprecedented rhodabenzene ensure the utility of here-developed method for the access to unexplored metallabenzenes. Experimental analysis and DFT calculation of the model complex suggested the aromatic character of iridabenzene **5**, whereas aromaticity of dianionic rhodabenzene **8** is still elusive.

## Acknowledgements

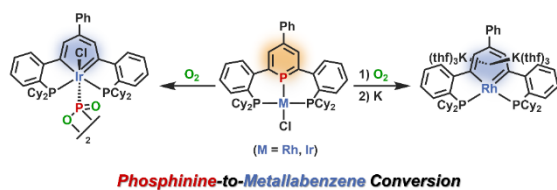
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**Keywords:** Phosphinine • Metallabenzene • Pincer Complex • Iridium • Rhodium

- [1] D. L. Thorn, R. Hoffman, *Nouv. J. Chim.* **1979**, *3*, 39–45.
- [2] a) J. R. Bleeker, *Chem. Rev.* **2001**, *101*, 1205–1227; b) C. W. Landorf, M. M. Haley, *Angew. Chem. Int. Ed.* **2006**, *45*, 3914–3936; *Angew. Chem.* **2006**, *118*, 4018–4040; c) L. J. Wright, *Dalton Trans.* **2006**, *60*, 1821–1827; d) J. Chen, G. Jia, *Coord. Chem. Rev.* **2013**, *257*, 2491–2521; e) B. J. Frogley, L. J. Wright, *Coord. Chem. Rev.* **2014**, *270–271*, 151–166; f) L. J. Wright, *Metallabenzenes: An Expert View*, John Wiley & Sons Ltd: Hoboken, NJ **2017**; g) B. J. Frogley, L. J. Wright, *Chem. Eur. J.* **2018**, *24*, 2025–2038; h) D. Chen, Y. Hua, H. Xia, *Chem. Rev.* **2020**, *120*, 12994–13086.
- [3] Y. Zhang, J. Wei, Y. Chi, X. Zhang, W. X. Zhang, Z. Xi, *J. Am. Chem. Soc.* **2017**, *139*, 5039–5042.
- [4] G. P. Elliott, W. R. Roper, J. M. Waters, *J. Chem. Soc. Chem. Commun.* **1982**, 811–813.
- [5] For representative reports, see: a) H. Xia, G. He, H. Zhang, T. Bin Wen, H. H. Y. Sung, I. D. Williams, G. Jia, *J. Am. Chem. Soc.* **2004**, *126*, 6862–6863; b) H. Zhang, H. Xia, G. He, T. Bin Wen, L. Gong, G. Jia, *Angew. Chem. Int. Ed.* **2006**, *45*, 2920–2923; *Angew. Chem.* **2006**, *118*, 2986–2989; c) G. R. Clark, G. L. Lu, W. R. Roper, L. J. Wright, *Organometallics* **2007**, *26*, 2167–2177; d) G. R. Clark, P. M. Johns, W. R. Roper, L. James Wright, *Organometallics* **2008**, *27*, 451–454; e) K. C. Poon, L. Liu, T. Guo, J. Li, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem. Int. Ed.* **2010**, *49*, 2759–2762; *Angew. Chem.* **2010**, *122*, 2819–2822.

- [6] For representative reports, see: a) J. R. Bleeke, Y. F. Xie, W. J. Peng, M. Chiang, *J. Am. Chem. Soc.* **1989**, *111*, 4118–4120; b) M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, V. Salazar, E. Oñate, K. Mereiter, *J. Am. Chem. Soc.* **2003**, *125*, 9898–9899; c) C. S. Chin, H. Lee, M. S. Bum, *Organometallics* **2005**, *24*, 4849–4852; d) G. R. Clark, P. M. Johns, W. R. Roper, L. J. Wright, *Organometallics* **2006**, *25*, 1771–1777; e) G. R. Clark, L. A. Ferguson, A. E. McIntosh, T. Söhnel, L. J. Wright, *J. Am. Chem. Soc.* **2010**, *132*, 13443–13452; f) M. Hernández-Juárez, V. Salazar, E. V. García-Báez, I. I. Padilla-Martínez, H. Höpfl, M. D. J. Rosales-Hoz, *Organometallics* **2012**, *31*, 5438–5451.
- [7] For representative reports, see: a) R. D. Gilbertson, T. J. R. Weakley, M. M. Haley, *J. Am. Chem. Soc.* **1999**, *121*, 2597–2598; b) H. P. Wu, S. Lanza, T. J. R. Weakley, M. M. Haley, *Organometallics* **2002**, *21*, 2824–2826. c) V. Jacob, T. J. R. Weakley, M. M. Haley, *Angew. Chem. Int. Ed.* **2002**, *41*, 3470–3473; *Angew. Chem.* **2002**, *114*, 3620–3623.
- [8] Y. Li, H. Wang, X. Li, X. Li, *Chem. Sci.* **2020**, *11*, 12249–12268.
- [9] For early reports, see: a) K. Dimroth, G. Neubauer, *Chem. Ber.* **1959**, *92*, 2042–2045; b) K. Dimroth, *Angew. Chem.* **1960**, *72*, 331–342; c) G. Märkl, *Angew. Chem.* **1966**, *78*, 907–908; d) F. D. Saeva, G. R. Olin, *J. Am. Chem. Soc.* **1980**, *102*, 299–303.
- [10] Z. Yoshida, S. Yoneda, H. Sugimoto, T. Sugimoto, *Tetrahedron* **1971**, *27*, 6083–6087.
- [11] J. R. Bleeke, R. Behm, Y. F. Xie, M. Y. Chiang, K. D. Robinson, A. M. Beatty, *Organometallics* **1997**, *16*, 606–623.
- [12] R. P. Hughes, H. A. Trujillo, J. W. Egan, A. L. Rheingold, *Organometallics* **1999**, *18*, 2766–2772.
- [13] H. P. Wu, T. J. R. Weakley, M. M. Haley, *Organometallics* **2002**, *21*, 4320–4322.
- [14] a) M. A. Iron, J. M. L. Martin, M. E. van der Boom, *J. Am. Chem. Soc.* **2003**, *125*, 13020–13021; b) M. A. Iron, A. C. B. Lucassen, H. Cohen, M. E. Van Der Boom, J. M. L. Martin, *J. Am. Chem. Soc.* **2004**, *126*, 11699–11710.
- [15] L. E. E. Broeckx, S. Güven, F. J. L. Heutz, M. Lutz, D. Vogt, C. Müller, *Chem. Eur. J.* **2013**, *19*, 13087–13098.
- [16] J. Zhu, G. Jia, Z. Lin, *Organometallics* **2007**, *26*, 1986–1995.
- [17] Rhodabenzene **8<sub>Me</sub>** has disordered rhodium atom, which requires careful discussion of the geometry. Please see the Supporting Information for the detailed discussion.
- [18] A. A. deL Paggio, R. A. Andersen, E. L. Muetterties, *Organometallics* **1987**, *6*, 1260–1267.
- [19] a) A. S. C. Chan, H. S. Shieh, J. R. Hill, *J. Organomet. Chem.* **1985**, *279*, 171–179; b) N. Mézailles, P. Rosa, L. Ricard, F. Mathey, P. Le Floch, *Organometallics* **2000**, *19*, 2941–2943; c) B. Longato, R. Coppo, G. Pilloni, C. Corvaja, A. Toffoletti, G. Bandoli, *J. Organomet. Chem.* **2001**, *637–639*, 710–718.
- [20] Dimerization of metaphosphite (PO<sub>2</sub><sup>-</sup>) ligands is reported: J. Abbenseth, F. Wätjen, M. Finger, S. Schneider, *Angew. Chem. Int. Ed.* **2020**, *59*, 23574–23578; *Angew. Chem.* **2020**, *132*, 23780–23784.
- [21] A. Hettche, K. Dimroth, *Chem. Ber.* **1973**, *106*, 1001–1011.
- [22] a) P. E. Garrou, *Chem. Rev.* **1985**, *85*, 171–185; b) A. W. Parkins, *Coord. Chem. Rev.* **2006**, *250*, 449–467.
- [23] P. V. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. Van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.
- [24] Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. von Ragué Schleyer, *Chem. Rev.* **2005**, *105*, 3842–3888.
- [25] R. Herges, D. Geuenich, *J. Phys. Chem. A* **2001**, *105*, 3214–3220.
- [26] D. Geuenich, K. Hess, F. Köhler, R. Herges, *Chem. Rev.* **2005**, *105*, 3758–3772.

## Entry for the Table of Contents



A novel synthetic method for metallabenzene by swapping a phosphorous atom in a phosphinine ring with transition metal fragments was developed. Oxidation of a phosphinine pincer iridium complex by  $O_2$  afforded iridabenzene via exchange of the phosphorous atom and the iridium fragment. Dianionic rhodabenzene was synthesized by  $O_2$  oxidation of an analogous rhodium complex followed by reduction by metallic potassium.

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